

Compact Electric Energy Storage for Marine Vehicles Using on-Board Hydrogen Production

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Abstract: The use of electric energy in marine vessels has been increasing in recent years. In general, it is motivated by the low ecological impact. However, in the case of underwater vehicles it is functionally essential. The objective of this study is to demonstrate the advantage of electric power generation and storage based on on-board hydrogen generation via the reaction between activated aluminum and water and application of the hydrogen in a fuel cell. The original activation process enabling a spontaneous reaction with water to produce hydrogen as well as a parametric study of hydrogen generation rate and yield are briefly described. The potential increase in specific energy (energy per unit mass) and energy density (energy per unit volume) vs. batteries and other means of hydrogen storage is presented. It is shown that the use of the present technology may result in a substantial increase of specific electric energy along with a reduction in volume or an increase in operating time for the same overall mass of energy storage and generation system.

Key words: Hydrogen production, aluminum-water reaction, activated aluminum, fuel cell, energy storage, marine electric power.

1. Introduction

Electric energy and power are required for variety of applications in modern marine vessels. Electric power for the main vehicle propulsion is essential for submarines in underwater operations as well as for surface and UUVs (underwater unmanned vehicles) or AUVs (autonomous underwater vehicles). UUVs and AUVs have shown increasing application for monitoring of sea water properties, pollutants, undersea flora and fauna, detection of oil spillage or operating problems around nautical oil rigs, as well as for military missions. Carreiro and Burke [1] present a variety of UUVs operated by the US Navy. Auxiliary and emergency electric power may be needed routinely in all kinds of vessels. Electricity can provide quiet and ecologically clean operation. However, electric energy storage (typically by means of batteries) is characterized by a fundamental

problem of low energy density (energy per unit volume) and specific energy (energy per unit mass).

1.1 Electric Energy Storage—Batteries

As has been stated before, most commonly electric energy is stored in batteries. Batteries are divided into two categories: primary batteries (non-rechargeable) and secondary batteries (rechargeable). The energy density of primary batteries is typically higher than that of secondary batteries. However, the latter may be recharged and used tens and hundreds of times. Good primary batteries may yield specific energy storage of about 300 Wh/kg. Some of them, e.g., Zn/air and Li/SOCl₂ (specific energy of 290-300 Wh/kg) can provide only limited power output which is adequate for small devices but not for high power operations. The Li/SO₂ primary battery with a typical specific energy of 260-280 Wh/kg may be a good choice for higher power, military or industrial applications [2, 3]. It is however a high cost device. Primary batteries may suit one-way or one-time missions. Usually, for multiple applications secondary, rechargeable batteries are preferred. Table 1 presents some

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commonly used rechargeable batteries and their characteristics. Note that good rechargeable batteries such as lithium/ion or lithium/polymer give electric energy density as high as 150 Wh/kg and even 200 Wh/kg. Nevertheless, special high performance rechargeable batteries with specific energy similar to that of primary batteries may be available. However, they are very expensive and would typically be used for special missions.

1.2 Hydrogen Storage and Fuel Cells

Hydrogen is considered an ultimate fuel due to its extremely high heat of reaction (low heating value of 120.9 MJ/kg and high heating value of 142.9 MJ/kg, about three times higher than that of hydrocarbon fuels) and due to its minimal ecological impact, as its reaction products are only water (in liquid or vapor state). Hydrogen is also an ideal fuel for application in fuel cells which convert directly chemical energy into electric energy at a relatively high efficiency (typically about 50%). As will be shown later, the use of hydrogen in a fuel cell may yield much higher specific energy compared to batteries. One of the often preferred fuel cell types for electricity generation from hydrogen is the PEM (proton exchange membrane) fuel cell, using hydrogen (fed from certain means of storage) and oxygen (typically from the ambient air) and operating at low

temperatures (typically between room temperature and 100 °C). Another type may be the alkaline fuel cell. Both batteries and fuel cells convert chemical energy into electric energy. The difference between those options for energy storage is the location of the active material (fuel and oxidant). In batteries the fuel and oxidant are part of the device, whereas in fuel cells they are supplied externally. This difference leads to several advantages of fuel cells over batteries: fast recharging, longer continuous run-time (approximately two to ten times longer, depending on the mission), constant voltage and lack of power decrease during operation, greater durability in outdoor environment under a wide temperature range, and less maintenance [4]. Additionally, fuel cells are characterized by a quiet operation. A schematic illustration of a PEM fuel cell is presented in Fig. 1.

