Aluminum and its role as a recyclable, sustainable carrier of renewable energy[*]

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Abstract

An energy system completely reliant on renewables requires an energy carrier to mitigate the geographic and seasonal variability of such resources. The cost of renewable electricity is now below the cost of hydrocarbon-generated electricity, and low enough that it is economically sensible to produce fuels using renewable electricity (Power-to-X). Aluminum is well suited to play the role of "X" in a power-to-X system. Aluminum possesses the characteristics that are most important for a sustainable energy carrier: high energy density, abundance, recyclability, and it is anticipated that the alumina-reduction process will soon be free of carbon emissions. Oxidation of aluminum yields a cycle efficiency of approximately 25% if the product(s) of oxidation are used to power a heat engine with an efficiency of 40%. This compares favourably to other proposed energy carriers, such as hydrogen and ammonia. These fuels yield cycle efficiencies of no more than 23% and 18% respectively, if the carbon-free production route is used to produce the hydrogen and ammonia. Aluminum fuel can be competitive with a $50 barrel of oil if the reduction process is powered by electricity priced at $26/MWh or less.

Keywords— Aluminum fuel, Recyclable energy carrier, Aluminum combustion, Aluminum-water reactions, Energy storage, Renewable energy, Power-to-X

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1 Introduction

A transition towards a power system based on clean, renewable energy is required to fight climate change. Currently, global power consumption is approximately 18 TW, and is expected to double within a few decades [1]. Over 90% of that power is supplied by hydrocarbons [2], the combustion of which is a major driver of climate change.

Electricity produced using renewable energy sources is now cost competitive with electricity derived through the combustion of fossil fuels; however, electricity cannot be stored, shipped and traded in the same way as hydrocarbons. Hydrogen, once expected to replace hydrocarbons, has failed to fulfill this expectation due to its low energy density and associated safety challenges. Thus, the development of an efficient, recyclable, clean energy carrier, with portability comparable to hydrocarbons, has emerged as the bottleneck in the transition to a renewable energy system.

1.1 Climate Change

The Paris Agreement calls for limiting the increase in global average temperature to 2°C above pre-industrial levels, preferably 1.5°C [3]. Currently, the global average temperature is estimated to be 1°C above pre-industrial levels [4], with a corresponding atmospheric carbon dioxide (CO_2) concentration of 412 ppm [5]. Cumulative emissions of CO_2 to the atmosphere are the key determinant of global mean surface temperature increase [6]. Limiting the cumulative CO_2 emissions to below $3650\,\mathrm{Gt}\,CO_2$ will provide a 66% chance of keeping the mean global temperature increase to below 2°C. The inclusion of non-CO_2 forcing factors drops the limit to $2900\,\mathrm{Gt}\,CO_2$ [6]. As of 2011, approximately $1900\,\mathrm{Gt}\,CO_2$ were emitted, leaving an emissions budget of $1000\,\mathrm{Gt}\,CO_2$ [7, 6]. Since then, global emissions have been estimated to be $36\,\mathrm{Gt}\,CO_2$ per year [8], indicating that the CO_2 budget will be depleted by 2038 if current trends continue.

Assuming no major removal of CO_2 from the atmosphere, the increase in temperature associated with CO_2 emissions are effectively irreversible on the timescale of the next few centuries [6]. Fossil fuel reserves have the potential to add another 3670–$7100\,\mathrm{Gt}\,CO_2$ to the atmosphere [6], a value inconsistent with limiting temperature increase to 2°C. Most fossil fuel reserves will need to remain unburned, and the fossil fuels that are used should be invested into the energy transition.

1.2 The need for a new energy carrier

Over 94% of CO_2 emissions are the result of the production and consumption of gas, oil and coal [9]. Jacobson *et al.* estimate that the global energy demand could be met using only wind, water and solar (WWS) as primary energy sources [10]. Using existing technology, solar energy alone could provide 580 TW of power [10]. This research suggests that neither the availability of clean energy nor appropriate harnessing technology is hindering the transition to a carbon-emissions-free energy system. The key remaining challenge is the development of technologies that would allow for the long-term storage of clean energy and the ability to transport and trade that energy globally.

