

Aluminum-Water Energy System for Autonomous Undersea Vehicles

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Aluminum-fueled energy systems that leverage the energy-dense aluminum-water reaction to produce both hydrogen and electrical power are maturing rapidly. These systems are safe, reliable, quiet, and completely air independent. Furthermore, they employ scalable designs and require few moving parts. These advantages are leading to the imminent use of aluminum-fueled systems in undersea applications.

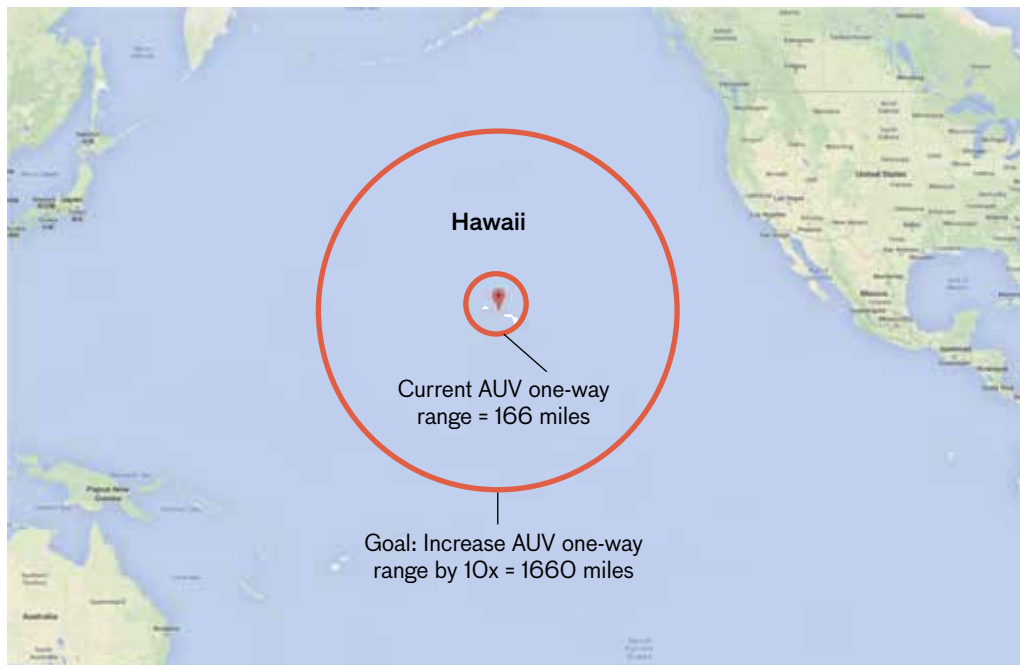


In recent years, autonomous systems have been developed for applications spanning air, ground, and both sea surface and subsurface domains. The technical challenges faced by these systems vary considerably from one domain to the next. This article describes a collaborative research effort between the Department of Mechanical Engineering at MIT and Lincoln Laboratory to address the problems inherent in powering autonomous undersea vehicles (AUV).

When operating below the sea surface, an AUV must navigate without access to the Global Positioning System (GPS) and with relatively short-range, limited-bandwidth communication links. These constraints make it difficult for operators to interact with the AUV, thereby placing a high demand on the autonomous behavior of the vehicle. Also, an AUV's lack of access to air while it is submerged significantly limits energy storage options. Currently, most commercial AUV systems use lithium-ion battery technology, which provides three days of endurance to a mid-sized AUV traveling at 3 knots. The goal of our research is to increase endurance by a factor of 10, expanding mission time for the same mid-sized AUV from 3 to 30 days. A tenfold increase in endurance could expand the uses of AUVs into new mission areas.

Background and Motivation

Recent advances in technology have enabled the development of highly capable AUVs for a wide range of applications, such as mapping the seafloor, characterizing

**FIGURE 1.**

The illustration shows the current one-way operating range (small circle) and the one-way goal range (large circle) for mid-sized AUVs launched from Hawaii.

subsurface ocean currents, and monitoring marine biology. Autonomous unmanned vehicles used for military activities are equipped with sensors to detect sea mines and characterize the undersea environment prior to the start of operations. Future military missions may also employ AUVs to collect data for intelligence, surveillance, and reconnaissance (ISR). In the civil and commercial sectors, AUVs are used for disaster recovery and for oil and gas exploration. In all these applications, the system's performance, thus the success of the mission, is limited by the total energy stored in the AUV power source.

Many fuel sources have been considered to power AUVs. Combustible organic fuels, such as gasoline or jet propellant, are energy dense but have not been used in AUVs because typical missions require extended periods of time below the surface without access to oxygen. Instead, electrochemical power sources such as lithium-ion batteries power most industry-built AUVs. In mid-sized AUVs, lithium-ion technology can power an AUV at 2 to 3 knots for three days [1]. However, because many missions demand timelines longer than three days, AUVs used in such missions require a power source with a high enough energy density to achieve the needed endurance. Currently, this energy density is not available.