Despite its outstanding properties, hydrogen poses difficult handling, storage, and transportation problems due to its extremely low density, 0.089 kg/m³ (gas), about 14 times less than air, and 71 kg/m³ (liquid), 14 times less than water, and its high flammability and explosion hazards. In addition, its cost is higher than that of conventional fuels. For many applications hydrogen is stored as gas in high pressure (200-700 bar) tanks, characterized by a relatively low overall hydrogen mass fraction of maximum 5-6%. Liquid hydrogen storage (at about 20

Table 1 Specific energy and characteristics of some commonly used secondary (rechargeable) batteries.

Type	Specific Energy (Wh/kg)	Characteristics	Applications
Lead-acid	35-40	Popular. Low cost. Low energy density. Moderate specific energy. Available in various sizes and shapes.	Automotive, golf carts, lawn mowers, tractors, aircraft, marine, industrial trucks, portable electronics, emergency power.
NiMH	75-80	Maintenance free.	Portable electronics, electric and hybrid vehicles.
NiCd	35-55	High cost. Good low temperature and high rate performance. Excellent cycle life. Maintenance free. Environmental not friendly—strongly regulated.	Biomedical, aircraft.
Li-ion	120-150	Moderate cost. High specific energy. High energy density. Long cycle life. Long shelf life.	Portable electronic equipment, electric vehicles, space applications.

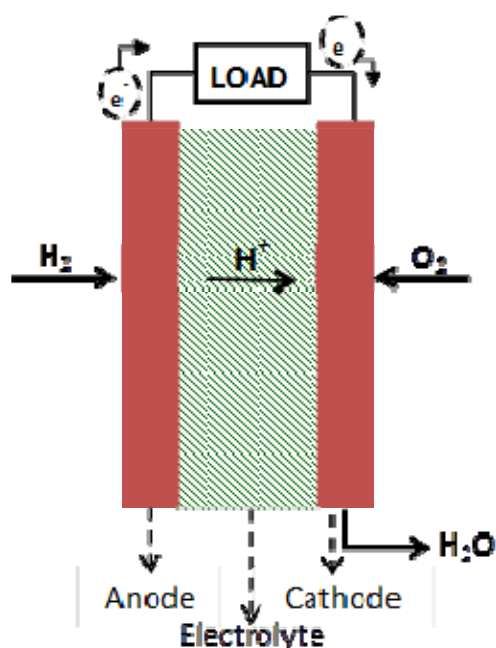


Fig. 1 Schematic illustration of a PEM fuel cell.

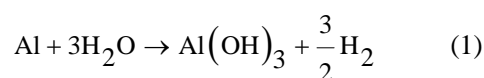
K) can yield a higher mass fraction (typically up to about 8-9%), but involves difficulties in handling and long-time storage, and its refrigeration requires substantial amount of energy (about 30% of the hydrogen energy). However, the overall hydrogen density in all those arrangements is very low and does not exceed about 60 kg/m³. Hydrogen storage challenges have been the subject of many publications, e.g., Refs. [5-10].

In order to increase the overall hydrogen density as well as to reduce the risks involved in storing high pressure hydrogen gas, solid materials that can store hydrogen and release it in a controlled and convenient manner have been sought. The most common materials for a compact storage of hydrogen are metal hydrides, which are chemical compounds of metals or metal alloys with hydrogen. There are many metal hydrides with mass fractions of hydrogen ranging from about 1% to over 20%. However, only few of

them can release hydrogen upon mild heating and are practically used. Table 2 presents a number of practically used metal hydrides and the content of hydrogen. As one can see, practical metal hydrides such as LaNi₅H₆ or FeTiH₂ contain only 1-1.5 wt% of usable hydrogen (hydrogen may be released only to a certain extent and not in full). It means that 1 ton of hydride can store only 10-15 kg of hydrogen. Nevertheless, due to the high density of these hydrides, the overall density of the contained hydrogen is about 115 kg/m³ for the former and about 100 kg/m³ for the latter [11, 12], higher than for liquid or high pressure gaseous hydrogen. This is an advantage for volume limited systems besides the improved safety. This type of hydrides has been used for power generation in underwater operation of submarines. Additional information is included in Refs. [13, 14].

2. Aluminum-Water Reaction for Hydrogen Production

Potentially, the chemical reaction between aluminum and water can yield very high (11%) mass of hydrogen compared to the aluminum mass, presenting a substantially higher hydrogen storage capacity and overall hydrogen density than in high pressure gas and even liquid hydrogen tanks and a much better mass fraction than in practical metal hydrides. Eq. (1) presents the reaction:



However, aluminum is naturally covered with a thin oxide film that practically prevents further chemical interaction with oxidizing species (air, water). Many researchers have tried different activation and catalytic methods as well as operating conditions to promote the

Table 2 Selected practical metal hydrides used for hydrogen storage.