Like hydrocarbons, WWS resources are not evenly distributed around the globe. Regions
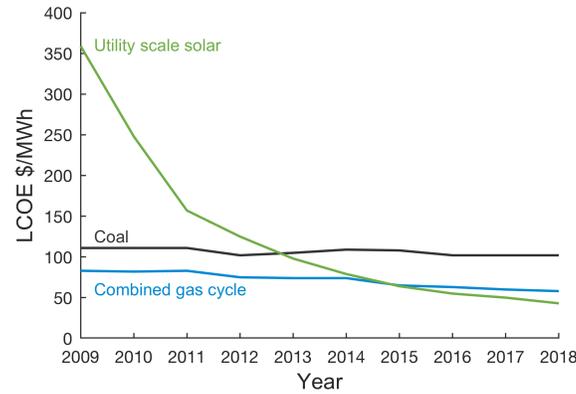
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Figure 1: Levelized cost of electricity. The levelized cost of unsubsidized utility scale solar electricity in the US has steadily declined since 2009. It is now less expensive than coal-fired electricity and combined-cycle natural gas [11].

with access to adequate hydroelectric resources, which can provide a steady power supply to the grid, largely do not need to supplement their power supply. However, regions rich in solar or wind resources must still rely on nuclear or carbon-based fuels for baseload power because of the intermittent and variable nature of wind and solar.

While, historically, cost has been a factor hampering the adoption of WWS energy systems, the economic picture is changing. The International Energy Agency (IEA) predicts that wind and solar photovoltaic (PV) power will be the most competitive power generation technologies for new power infrastructure, based on cost and value, under most conditions [1]. As shown in Fig. 1, in the US, the levelized cost of electricity (LCOE) of unsubsidized solar PV dropped below that of coal-fired plants in 2012. In 2013, the LCOE of solar PV was $104/MWh [1] while the cost of coal-fired electricity was $105/MWh [11]. The LCOE of solar continued to decline. By 2016 the cost was $55/MWH, lower than the $63/MWh of combined-cycle gas [11], and is headed to $30/MWh.

Industrial electricity rates in OECD countries currently range from $45–143/MWh with a mean of $100/MWh [2]. In regions already generating renewable energy, such as Norway and Quebec, industrial electricity rates are as low as $45/MWh and $27/MWh [2], respectively [2, 12].

Historically, electricity has been made from carbon-based fuels because hydrocarbon fuels can provide stable power and were less expensive than WWS power. However, as technology improves and the cost of WWS electricity decreases, a paradigm shift emerges: it becomes cost-effective to make fuels using electricity rather than the *status quo* of using fuels, largely hydrocarbons, to make electricity. Fuels, or energy carriers, produced from WWS power sources would also remove the last hurdle to a complete transition to low-carbon power, because they would act as a mechanism for the storage and transportation of renewable energy.

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[1] US dollars unless otherwise noted

[2] CAD$35 exchanged at rate CAD$1.3 to USD$1

2   The Ideal Energy Carrier

Regions with access to solar resources, or any other economically viable WWS power, are well positioned to capitalize on this paradigm shift. A region with WWS energy resources that surpass local needs can use that excess renewable energy to produce an energy carrier (power-to-X). These energy carriers, "X", would need to be energy dense and have high specific energies, making them easy to store and transport. Their base material(s) would need to be:

- inexpensive
- abundant
- recyclable using renewable electricity
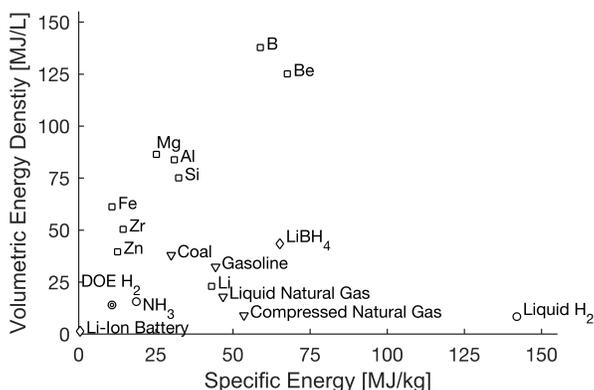- GHG-emissions-free over its lifecycle