The map in Figure 1 illustrates the benefit of increased AUV endurance. Operating radii are shown for

mid-sized AUVs deployed from Hawaii. The smaller circle represents the one-way operating range given a platform speed of 2 knots for three days, or approximately 166 miles. If the platform endurance is increased by a factor of 10, then the one-way operating range increases to 1660 miles, which is denoted by the larger circle.

In addition to extending AUV endurance, a higher energy density allows higher-speed operations that enable an AUV to perform ship tracking and interception. Other components of an undersea network, including sonobuoys and bottom-mounted sensors, will also benefit from increased endurance.

Energy System Options

Over the years, researchers looking to maximize AUV endurance, given the constraint of a fixed hull volume at neutral buoyancy, have explored various fuel options for powering underwater systems. In undersea applications, the available volume within the hull of a vehicle imposes a volume constraint on the vehicle's energy system, and the need to maintain neutral buoyancy imposes a constraint on the system's mass. Hence, for undersea systems, both volumetric and gravimetric energy densities are important. These constraints apply to the complete energy system, which includes the fuel, the oxidizer (if any), all the plumbing, electronics, and any unfilled hull

volume. Thus, the specific gravity of the fuel itself can vary, so long as the final energy system maintains a specific gravity of 1. Fuel options that exhibit high volumetric energy density and are considered safe to handle include aluminum, anthracite, and silicon. Figure 2 illustrates the energy density for a number of fuel options. The energy density per unit mass is on the x -axis, and energy density per unit volume is on the y -axis.

An energy source for an AUV must operate without access to air or oxygen, be reliable, and be easy to refuel even under nonideal conditions. For military applications, the energy source also must be marine-safe for transportation and exhibit a low acoustic signature for covert missions. In some applications, power demand varies widely during a mission. For example, the vehicle may need to first loiter at a low speed and then accelerate to a higher speed for a short period of time. In such a situation, the energy subsystem must be sufficiently flexible to output the appropriate power levels to meet

the changing demands during the mission. Finally, an additional advantage for the energy source is to produce minimal impact on the environment.

Table 1 compares the most relevant characteristics for a number of different energy options. As indicated, an energy source based on an aluminum-water reaction has an extremely high energy density and uses water as an oxidizer, making it a particularly attractive fuel for AUVs.

Currently, the most common energy sources used in undersea systems are lithium-ion batteries. Batteries, which can be custom fabricated from individual cells, fit well into AUV hulls. They can also supply power on demand, work during submerged operations, and are reliable and silent. Despite the technological advances in lithium-ion batteries, they have limited energy density and must be recharged. In addition, because large lithium-ion batteries can become hot enough to ignite nearby materials or even erupt into