Metal/Alloy	Hydride	Hydrogen capacity (wt%)	Hydrogen density (kg/m ³)	T for 1 bar (°C)
LaNi ₅	LaNi ₅ H ₆	1.37	115	12
CaNi ₃	CaNi ₃ H _{4.4}	1.8		25
FeTi	FeTiH ₂	1.89	100	-8

reaction. Vlaskin et al. [15] and Yavor et al. [16] showed good reaction rate and hydrogen production yield when reacting aluminum powder (of a micron size range) with high-temperature water (typically 150-300 °C) at elevated pressure. Ball milling [17, 18] and mechanical cutting [19] have also been investigated for enhancing the reaction between aluminum and water. The latter related the research to power generation. The use of gallium and other alloying elements with aluminum have been studied as well [20]. Reaction of aluminum in alkali solution [21] could also yield hydrogen.

The authors of this article have proposed, studied, and patented an original method of a thermo-chemical treatment of aluminum particles with a small amount (typically 1-2.5%) of lithium based activator, enabling the aluminum to react spontaneously with water at room temperature and produce hydrogen [22-24]. Starting with lithium hydride the activator or its components diffuse into the aluminum lattice and help modifying the oxide layer around the particles to become non-protective. This method of aluminum activation seems ideal for hydrogen production and storage. It is safe, easy to handle, does not need additives in the water, and gives high yield of hydrogen production (about 90% and more). A brief summary of a parametric study of the activated

aluminum reaction with water is given below. Fig. 2 shows the effect of water/aluminum mass ratio on the hydrogen production rate vs. time. One can see that the reaction rate is higher for a lower mass ratio. The main reason is the faster temperature increase during the (exothermic) reaction and its substantial effect on the reaction rate. The stoichiometric water-aluminum mass ratio is 2. However, when reacting in an open vessel the water boils and partially evaporates. Hence, excess water was used in the experiments. One can see that the reaction comes to completion in a few minutes.

It is most interesting to learn that the activated aluminum reacts in a similar manner with any type of water (Fig. 3). The fact that sea water may be used is very significant for marine applications, as water can be pumped directly from the sea and should not be carried along.

3. Combined Hydrogen and Electric Energy Production and Storage

3.1 Performance and Specific Electric Energy

As was stated before, the aluminum-water reaction may be considered as compact hydrogen storage. Channeling the hydrogen produced to a fuel cell can generate electricity on-board and on-demand safely and

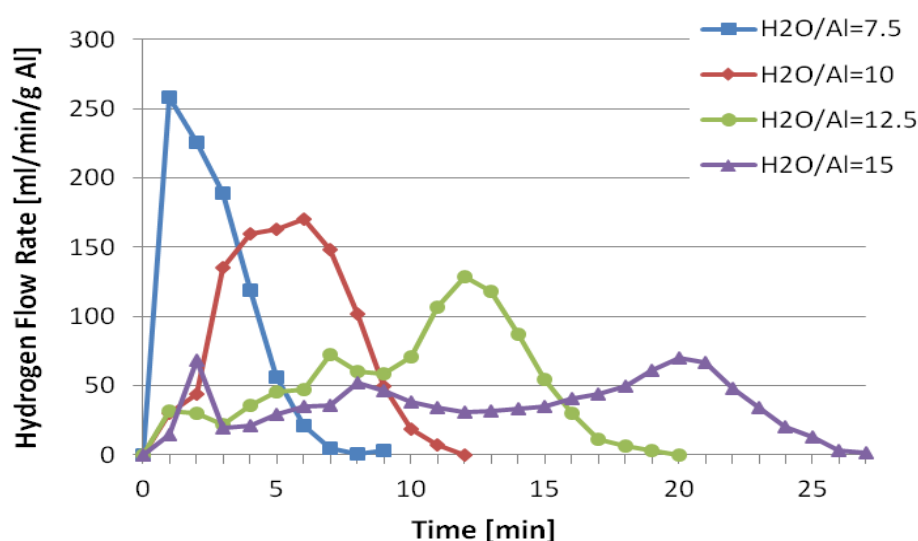


Fig. 2 Effect of water/aluminum mass ratio on the hydrogen production rate vs. time. Activator fraction 2.5%.