Figure 2: Energy density of various materials. The specific energy of aluminum is similar to that of conventional hydrocarbons but has twice the energy density.
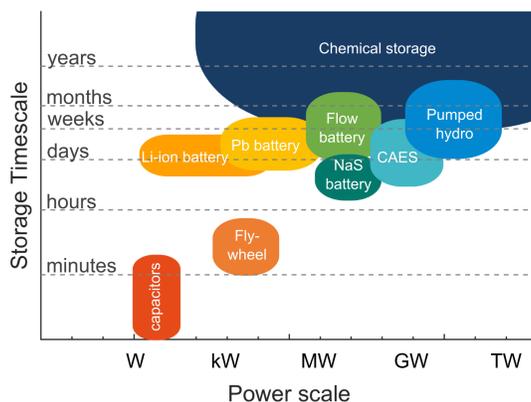

Figure 3: Energy storage devices. Chemical storage is the only energy storage mode that features both the high energy density and the portability required in an energy carrier that can facilitate the long-term storage and trade of clean energy. Adapted from [13].

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Batteries, appropriate for small-scale, short term energy storage, and for use in devices with low power needs, are not suitable as an energy carrier because of their low specific energy and energy density as shown in Fig. 2 [14, 15]. While batteries can provide high power, they can only do so for short periods of time, typically on the order of minutes, before depleting their stored energy. Furthermore, premature discharge in batteries makes long-term storage in batteries inefficient. Premature discharge can be reduced by increasing the internal resistance of the battery but this approach also serves to limit the power density of the device [16]. This inability to provide sustained high power, the typical power requirement in applications such as long-distance shipping, renders battery-powered motors unsuitable for such applications.

Figure 4: Periodic table. Only Al and Fe remain as candidates for a clean energy carrier after factors such as specific energy, availability, toxicity and appropriate reactivity with oxygen are considered.

Fig. 3 shows various options for energy storage devices and illustrates the challenges related to self-discharge and low power densities of batteries. From this figure it is clear that chemical energy storage devices are the most suitable for the time scales and densities needed.

Hydrogen, produced using renewable electricity via an electrolysis process, emits no GHGs when produced or when combusted with air. It has a high specific energy and can deliver sustained, high power when combusted. However, hydrogen's energy density, even as a cryogenic liquid, is very low, necessitating large volumes which are difficult to store and dangerous to transport.

Hydrogen energy research has tended to focus on the development of compounds that allow for the storage of hydrogen in a chemically bonded from. These approaches suffer from high cost, safety concerns and the scaling-up of these technologies would require the creation of untested, large-scale industrial installations for their synthesis and recycling.

At the same time, hydrogen can be generated from water, anywhere on Earth, *via* the highly exothermic reaction of water with light metals such as lithium, magnesium and aluminum. Producing hydrogen *in situ* and on-demand would greatly improve the safety and convenience of hydrogen-fuelled systems by removing the need to store or transport the hy-

drogen [17]. The large-scale industry for metal smelting, especially aluminum, already exists and the (hydr)oxide product of the reaction can be easily recycled.

Ammonia (NH_3), a compound containing only hydrogen and nitrogen, could be made using the primary inputs of air, water and renewable energy (AWRE) so as to not emit GHGs [18]. However, it should be noted that ammonia presents a serious environmental hazard to water systems and some wildlife [19]. Furthermore, direct combustion of ammonia may lead to the formation of NO_x which has a global warming potential (GWP) of 298 on a 100-year horizon [20].

Looking to the periodic table in Fig. 4, it becomes clear that only two elements could reasonably serve as a large-scale energy carrier for renewable energy [15, 21]. Elements in the 15th through 18th groups of the periodic table are eliminated because of their poor or non-existent reactivity with oxygen.

Elements in the 5th period and higher are eliminated because their high molecular mass renders their specific energy too low. Known reserves of scandium, titanium, vanadium, gallium and germanium are too low for them to serve as an energy carrier on the scale required. Beryllium, chromium and manganese are toxic or form toxic oxides. Cobalt, nickel and copper react very slowly with both air and water, while sodium, calcium and potassium react too fast with water thereby posing a safety risk. While silicon holds promise as an energy carrier, only nano-sized silicon particles have, so far, been demonstrated to have reasonable oxidation rates [22, 23, 24]. Carbon must be excluded because its oxides, CO_2 and CO, are known GHGs and hydrogen is also eliminated because of its low energy density.

Of the remaining elements (lithium, magnesium, iron, zinc, boron, and aluminum), only iron and aluminum have known reserves that are greater than the potential demand of that fuel. It is estimated that there is enough bauxite to produce 11 000–15 000 MT of aluminum and enough iron ore to produce 27 000 MT of iron [25]. One TW of power on an annual basis would require approximately 9% of the conservative aluminum estimate or 13% of the iron reserves. The ease of recycling of both metals would mean that supplies would not deplete, a high risk with fossil fuels. Both aluminum and iron are active areas of research [26, 15] and this document will focus on the former.