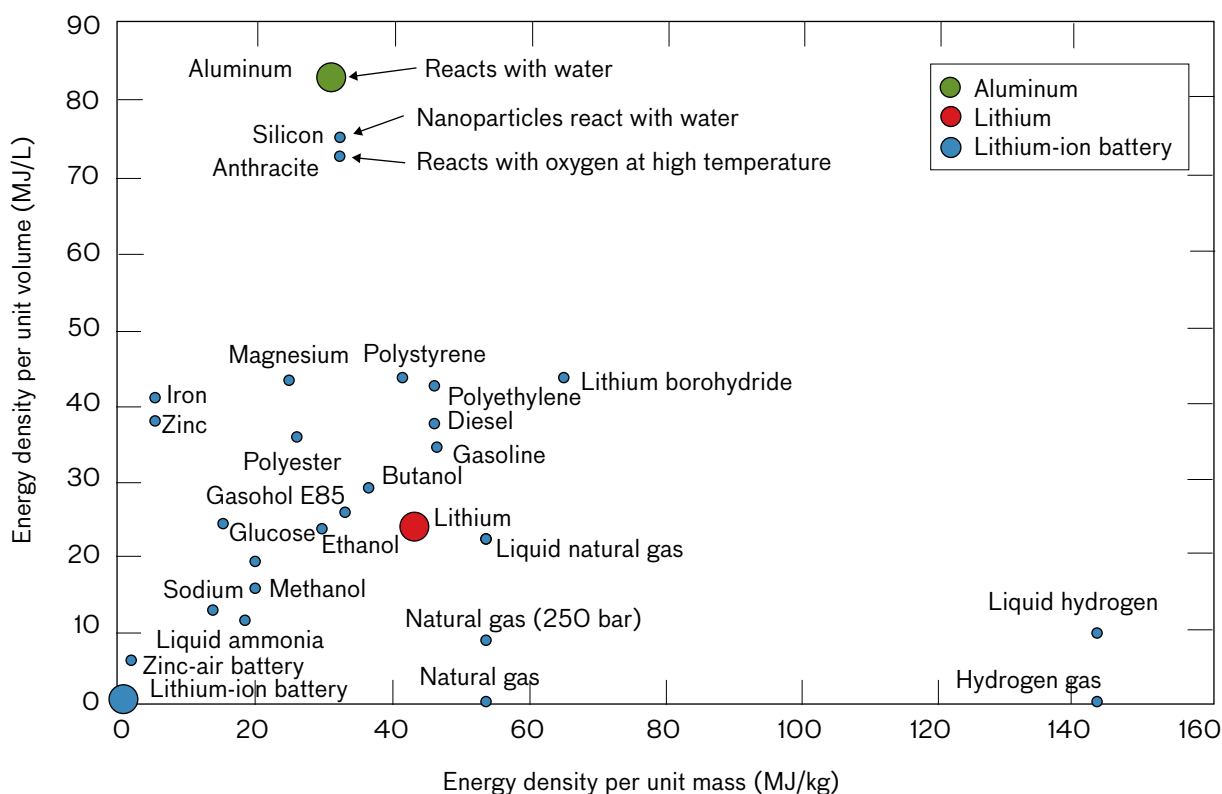


FIGURE 2. Energy densities of select fuels are compared. These data are for relative comparison only; the volume and mass penalties of oxygen and water are not included. Data for lithium-ion and zinc batteries (which are complete energy storage systems and not fuels) are also included for relative comparison.

Table 1. Comparison of Energy Options for Underwater Vehicles

Energy options	Energy dense	Submerged operation	Reliable	Easy refuel	Safe	Low noise	Power on demand	Eco-friendly
Battery		✓	✓	✓	✓	✓	✓	
Wave energy	N/A			N/A	✓	✓		✓
Solar				N/A	✓	✓		✓
Docking	N/A	✓		✓	✓	✓		✓
Tether to shore	N/A	✓			✓	✓		✓
Combustion	✓		✓	✓	✓			
Ga/Al-H ₂ O*	✓	✓	✓	✓	✓	✓	✓	✓
Monopropellants	✓	✓	✓				✓	
Nuclear	✓	✓	✓	N/A	✓	✓	✓	

*gallium/aluminum-water

flame themselves when damaged, they present a major safety concern on board marine vessels.

Fuel cells and hybrid energy systems have the potential to increase power density in underwater systems while also lowering construction and maintenance costs. Fuel cells that convert chemical energy directly into electrical energy are particularly advantageous for AUVs on covert missions because the cells utilize few moving parts and, consequently, have a low acoustic signature. The main drawback of commercial air-breathing fuel cells is packaging. The overall energy density decreases with the addition of the valving and control circuitry needed to operate an air-breathing fuel cell in a hermetically sealed environment. Most commercial fuel cells below ~1 kW are powered by the reaction of hydrogen with oxygen. For example, see the 200 W Horizon fuel cell in Figure 3. This approach introduces the risk of gas leakage and combustion within the sealed hull of an AUV. However, the amount of energy released by a few cubic feet (= 10s of grams) of burning gas is orders of magnitude less than that released by the unintended ignition of the lithium-ion battery our power system is designed to replace.

Anthracite, a lustrous carbon-rich coal, has a high energy density of approximately 72 MJ/L when burned to completion in air. Unfortunately, when anthracite is reacted with water, high temperatures are required

for the water-gas reaction to proceed efficiently. Also, the carbon monoxide waste is difficult to separate from the hydrogen; it “poisons” the fuel cell catalyst; and it is difficult to store and dispose of safely.

Silicon, with a volumetric density of approximately 76 MJ/L, is another potential high-density fuel. Researchers at the University of Buffalo have demonstrated that nano-sized particles of silicon react with water to release hydrogen gas [2]. The hydrogen can then be used to power a fuel cell. The process to generate nano-sized particles of silicon is expensive; nonetheless, it is an interesting fuel option.

Aluminum has the highest volumetric density of all the fuels identified in Figure 2. Elemental aluminum reacts with water and releases approximately 83 MJ/L of energy, making aluminum-water an extremely attractive fuel or oxidizer option. In addition to having high energy density, aluminum fuel is reliable, easy, and safe to handle; reacts quietly; and produces eco-friendly aluminum hydroxide waste.

Prior Efforts Using Aluminum as a Fuel Source

Research in using aluminum as a fuel can be traced back more than 50 years. Note that all previous attempts to produce power from an aluminum-water reaction have been hindered by passivation from the oxide layer. The thin aluminum oxide layer that forms naturally on the