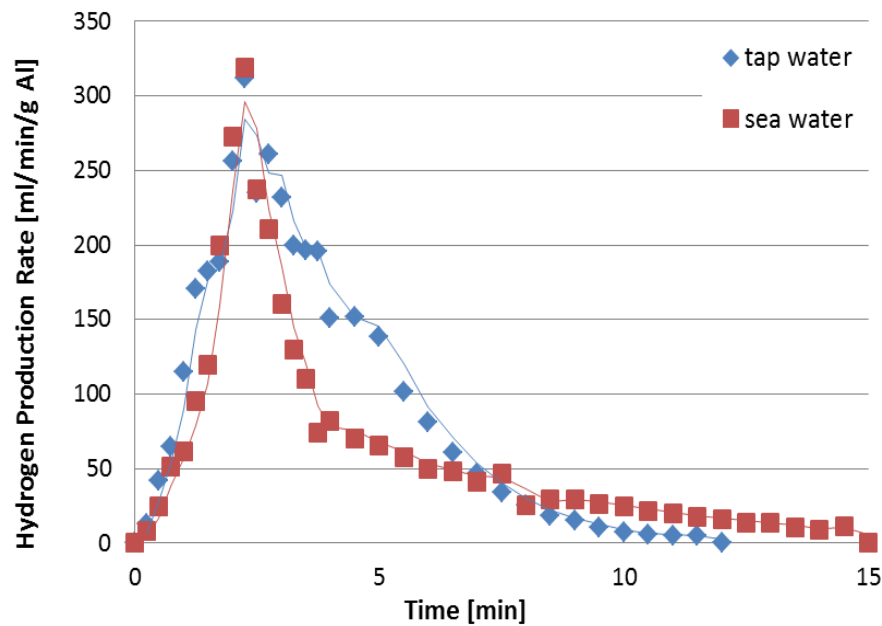


Fig. 3 Effect of water type on the hydrogen production rate vs. time. Activator fraction 2.5%.

conveniently, as the hydrogen gas is used upon its production and should not be accumulated. One can show that the application of this technology for electric marine propulsion can yield very high specific electric energy storage. In surface vessels both the water needed for the reaction with aluminum and the air required for the fuel cell are acquired from the surrounding. In underwater applications water is available from the ambience, whereas oxygen has to be stored in some form for the fuel cell operation. The specific electric energy storage when using a PEM fuel cell with 50% efficiency is 2,200 Wh/kg Al, greater by an order of magnitude than the storage by batteries. Indeed, when considering the overall specific energy one should take into account also other components including the fuel cell system and controls, the hydrogen reactor, and the oxygen storage in case of underwater vehicles (submarines often carry liquid oxygen for undersea operation). A conservative estimate of the system mass (fuel cell and reactor) is about 10 kg per kW of electric power capacity (scaled with the power). The longer the operating time the higher the specific energy, as the fixed mass of the fuel cell and reactor represents a smaller fraction of the overall mass, and the fuel component becomes

dominant. Table 3 presents the specific electric energy for different marine operation scenarios and mission duration with regard to the present Al-water-fuel cell technology in comparison to other storage means. Some of the data also appeared in the work by Elitzur et al. [25], which assessed the technology for surface and aeronautical applications as well.

Considering that batteries can store between 100 and 200 Wh/kg, and special high performance batteries up to 300 Wh/kg (independent of the mission duration), one concludes that for short missions of the order of one hour duration, batteries are superior to the Al-water-fuel cell technology with regard to specific electric energy storage. However, for longer missions of 10 hours and more, our technology reveals substantial advantage. At very long missions (1,000 hours) one extracts almost the entire specific energy potential of the aluminum-water reaction.

Referring to metal hydride energy storage: their maximum potential of specific electric energy (when using the hydrogen released in a PEM fuel cell) is about 300 Wh/kg (assuming 1.5% usable hydrogen mass fraction). Nevertheless, for underwater operation oxygen has to be carried along, reducing the maximum specific energy to about 260 Wh/kg (assuming

Table 3 Specific electric energy storage via Al-water hydrogen production reaction and PEM fuel cell compared to other storage means for surface and underwater marine vehicles as a function of operating time.

Application, mission	Specific Energy (Wh/kg)					Remarks
	Without fuel cell mass ⁽¹⁾	With fuel cell mass ⁽²⁾				
		Operating Time				
		1 hr	10 hr	100 hr	1,000 hr	
Marine surface vessels, Al-water technology	2,200	96	688	1,803	2,150	Al mass only. Water and air available
Marine underwater vehicles, Al-water technology	1,165	92	538	1,043	1,150	Al and oxygen mass. Water available
Hydrides, underwater	267	73	211	260	267	Hydride and oxygen mass
Batteries, both surface and underwater	100-300	100-300	100-300	100-300	100-300	Battery mass ⁽³⁾

(1) Aluminum mass 0.455 kg/kWh.