Aluminum has a high specific energy ($\approx$31 MJ/kg), is safe and easy to store and transport, has a low risk of premature or accidental oxidation if particles are coarse enough, and can be recycled indefinitely. When aluminum oxide is reduced to aluminum, the energy state of the material increases. Similarly to a battery being charged, the aluminum is storing that energy. However, unlike a battery, the aluminum will not self discharge and has a high specific energy and energy density thereby providing a convenient storage and transportation package for the energy. When the stored energy is needed, it can be released through oxidation with water to produce a hot hydrogen-steam mixture [27]. The hydrogen can be used in a fuel cell or combusted in air to power a heat engine. Another alternative is the direct combustion of the aluminum, which releases the energy in the form of heat [26] that can be fed to a heat engine. In both cases the metal oxide (or hydroxide) that is produced can be collected and recycled.

The energy carrier not only allows for the long-term storage of the renewable energy, but also commodifies it. The energy could then be traded globally, to regions with inadequate WWS resources, or stored locally to meet energy demand due to seasonal variability [28].

An energy carrier made from renewable energy would offer a second advantage: a fuelling

system for power applications that cannot use WWS electricity directly. The engines used in applications that require sustained access to high power and have few refuelling opportunities, such as trans-oceanic shipping and long-distance transportation, could be fuelled by aluminum as a clean energy carrier.

The commodification of renewable energy is already taking place. Hydro Quebec, a state-owned power utility, has a hydroelectric power capacity of 45 GW [29]. Quebec's annual electricity demand is approximately 611 PJ, compared to its 720 PJ hydroelectric capacity [29]. The excess of hydroelectricity allows the utility to offer competitive industrial rates which have attracted electricity-intensive industries such as aluminum smelting. The result is that Quebec is the fourth largest aluminum producer in the world [30], despite non-existent bauxite reserves.

In 2018, Sun Metals built a 125 MW solar facility in Australia to supply approximately one-third of the electricity to its zinc refinery [31]. By shifting to solar power, Sun Metals avoids reliance on the coal-fired electricity which the company describes as unstable both in terms of supply and pricing [32]. Although the metals being produced in these examples are not being used as a fuel, it does demonstrate that inexpensive renewables can be exported globally if that energy is used to produce a commodity. Metals are already traded globally as commodities for industry and manufacturing. Metals can also serve as renewable energy commodities for a global clean energy trade.

3 Aluminum Fuel

3.1 Aluminum Production

There are two distinct phases to primary aluminum production. In the first stage, bauxite ore is refined *via* the Bayer process to alumina (Al_2O_3) and, in the second, alumina is reduced to aluminum.

Bauxite typically contains 30–50% Al_2O_3, the balance comprises of silica, iron oxides and titanium oxide [18]. Each tonne of aluminum requires two to three tonnes of bauxite, depending on the Al_2O_3 content. The first step in the Bayer process is the digestion of the bauxite after it has been crushed, milled and washed to increase specific surface area. The crushed bauxite is mixed with caustic soda and fed into a pressure vessel, which contains a solution of sodium hydroxide, and is heated to temperatures ranging from 415 K to 550 K [33]. The temperature, pressure and alkalinity conditions inside the digester are adjusted based on the mineral content of the bauxite [33]. During digestion, any aluminum present dissolves in the form of sodium aluminate and the caustic soda causes any silica present to precipitate as calcium silicate. The contents of the digester are then cooled, the solid impurities are filtered out, and the caustic soda is retrieved for use in future digestion.

The liquid left after filtering is a supersaturated sodium aluminate solution. The solution is control-cooled and seeded with aluminum hydroxide which will allow for the formation of aluminum trihydroxite ($Al(OH)_3$) crystals. Smaller crystals resulting from this process are retained for use as future seeds and the larger ones are calcinated [34]. During calcination, the $Al(OH)_3$ crystals are heated to 1375 K to dehydrate the $Al(OH)_3$ and form Al_2O_3 [33].