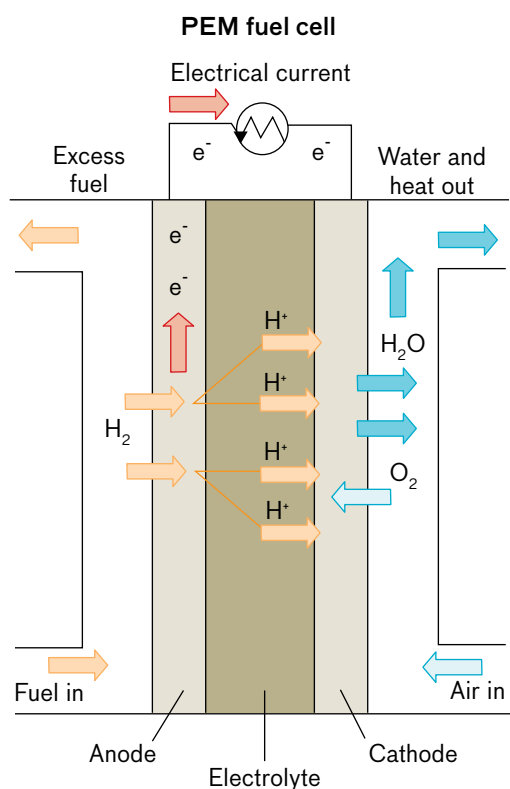


FIGURE 3. A Horizon H-200 hydrogen/oxygen fuel cell is above top. The controller module and solenoid valves are not shown. On the bottom is a schematic of a polymer electrolyte membrane (PEM) fuel cell.

surface of elemental aluminum protects it from environmental corrosion by water. However, this corrosion is the reaction needed for the energy system. The passivation layer forms almost immediately; even freshly machined aluminum will not react with water. Previous attempts to overcome the passivation layer include extreme heating and alloying with other metals such as gallium.

In the early 1960s, rocket propellants were developed using solid oxidizers and reactive metal fuels composed of fine powdered aluminum [3]. While the solid aluminum oxide ash itself provided little volume change, the enormous energy released during combustion significantly raised the exhaust temperature, leading to a large increase in thrust. By the 1970s, the United States began transitioning the fuels for their strategic missiles to these aluminized solid rocket propellants. Unfortunately, once they are ignited, solid fuels are difficult to control, and the power output is not easily throttled.

In the 1970s, the U.S. and Soviet militaries explored the use of aluminum to power submarines. These efforts were abandoned, and today U.S. submarines are nuclear powered and Russian submarines are either nuclear or diesel-electric powered. In the 1990s, several researchers developed aluminum-powered primary batteries with hydrogen peroxide as an electrolyte [4]. However, concentrated hydrogen peroxide is a dangerous, corrosive oxidizer that can release enormous amounts of both heat and oxygen when exposed to certain metals. Because hydrogen peroxide requires special handling, the U.S. Navy was unwilling to approve its use on Navy platforms. More recently in 2002, researchers at the Applied Research Laboratory at Pennsylvania State University developed an aluminum combustion engine that reacts finely powdered aluminum metal with seawater [5]. Their concept involved heating aluminum to a high temperature to remove the naturally formed aluminum oxide layer and then reacting aluminum with water. The heat from this reaction was used to power a turbine that drives the vehicle's propulsion. This technique involves a rather complex mechanism, is difficult to control, and operates at a high temperature.

In an alternative strategy, researchers at Purdue University developed and patented an approach for removing the tightly adherent aluminum oxide layer by forming an aluminum alloy. The alloy is primarily aluminum but also contains small amounts of gallium, indium, and tin. This technique naturally disrupts the oxide layer and enables a reaction with water at room temperature [6]. It was found, however, that the average amount of aluminum fuel consumed in their reaction was approximately 84% [7]. Therefore, about 16% of the aluminum fuel did not react with water because aluminum hydroxide waste suppressed the reaction. MIT research-

