

## Metal-water combustion for clean propulsion and power generation



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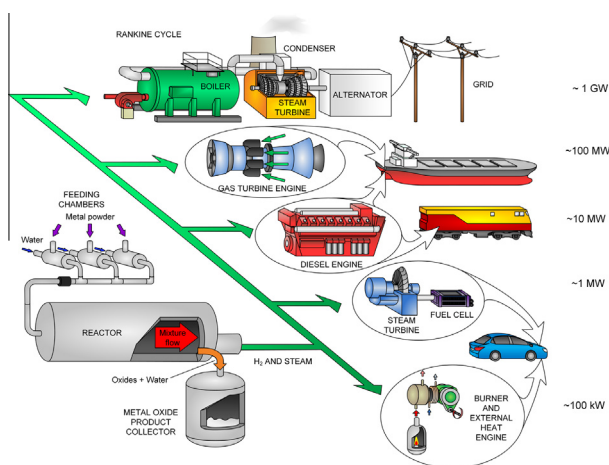
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### HIGHLIGHTS

- Many metals react with water to produce H<sub>2</sub> on demand in exothermic reactions.
- Metal-water combustion leads to higher energy density than batteries or H<sub>2</sub> storage.
- High-temperature metal-water flames maximize system power density.
- Hot H<sub>2</sub> from metal-water reactions is a promising fuel for compact power systems.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Metals are energy-dense fuels that can react exothermically with water to produce hydrogen, and this hydrogen is useful as a propellant for rockets and underwater vehicles or as a fuel for engines and fuel cells. Propulsion systems usually rely on high-temperature combustion ( $T > 3000$  K) of metal-water propellants, while hydrogen-production systems typically employ low reactor temperatures ( $T < 100$  °C). This paper reviews the current state of knowledge of both low-temperature and high-temperature metal-water reactions. Low-temperature reactions allow only the chemical energy contained in the hydrogen to be used, with the thermal energy released during the metal-water reaction being wasted. Metal-water propulsion systems typically make use of only the thermal energy of the metal-water reaction, with the hydrogen being exhausted to produce thrust. This paper proposes several novel applications of high-temperature metal-water combustion that allow the full chemical energy within the metal fuel to be harnessed, including high-speed air-breathing engines and high-power, compact, low-emissions power-generation systems. These technologies promise improved performance by maximizing the conversion of the chemical energy, stored within the metal fuel, into useful work at sufficient rates for high-power applications.

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## 1. Introduction

### 1.1. The need for clean energy carriers and energy-trading commodities

Hydrocarbon fuels, from fossil sources, currently dominate global energy trade and are used in nearly all applications where high power density,  $\mathcal{P}_V$  [kW/L], is required [1]. It is widely recognized that our economy should transition away from energy sources based on fossil fuels to clean and, preferably, renewable low-carbon energy sources [2,3]. Biofuels are one option that has been widely studied [4,5], but estimates indicate that biofuels alone cannot be produced sustainably in the quantities needed to offset current fossil fuel consumption or our future energy needs [6]. It is envisioned that in 50–100 years, most of the energy produced globally could come from clean primary sources [7,8], based on solar, wind, hydroelectric, geothermal, clean nuclear and, eventually, thermonuclear power [9].

Producing electricity from clean energy is, however, only part of the quest. Another key challenge is the development of energy carriers, or renewable-energy commodities, to store, trade, and distribute this clean energy to consumers, such as transportation vehicles, industries, households, remote locations, or foreign countries, in a way that does not undermine its clean production [10,11]. Electrical energy cannot be stored and traded in the same flexible way as hydrocarbon fuels. Losses limit the distance that electrical power can be delivered via power lines, and such infrastructure is costly to build. Electrical storage devices, such as batteries or capacitors, cannot attain the energy densities of chemical fuels [12] and, thus, are not suitable for long-distance inter-continental global trading routes or for high-power vehicles and machinery [11].

### 1.2. Hydrogen as a clean energy carrier?

It has been widely assumed that hydrogen, produced using clean energy sources, will be the future energy carrier that will replace the crucial roles of hydrocarbon fossil fuels in our global economy [2,13,14]. Hydrogen is an attractive energy carrier since it can be produced using clean primary electricity or solar energy [15–17]. Hydrogen has a high specific energy  $\mathcal{E}_{m,f}$ , or energy per unit mass of fuel [MJ/kg or kW.h/kg], and is a highly-reactive fuel [18] that can be used in a wide variety of internal-combustion engines [19,20] or fuel cells [21].