The reduction of alumina to aluminum is done using the Hall-Héroult process. Prior to the development of this process, the alumina was melted at temperatures of 2300 K and

a current passed through the molten alumina. Because of the energy intensive nature of melting alumina, the resulting aluminum was very expensive and treated as a precious metal [35]. Rather than melting the alumina, the Hall-Héroult process starts by dissolving the alumina into molten cryolite. This process is more energetically advantageous as it only requires temperatures in the range of 1200 K [36]. The electrical resistance of the molten cryolite helps maintain the cell temperature, as does the thermal insulation provided by a crust which forms at the top of the cell.

A cell potential, usually 3–5 V, causes the oxygen anions (O^{2-}) to migrate towards the carbon anode and the aluminum cations (Al^{3+}) to migrate toward the graphite cathodes. The electrons move from the O^{2-} ions to the Al^{3+} ions forming oxygen and aluminum. The resulting aluminum metal sinks to the bottom of the cell where it can be collected [36].

The use of carbon anodes and cryolite in the Hall-Héroult process pose some significant environmental challenges. The carbon from the anodes, as they are consumed, combine with the oxygen gas to form CO_2. The stoichiometric amount of CO_2 is approximately 1.2 tonnes of CO_2 per tonne of aluminum. The production of the anodes required to produce 1 tonne of aluminum emits another approximately 0.4 tonnes of CO_2, largely due to the combustion of natural gas to power the oven and the volatile organic compounds present in the pitch [34].

The use of cryolite results in the formation of perfluorocarbons (PFCs) gases when the cyrolite electrolytically decomposes. The resulting CF_4 and C_2F_6 have a 100-year GWP of between 6500 and 9200 [37]. Although released in exceedingly small amounts, their high GWPs translate to emissions equivalent to approximately 0.6 tonnes of CO_2 per tonne of aluminum [38], rendering total emissions to 2.2 tonnes of CO_2-equivalent per tonne of aluminum.

3.2 Recycling technologies

Inert anodes, to replace the use of carbon anodes, has been an active area of research for two decades [39, 40]. The challenge is finding anode materials that are electrically conductive, physically and electrochemically stable at the operating temperature of the cell, resistant to corrosion by oxygen and fluoride electrolyte, and both mechanically and thermally robust. The result of this research is the filing of two patents [41, 42] and the formation of Elysis, a consortium which includes Alcoa, Rio Tinto, the Canadian and Quebec government and Apple. The consortium is expected to deploy the inert anode technology widely on a five-year time scale [43] and a commercial-scale batch has already been sold to Apple [44]. The consortium claims that their technology will eliminate all direct and process GHGs from alumina reduction and that existing smelters can be retrofit with the inert anodes, further facilitating the transition to "green" aluminum [45].

3.3 Power generation using aluminum fuel

Both aluminum-air combustion and aluminum-water reactions offer the advantage of scalability to meet the power needs of various applications. In many cases, existing equipment such as diesel engines, gas turbine engines or external combustion engines may be modified to run on the oxidation products of heat and/or hydrogen. Of particular interest are engines used in applications with a sustained demand for high power, such as those used in freight

transport or power generation when renewable electricity is not available. Renewable energy technologies do not currently offer a practical fuelling option for these engines and, as a result, these sectors are still reliant on hydrocarbons.

3.4 Aluminum combustion

Aluminum has previously been used as a fuel in aluminized solid rocket propellants [46, 47, 48] and pyrotechnics [49] because of its high energy content. When using aluminum in a direct-combustion regime, it is more practical to use the resulting heat for process heating or to power external combustion engines (ECEs) because the combustion times of micron-scale metal powders are too slow for internal combustion engines (ICEs) and pose other challenges for engine designers [15, 50]. The combustion of nano-metric powders results in nano-oxides which are difficult to separate from the hot exhaust gas and capture for recycling [15].

In aluminum-air combustion, as with all flames, the reaction kinetics, as well as heat and mass diffusion, are important. In metal flames, two combustion regimes have been recognized: the diffusion limited regime and the kinetically-limited regime [51]. The latter regime is similar to that of any gas-phase mixture with the reaction rates exponentially dependent on local temperature and linearly dependent on oxygen concentration. Diffusion-controlled combustion begins in the kinetic regime but, if the reaction kinetics are sufficiently fast, the aluminum particles can ignite and transition to the diffusion-limited regime [51]. Ignition of a particle is the point at which the rate of heat release from the surface of the particle exceeds the rate of heat loss, allowing the sudden transition to the diffusion-limited regime.