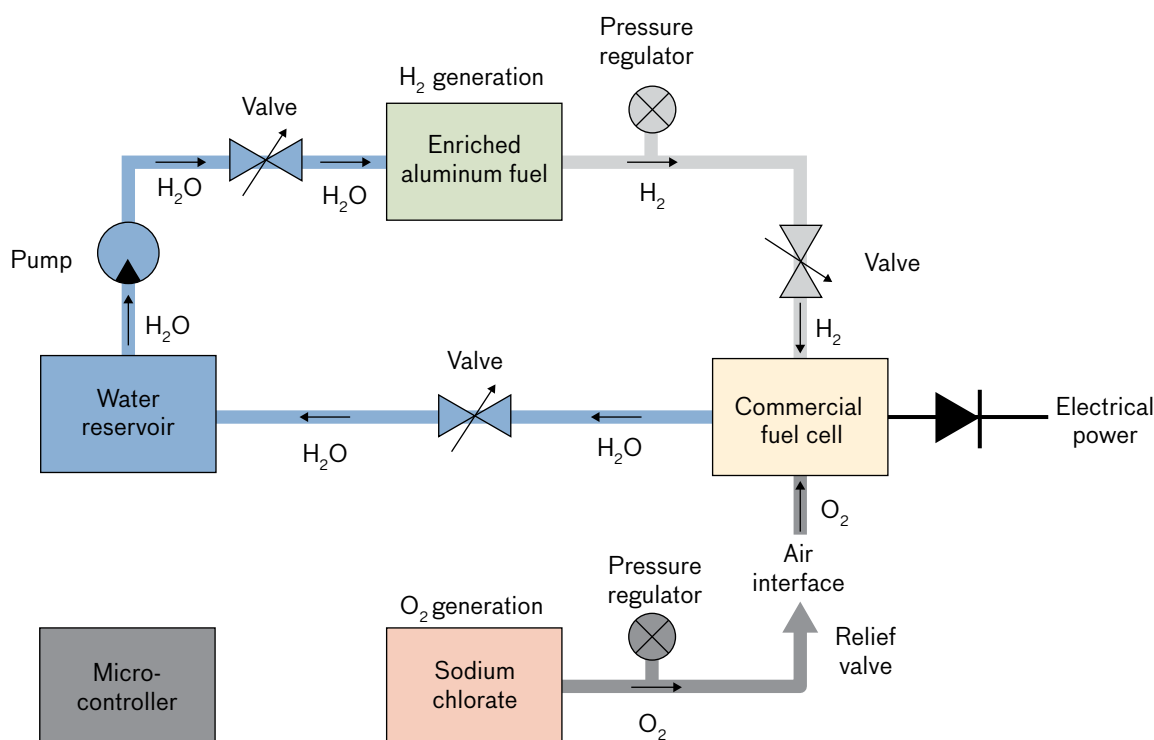


FIGURE 4. The block diagram of the aluminum-chlorate power system shows its basic building blocks and their interconnections.

ers recently attempted to generate this same alloy and react it with water, but they met with similar challenges.

In our approach, we propose to incorporate a refined mixture of aluminum with other metals in Group 13 (gallium, indium, and thallium) and Group 14 (carbon, silicon, germanium, tin, and lead). These other metals physically disrupt the integrity of the passivation layer, thus allowing the reaction of aluminum with water to proceed.

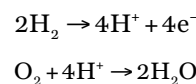
Electrical Power Generation Concepts

Two novel concepts that use the thermal and chemical energy released when aluminum reacts with water were investigated for generating the electrical power to run an AUV.

Aluminum-Chlorate Fuel Cell Power System

This concept uses both an aluminum alloy and sodium chlorate to generate hydrogen and oxygen to feed a commercial 200 W fuel cell stack (Horizon H-200). The fuel cell then converts the hydrogen and oxygen into water, heat, and electrical power. Fuel cells are

particularly advantageous for AUVs on covert missions because they quietly convert chemical energy directly into electrical energy; the dominant noise source is the turbulent airflow generated by the air supply fans. Current is generated via the two separate half-reactions that follow:



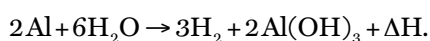
The voltage developed between the anode and cathode of 40 individual cells wired in series forces this current through an external load to deliver up to 200 W of electric power.

Fuel cells are most efficient when operated at the upper end of their power range, so the power produced by a 200 W fuel cell is used to continuously charge lithium-ion batteries on board the AUV and to provide power to the AUV circuitry, both of which functions present a stable load. In this way, a relatively small fuel cell can always operate at its maximum efficiency while the batteries handle the variable-power demands, which include pro-

viding the many kW of peak power occasionally required to propel the vehicle out of harm's way.

In this concept, hydrogen is produced from the aluminum-water reaction while oxygen is produced by thermal dissociation of sodium-chlorate. A block diagram of the aluminum-chlorate power system is shown in Figure 4.

H₂ generation in Figure 4 refers to the facilitated reaction of aluminum fuel with water to form hydrogen gas, aluminum hydroxide, and heat according to the following chemical equation:



Energy from this reaction is released in two forms. About half of the energy is released as heat (41.9 MJ/L Al), and the other half is released as potential energy in the form of hydrogen gas, which can then be reacted with oxygen (41.1 MJ/L Al). The aluminum-chlorate fuel cell concept only harvests energy in the form of hydrogen gas; the excess heat energy is released as waste.

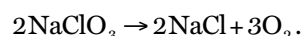
Aluminum fuel is prepared for the reaction through alloying a mixture of gallium, indium, and tin. The activated aluminum fuel readily reacts with water to release hydrogen. MIT researchers have demonstrated that the interdiffusion of a small amount of gallium, indium, and tin within the bulk aluminum disrupts the aluminum oxide layer and exposes enough elemental aluminum to allow the reaction with water to proceed rapidly at ambient temperature. This disruption of the surface film can be seen in the micrograph in Figure 5 and in the photograph in Figure 6.

Activated aluminum fuel is loaded into the hydrogen reactor in the form of spherical pellets. A small reciprocating pump controls water flow into the reactor vessel so that it can react with the abundance of aluminum fuel, generating hydrogen under pressure. A pressure regulator is then used to reduce and stabilize the hydrogen pressure reaching the fuel cell. The use of spherical aluminum gallium indium (AlGaIn) alloy fuel pellets provides solutions for two major challenges in utilizing aluminum as a fuel source: (1) the aluminum can react to completion because the interstitial volume between the pellets provides space for hydroxide waste to accumulate; (2) hydrogen can be produced at a rate commensurate with the relatively stable demand of the

fuel cell by monitoring the reactor pressure and filtering water flow accordingly.