(2) Estimated system mass of fuel cell and auxiliary equipment 10 kg/kW.

(3) For high power and missions of long duration, batteries with specific energy of 100-150 Wh/kg such as rechargeable lithium-ion batteries are likely to be used.

the use of liquid oxygen). For long underwater missions hydride/fuel cell technology exhibits almost twice the specific energy compared to the commonly used lithium-ion batteries which are in the range of 100-150 Wh/kg. Their specific energy is, however, far below that of the presented Al-water technology.

In assessing the practical use of the aluminum-water technology, one should note that the concept described here is based on laboratory scale experiments. Tests have shown good scaling capability of a factor of 10 and more, yet did not exceed hydrogen production rate of about 20-30 liter per minute, which is equivalent to an electric power generation in the range of 1 kW. The experiments revealed good reproducibility and good safety features. Further scaling up seems feasible. Nevertheless, all experiments have taken place in a batch reactor. One of the main challenges for extended operation should be technical solutions for reliable and controllable continuous reactants feeding to the hydrogen reactor.

3.2 Marine Vehicles and Sample Calculations

The application of fuel cell technology for electrically operated marine vehicles has been gaining interest, and actual vessels apply this technology. In 2007 Voller Energy Group announced the installation of a 1 kW fuel cell generator on-board a sailing yacht

[26]. Siemens Industries, Inc. have long been developing and installing PEM fuel cells for submarines [27]. The source of hydrogen is metal hydride, whereas oxygen may be stored as a cryogenic liquid. It may also be produced from oxygen containing solids such as sodium chlorate.

As mentioned before, providing compact (high specific energy and high energy density) electric energy storage for underwater autonomous vehicles (UUVs, AUVs) is essential for enabling longer missions or larger space for instrumentation, as the use of batteries may occupy most of the vehicle space, leaving little space for instrumentation, as well as limiting the mission range and duration.

In the following section evaluation of the outcome of replacement of an existing battery power source by the present Al-water-fuel cell technology in a small AUV is presented.

The following data are available for this vehicle.

Data on the battery characteristics were taken from the website of Bluefin Robotics [28]:

Total electric energy: 4.5 kWh.

Energy storage: lithium-polymer battery packs.

Endurance: 26 hours.

Specific energy: unpacked 200 Wh/kg; packed 80-120 Wh/kg (average 100 Wh/kg).

From these data one can deduce that the overall



Fig. 4 A model boat as technology demonstrator for electric marine vehicle operation using on-board an Al-water hydrogen reactor and a PEM fuel cell.

energy storage package weighs 45 kg and the average power is 173 W.

Using the Al-water-fuel cell technology for the same overall energy and average power will result in:

Fuel cell and reactor mass: 1.8 kg.

Activated aluminum mass: 2.1 kg.

Oxygen mass, stored as liquid: 1.9 kg; or stored in sodium chlorate: 4.2 kg.

Overall energy storage mass: about 6 kg for liquid oxygen storage or about 8 kg for sodium chlorate as the oxygen source.

This is a noticeable mass saving. Alternatively, for the same mass of the battery pack one could increase the operating time by a factor of about 5 to 11, depending on the oxygen storage method, namely from the original 26 hours to about 140-300 hours.

4. Technology Demonstration

The combined technology of in-situ hydrogen production from the reaction of activated aluminum and water together with electric energy generation by a fuel cell has been demonstrated by designing and constructing a model boat (as well as a model car) with on-board hydrogen reactor, PEM fuel cell (Horizon H-30, rated power 30 W), and electric motor. Fed by 5 gram of activated aluminum powder the boat could operate for more than 40 minutes. The model boat and installation is presented in Fig. 4. A short video clip appears in the link by Gany, Rosenband,

and Elitzur [29].

5. Summary

This work deals with the use of aluminum-water reaction for hydrogen and electric energy production and storage on-board marine vehicles. Using an original method for aluminum activation, it is demonstrated that high reaction rate and hydrogen production yield may be obtained at room temperature. The combination with a PEM fuel cell exhibits compact electric energy storage compared to batteries that may be essential for long range and long duration AUV operation. A model boat equipped with hydrogen reactor, fuel cell, and electric motor has been constructed and operated, demonstrating the technology.

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