In the diffusion-limited regime, diffusion of the oxidizer to the reaction surface limits the rate of reaction, therefore reaction rates are relatively independent of the surrounding temperature conditions. Ignition takes place at the level of individual particles forming a flame, in effect each particle burns as a "micro reactor" once ignited.

The advantage of direct combustion can be understood by examining the power density, P/V [kW/m^3], expression below. Equation 1 shows that the power density of a chemically-fuelled power system can be estimated as the product of efficiency, η, the specific energy of the fuel, ε_m [kJ/kg], and the density of the reactants, ρ_m [kg/m^3], (or the energy density, ε_V (kJ/m^3)) and the characteristic reaction rate $\dot{\omega}$ (1/s) [26]:

$$P_V \propto \eta \varepsilon_m \rho_m \dot{\omega} = \eta \varepsilon_V \dot{\omega} \tag{1}$$
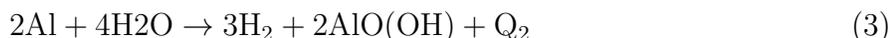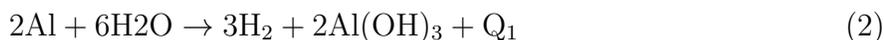
Equation 1 implies that high specific energy and fast reaction rates are necessary to achieving high power densities. High specific energy is a characteristic of the fuel and air mixture. High pressure air is used to increase density, and enables the extraction of mechanical work. Fast reaction rates are characteristic of a combustion regime.

3.5 Aluminum-water reactions

The water oxidation mode of aluminum yields heat and hydrogen, both of which can be used for stationary power [52, 53, 54]. The use of aluminum-water reactions for underwater propulsion has also been studied [55, 56]. The reaction of metals with water to produce hydrogen has been studied since the 1920s, starting with ferrosilicon and sodium hydroxide

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[57]. The advantage was that hydrogen, needed to fill naval balloons, could be produced in the field using relatively safe, compact reactants. Attention has shifted towards aluminum as the fuel in such systems because it has a high hydrogen yield of approximately $1.2\,\mathrm{L_{STP}}$ of hydrogen per gram of aluminum.

The aluminum-water reaction follows one of three reaction pathways:

$$2Al + 6H2O \rightarrow 3H_2 + 2Al(OH)_3 + Q_1 \tag{2}$$

$$2Al + 4H2O \rightarrow 3H_2 + 2AlO(OH) + Q_2 \tag{3}$$

$$2Al + 3H2O \rightarrow 3H_2 + Al_2O_3 + Q_3 \tag{4}$$

All three reactions yield the same amount of hydrogen from aluminum, as well as thermal energy $(Q_{x=1,2,3})$ on the order of 800–900 kJ, with only the stoichiometric amount of water (and subsequent reaction product) changing [58]. The solid reaction product of aluminum (hydr)oxide can be recycled. Recent work has shown that the reaction product can be tuned by controlling the pressure conditions of the reaction [59].

Although thermodynamically predicted to react with water above 273 K, a passivating layer of dense aluminum oxide prevents oxidation [60]; Aluminum's readiness to react with air causes this layer to form after any exposure to air. The layer grows to be 2–3 nm thick, before stopping, regardless of the amount of bulk aluminum beneath [58]. The passivation layer contributes to the safety and longevity of aluminum as a fuel because it protects the bulk aluminum beneath from oxidation, either by air or by water, under ambient conditions, and does not grow over time.

The aluminum-water reaction occurs at the interface between the protective oxide layer and the bulk aluminum, rather than on the surface of the aluminum oxide [61] . In order for the reaction to proceed, the passivation layer must be compromised by creating the right conditions. This property renders aluminum a very safe vector for energy storage.

4   Scaling aluminum to one TW

To provide one TW of power for one year, approximately $1025\,\mathrm{MT}^{3}$ of aluminum would be needed, assuming that both the thermal and any chemical energy evolved during the oxidation process are utilized. This also assumes that the period for recycling is one year; less aluminum would be needed if the recycling period were more frequent. For comparison, global steel production currently sits at 1800 MT per year [62]. Current production of primary aluminum is 60 MT per year, with a global capacity of 77 MT [30].