The fuel cell requires oxygen in addition to hydrogen. Because oxygen is not readily available while the fuel cell is operating submerged within an AUV, it is supplied by heating sodium chlorate in a specially designed continuous-feed oxygen generator, or pyrolyzer. The chlorate pyrolysis reaction releases oxygen in a controlled fashion.

Sodium chlorate was selected as the oxygen source because it is stable in crystalline powder form at room temperature; its storage method is safer than storage for most other oxygens, such as hydrogen peroxide and liquid oxygen; its oxygen storage density is very high (~600 kg O₂/m³); and it produces a relatively harmless waste product: table salt. Pure sodium chlorate begins to dissociate at about 450°C, producing both oxygen and chlorine. Adding a few percent of an inorganic transition-metal catalyst, such as iron oxide, reduces this dissociation temperature to around 300°C, extending the life of the pyrolyzer and reducing chlorine production significantly. The pyrolysis reaction primarily produces oxygen and sodium chloride per the formula below:



The reaction is weakly exothermic (-30 kJ/mole of O₂); however, the effect of this added heat on the reaction rate is small when compared to the amount of heat lost because of conduction.

Oxygen production is adjusted by controlling the amount of sodium chlorate powder entering the stainless steel pyrolyzer tube via a bead-chain feed mechanism as shown in Figure 7. The oxygen generator was built to store and pyrolyze the sodium chlorate/catalyst feed and to contain the sodium chloride waste. Furthermore, the bead-chain system was designed such that sodium chlorate delivery and pyrolysis (and hence oxygen production) are inherently safe; if either the feed mechanism or the pyrolyzer were to fail in any fashion, oxygen production would slow or stop.

A pressure regulator on the outlet port of the generator controls the oxygen pressure (and hence oxygen partial pressure) within the hull of the undersea energy

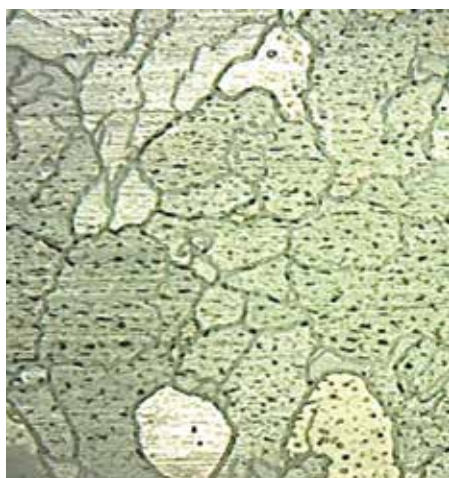


FIGURE 5. A scanning electron microscope (SEM) image of an aluminum pellet before treatment with gallium, indium, and tin is on the far left, and a SEM image of the pellet after treatment is on the left. Notice the smooth surface of the aluminum oxide on the pellet before treatment in contrast to the rough surface on the pellet after treatment.



FIGURE 6. The dull surfaces of the 6 mm diameter aluminum pellets, shown after treatment with gallium, indium, and tin, are caused by the disruption of the aluminum oxide layer.

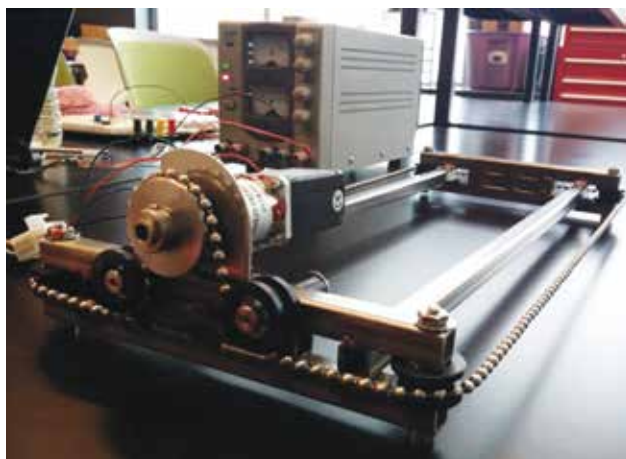


FIGURE 7. The bead-chain feed mechanism used in the chlorate oxygen generator controls the sodium chlorate powder entering the pyrolyzer tube. The pyrolyzer tube is not shown.