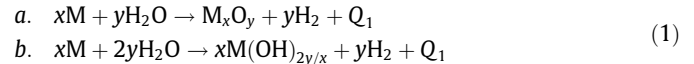
It has become apparent, however, that hydrogen is not an attractive candidate for energy storage and long-distance energy trade due to its very low density, both as a compressed gas or even as a cryogenic liquid [11,13,22]. The boil-off of hydrogen needed to maintain it as a cryogenic liquid also makes it impractical for long-distance energy trade or long-term storage [12,13]. The inherent danger of fire and explosion associated with the extremely flammable hydrogen-air mixtures, due to the high reactivity of hydrogen, is another serious issue that is difficult to address [14,22]. Solids that store hydrogen via chemical bonding, such as metal hydrides, or by molecular trapping, such as carbon nano-tube matrices, have been widely investigated as a way to deliver hydrogen to consumers, yet no practical hydrogen storage technology has yet been developed that can meet the U.S. Department of Energy hydrogen-storage targets [23–26], which are, effectively, targets for the specific energy,  $\mathcal{E}_{m,fs}$  [kW.h/kg], and energy density,  $\mathcal{E}_{V,fs}$  [kW.h/L], of the clean fuel system.

### 1.3. On-demand hydrogen production by reacting metal fuels with water

In contrast, a common chemical compound based on hydrogen is available everywhere on earth for free – ordinary fresh or sea

water – and water contains more hydrogen per unit volume than liquefied cryogenic hydrogen itself. Thus, instead of manufacturing and shipping hydrogen-based compounds, chemical fuels that react with water to free the hydrogen from its bonds with oxygen can be used. Metals are the most obvious candidates due to their high reactivity with water, large energy density, and wide availability. Metals can be produced with clean primary energy through electrolysis, or other methods, and then store this primary energy as chemical energy in the metal fuel that can be released through their oxidation by air, water, or other oxidizers [11,27–33].

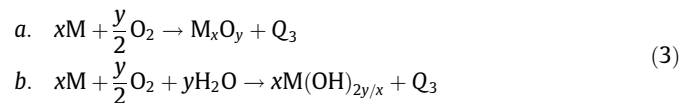
The reaction of a metal (or metalloid) element, M, with water releases the chemical energy stored in the metal as thermal energy and hydrogen. The reaction may occur through different paths:



where  $x$  and  $y$  depend on the stoichiometry of the specific metal-water reaction, and the thermal energy released by the metal-water reaction,  $Q_1$ , may be different between the paths. The products of the metal-water reaction are hydrogen gas and either a metal oxide or hydroxide. The resulting hydrogen from the water-splitting reaction can then be reacted, or burned, with oxygen from the air to release more thermal energy:



The two-step metal-water and hydrogen-air reaction sequence is equivalent, thermodynamically, to the reaction of the metal fuel with oxygen from the air, with or without excess water depending on the reaction path:



where the heat of metal combustion,  $Q_3$ , is equal to the sum of the heat produced from Reactions 1 and 2,  $Q_3 = Q_1 + Q_2$ . Thus, the metal-water reaction can be thought of as a type of chemical-looping system where the hydrogen is simply an intermediate that facilitates the overall metal-oxidation process. The metal-water reaction is often exothermic, producing significant thermal energy,  $Q_1$ , such that  $Q_1$  and  $Q_2$  are nearly equal for many metal-water systems, including aluminum [30–32].

Two main approaches have been investigated to date for harnessing the energetic potential of metal-water reactions: low-temperature metal-water reactors, primarily using aluminum, as compact hydrogen generators for fuel cells or other power systems [30,34–40], or high-temperature combustion of metal-water propellants for underwater [41–48] or space [49–55] propulsion, where hydrogen is typically exhausted to produce thrust. The key limitation to these previous approaches is that the low-temperature reaction wastes the thermal energy of the metal-water reaction,  $Q_1$ , while the high-temperature propulsion applications typically waste the chemical energy contained within the exhausted hydrogen,  $Q_2$ . In either case, the energy-cycle efficiency, defined as the percentage of the energy contained within the metal fuel that is converted to useful energy, and the energy density of the system are significantly reduced.

### 1.4. Specific energy and energy density of metal-fuel technologies

The specific energy,  $\mathcal{E}_{m,f}$  [kW.h/kg], of either a metal-water mixture for producing hydrogen or a metal-water propellant would be given by  $Q_1$  or  $Q_2$ , as appropriate, divided by the mass of the metal-water mixture,  $m_{mix}$ . Lightweight and energetic metals/metalloids, such as boron [56–58], aluminum [30,31,37,41,45,47,59–62], mag-

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