Adoption of aluminum fuel technology, as with adoption of any new technology, would likely follow a logistic growth model as a function of time, t:

$$f(t) = \frac{C}{1 + \alpha e^{-\beta t}} \tag{5}$$

where C, in this case, is the total required capacity of 1025 MT, β is the logistic growth rate constant, and α is a constant related to the ratio of the final to the initial amount of aluminum available for fuel:
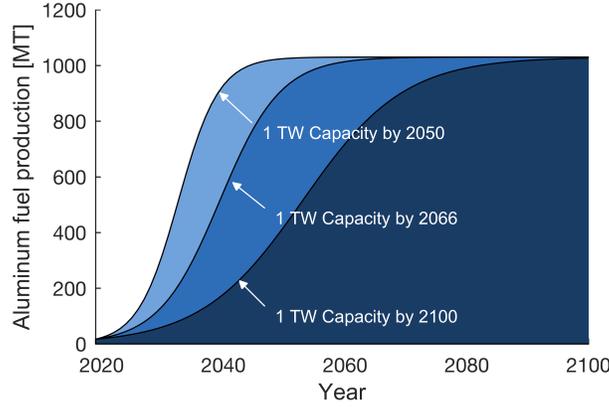
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[3] 1 MT=1 million tonnes=1 billion kg

Figure 5: Required aluminum production. Scaling aluminum fuel production to 1025 MT per year, the fuel needed for 1 TW capacity, would require an average growth rate of 26% during the first 15 years. Average growth rates of 18% or 11% during this time period would see this target hit by 2066 or 2100, respectively.

$$\alpha = \frac{C}{f(0)} - 1 \qquad (6)$$

Here, we assume the delta between current primary aluminum production and capacity is immediately put into service, yielding an initial amount of aluminum available for fuel: $f(0)$=17 MT. Based on these assumptions, an average growth rate of 25% in the aluminum fuel sector over the first 15 years would put the sector on track to achieve 1025 MT aluminum fuel production by 2050, as shown in Fig. 5. The translates to a 12% growth in the overall primary aluminum in the same time period. An average growth rate of 18% and 10% over the same period would see this target reached in 2066 and 2100, respectively. Growth in early years would be limited by the availability of reduction facilities, installed WWS capacity, as well as the technologies to convert the stored energy to work.

4.1 Energy requirements for aluminum production

The world average energy intensity is approximately 73 PJ per MT of primary aluminum [63, 64]. Secondary aluminum production typically only involves the re-melting of aluminum and therefore requires approximately 5% of this initial energy input [38]. However, the recycling of aluminum fuel oxidized in air or with water would require the reduction step, but not the ore refining step, and should be thought of as being closer to primary aluminum production than secondary aluminum production.

To recycle alumina, the product of aluminum oxidation, back to aluminum requires 50 PJ per MT of aluminum [65]. The products of the aluminum-water reaction, $Al(OH)_3$ and $AlO(OH)$, would need to be re-calcinated, a process which could add approximately 4.25 PJ to the process [66]. Re-calcination could be avoided if conditions inside the aluminum-water reactor, *e.g.* temperature and pressure, were tuned to favour the production of Al_2O_3 [59].

A global increase of between 1.6 TW and 1.8 TW of renewable electricity capacity would be needed to provide the energy required to produce and recycle 1025 MT of aluminum per

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year. The 0.2 TW range reflects the power requirement for re-calcination, should this step be necessary. The growth rate of renewable energy capacity is directly linked to the growth rate of aluminum production. Such smelters would necessarily be located in regions with minimal seasonal variability in their access to renewable energy.

5 Cycle efficiency and economics

5.1 Cycle efficiency of aluminum fuel

The environmental, energetic (approximately 23 PJ per MT of aluminum) and monetary cost associated with the Bayer process need only be "paid" once. After the first oxidation cycle, the aluminum oxide would only need the energy inputs associated with the reduction process. Considering the energy content of the aluminum is 31 PJ per MT, the energy storage efficiency of aluminum fuel is approximately 62%. A cycle efficiency of almost 25% is achieved if the heat from the oxidation reaction is fed to a heat engine with an efficiency of 40%. The same cycle efficiency is reached if the water oxidation route is taken and both the heat and hydrogen produced are used for power in the same heat engine. If re-calcination is required, then the cycle efficiency is about 23%.

A potential early use case for aluminum fuels is to use existing scrap aluminum that has accumulated in remote regions or regions that have suffered natural disasters, and where collecting and transporting the metal for recycling is not cost efficient. Besides the "free" power provided, the use of such scrap for power would resolve the issue of waste and provide a valuable by-product of aluminum oxide or hydroxide.