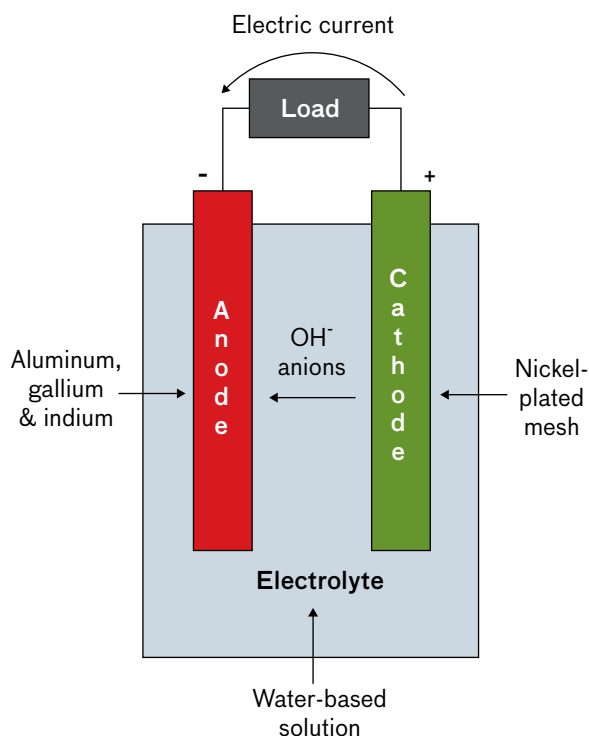


FIGURE 8. The aluminum-water primary cell uses an aluminum gallium indium anode, a nickel-plated cathode, and a water-based electrolyte to provide high energy density and achieve good efficiency. Hydrogen gas, a byproduct of the reaction, is vented in this design, causing its potential energy to be lost.

system. Fans on the fuel cell then circulate this oxygen-replenished gas mixture through the fuel cell stack from within this volume. As oxygen is consumed, the hull pressure will slowly drop, allowing the pressure regulator to release more oxygen from the generator housing as needed. We plan to use nitrogen and argon, from atmospheric gas trapped in the hull when it was sealed, as diluents to maintain roughly 20% oxygen at an absolute pressure of about 1 bar—the same oxygen concentration and pressure at which our commercial fuel cell was originally designed to operate. It may be possible to increase efficiency by operating the fuel cell at higher oxygen partial pressures. However, because this fuel cell also uses airflow for cooling and moisture removal, our initial plan is to maintain normal atmospheric conditions as closely as possible.

The aluminum-chlorate fuel cell concept offers several advantages over other aluminum-fueled power sources. First, because this design has few moving parts, the risk of mechanical failure is reduced. Second, because the aluminum-water reaction proceeds at a low temperature and is easy to control, we can start, stop, and throttle hydrogen production on demand. Finally, the design allows for easy refueling: waste aluminum hydroxide and sodium chloride are removed, and fresh activated aluminum fuel and catalyzed sodium chlorate are added.

Aluminum-Water Primary Battery

Another way to exploit the energy released by the aluminum-water reaction is to use aluminum to construct a battery. For this second concept, our goal was to design, build, and test a primary battery using an aqueous electrolyte and an aluminum alloy anode. A proof-of-concept prototype of this battery was initially fabricated and demonstrated as a collaborative project between Lincoln Laboratory and the Department of Mechanical Engineering at MIT. Test results indicated a volumetric energy density of approximately 12 MJ/L. In addition, the energy conversion for this prototype was extremely efficient: approximately 65% at 1 W output power. Several of the MIT researchers involved in this collaboration are currently commercializing the technology in a start-up company, OpenWater Power, located in Somerville, Massachusetts [8].

In addition to its high energy density and efficiency, the aluminum-water battery uses few moving parts and is

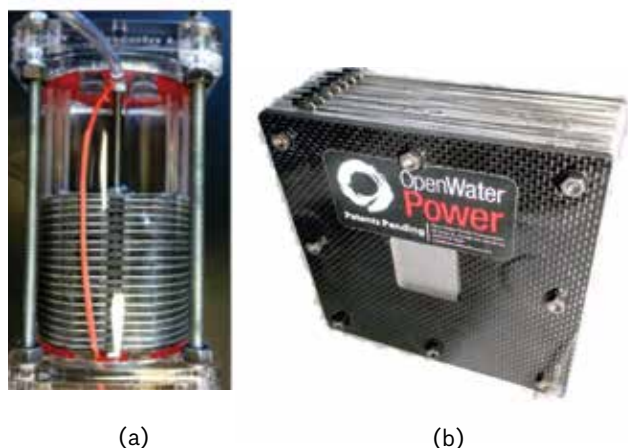
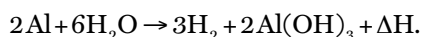


FIGURE 9. This figure shows two prototype aluminum batteries: an early prototype built at MIT (a) and a more recent prototype built at OpenWater Power (b).

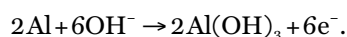
easily scaled to meet system requirements. The illustration in Figure 8 shows the basic elements of an individual cell consisting of an aluminum alloy anode, a nickel-plated cathode, and a water-based electrolyte.

To understand the operation of an aluminum-water cell, first consider the reaction of aluminum with water to form hydrogen gas, aluminum hydroxide, and heat according to the same reaction discussed earlier,

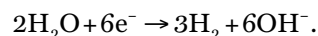


About half of the energy is released as heat, and the other half is released as potential energy in the form of hydrogen gas. This battery design effectively leverages the heat energy from the reaction while the hydrogen gas is released as waste.

The aluminum-water cell physically separates the reaction of aluminum with water into two half-reactions. The chemical reaction occurring at the aluminum-gallium anode is



In this reaction, the aluminum anode is being oxidized by hydroxyl ions, releasing its electrons into the anode terminal to flow through an external circuit. The chemical reaction occurring at the cathode is



In this reaction, water is being reduced by the electrons, releasing hydrogen gas and generating hydroxyl ions as a result.

The key to this technology is alloying the aluminum with a controlled amount of liquid gallium indium solution. This liquid alloy disrupts the oxide layer that normally coats and protects the aluminum surface from corrosion. In addition to depassivating the anode, the liquid metal has low activity for H_2 evolution [9], making it hard for the water reduction reaction to occur spontaneously on the aluminum alloy surface. Consequently, when an electrical load is connected between the anode and cathode, and both electrodes are placed in an electrolyte solution, the electron flow delivers power to the load and hydrogen evolution occurs predominantly at the cathode, according to the second half-reaction above.

As soon as the cell is activated by adding water, hydrogen production (“spontaneous corrosion”) begins at the aluminum anode. While spontaneous corrosion was a desired outcome in our hydrogen generator discussed earlier, in the aluminum-water cell it decreases energy efficiency and reduces the cell’s shelf life. A novel corrosion inhibitor that reduces spontaneous corrosion at the anode was discovered [9] and is proving useful for our design.

Prototype batteries were initially designed and built at MIT, and later greatly refined at OpenWater Power (Figure 9). The most recent prototype had a volumetric energy density of 12 MJ/L.

Future Directions

The aluminum-water reaction is a promising fuel source that can be transitioned to a number of undersea systems. Increases in endurance can significantly enhance capabilities and expand mission roles for both current and future undersea systems. In the two aluminum-fueled power system concepts discussed in this article, energy is extracted from the aluminum-water reaction in different yet complementary ways.

Our next steps in aluminum power system development are to build and test full-scale operational pro-

totypes for both the aluminum-chlorate fuel cell power system and the aluminum-water primary battery. We are planning to design and construct systems that integrate into mid-sized AUVs for system characterization and at-sea tests and demonstrations.

Acknowledgments

The authors would like to thank Bernadette Johnson and Robert Shin of MIT Lincoln Laboratory and Mike Wardlaw of the Office of Naval Research for funding this work. The authors would also like to recognize all of the long hours and hard work put in by the MIT students enrolled in the Engineering Design and Development courses in the Department of Mechanical Engineering. Finally, we express gratitude to the researchers at OpenWater Power and at Woods Hole Oceanographic Institution for their participation on this project. ■

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Douglas P. Hart is an MIT professor of mechanical engineering and an inventor, cofounder, and board member of three venture-funded companies, including Brontes Technologies Inc., an MIT Deshpande Center spinout acquired by 3M in 2006, and Lantos Technologies, a Deshpande Center spinout founded in September 2011. He is also an advisor

for numerous companies and professional organizations. Prior to joining the faculty at MIT in 1993, he worked as a research engineer for Electromagnetic Launch Research Inc. (now Kaman Electromagnetics Corporation) on satellite propulsion and as a senior systems engineer for Northrop Corporation (now Northrop Grumman) on unmanned drones. He currently teaches and conducts research in the areas of fluid mechanics, design, and instrumentation. His awards include the American Society of Mechanical Engineers' Robert T. Knapp Award for his work in the area of flow diagnostics, and MIT's Joseph Henry Keenan Award for Innovation in Undergraduate Education and Junior Bose Award for Excellence in Teaching. He holds a bachelor's degree in aeronautical/astronautical engineering from the University of Illinois, a master's degree in mechanical engineering from MIT, and a doctoral degree in mechanical engineering from the California Institute of Technology.



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Joseph R. Edwards is a member of the technical staff in the Advanced Undersea Systems and Technology Group. Since joining Lincoln Laboratory in 2008, he has developed beamforming algorithms for submarine sonar arrays and vector-sensor fixed arrays, real-time signal processing strings for towed arrays on unmanned undersea vehicles and autonomous fixed

arrays, and automation for fixed sensor array fields. He earned bachelor's and master's degrees in mechanical engineering at Virginia Tech. After working several years in submarine silencing research and development, he completed a doctoral program in ocean acoustics at MIT, where he focused on using active sonar on unmanned undersea vehicles to hunt for buried mines. He then worked in small business, developing sonar simulation software and analysis tools for a variety of naval applications.



Kristen E. Railey is a graduate student in the joint MIT and Woods Hole Oceanographic Institution program in Applied Ocean Science and Engineering. She was previously a member of the technical staff in Lincoln Laboratory's Advanced Undersea Systems and Technology Group. Her research focused on signal processing and controls in

robotics. Prior to joining Lincoln Laboratory, she was a student in the MIT Beaver Works senior capstone class developing alternative energy systems in autonomous underwater vehicles. Her thesis work resulted in her coauthorship of the winning entry in the 2013 American Society of Mechanical Engineers, Fluids Engineering Division, Young Engineer Paper contest. She holds a bachelor's degree in mechanical engineering from MIT.