5.2 Cycle efficiency of hydrogen

It is useful to compare the cycle efficiency of aluminum fuel with other renewable energy carrier candidates that would not emit any GHGs during their lifecycle. Although its energy density is very low, hydrogen is worth addressing because it is a viable fuel to replace hydrocarbons in many high-power applications. The efficiency of producing hydrogen via electrolysis ranges from 63–71% for alkaline water electrolysis (AEL) and 60–68% for proton exchange membrane (PEMEL) processes in commercial settings [67, 68]. The energy required to compress hydrogen to 700 bars for transportation is approximately $5 \, MJ/kg_{H_2}$, however the real value is closer to 10% of the energy content of the fuel due to losses during filling of the tank and pre-cooling procedures [68]. To compress hydrogen to a liquid requires approximately 30% of the energy of the fuel [68].

Assuming the hydrogen is used to fuel a heat engine with an efficiency of 40%, the cycle efficiency would be between 20% and 26%. The 26% cycle efficiency could be realized using the most efficient AEL process and compressing the hydrogen to 700 bars.

5.3 Cycle efficiency of ammonia

Ammonia requires hydrogen and nitrogen as inputs. The hydrogen component of ammonia can be made via electrolysis of water using renewable electricity, the nitrogen captured from air and the two gases are fed into a Haber-Bosch reactor. This method of ammonia

production requires an energy input of 36–43 PJ per MT_{NH_3} of ammonia [18], which has a specific energy of approximately 19 PJ per MT.

If the ammonia is not to be used directly, but rather simply using the nitrogen as a means of stabilizing hydrogen molecule (similar to the role of carbon in hydrocarbon fuels), then the ammonia would require a "cracking" process to retrieve the hydrogen. Ammonia "cracking" requires an energy input of 5 PJ per MT_{NH_3}, or 7 PJ if the process is to include compression of the resulting hydrogen [18]. The energy efficiency at this stage is approximately 38–44%. If the resulting hydrogen is used to fuel the heat engine described above, then a cycle efficiency of between 15–18% can be expected. Higher cycle efficiencies may be realized if the hydrogen is used to power a fuel cell or if the ammonia is combusted directly [18], but the latter carries the risk of NO_x formation and along with other environmental risks.

6 Economic considerations of aluminum fuel

All but one of the eleven recessions since the Second World War immediately followed a spike in energy prices [69] indicating that there is an economically tolerable price range for energy. Below the lower price limit, the incentive to produce the energy is not present and, above the upper price limit, the market is not willing or able to buy the energy and the economy slows. The World Energy Agency states that oil prices around $100 per barrel is the upper limit to what the global economy can tolerate without risking recession, however prices around $50/barrel are preferable for growth scenarios.

The price of crude oil represents 45% of the retail price of diesel and refining of diesel represents another 13% [70], placing the cost of diesel at approximately 28% higher than crude oil. A barrel of oil contains approximately 1.7 MWh of energy. The cost of diesel derived from a $100-barrel of oil is $128, translating to an energy price of $80/MWh. A $50-barrel of oil provides energy, in the form of diesel, at $40/MWh

Fig. 6 compares the price of energy in the form of potential clean energy carriers to the price of energy derived from diesel. The energetic content of one barrel is equal to approximately 197 kg of aluminum, therefore, to be competitive with an energy price of $80/MWh, the net commodity price of aluminum fuel would have to be $652/tonne or better.

A key component of the aluminum fuel cycle is the collection and recycling of the aluminum oxide. Each kilogram of aluminum produces 1.8 kilograms of aluminum oxide. If that oxide is sold at the commodity price of $330/tonne [71], users of aluminum fuel would receive $594 for each tonne of aluminum fuel used. This means that the commodity price of aluminum could be as high as $1247/tonne while keeping the net commodity price at $652/tonne. The value of the solid product incentivizes the recycling of this commodity.

The cost of electricity accounts for as much as 40% of the cost of primary aluminum [38], which means that the cost of electricity to produce aluminum at $1247/tonne could not exceed $498. One tonne of aluminum requires approximately 14 MWh of electricity [65], capping the price of electricity at $36/MWh, a value which is below some industrial electricity rates today. An electricity price of $26/MWh would enable aluminum to be competitive with diesel produced from a $50 barrel of oil. The maximum electricity price is not simply halved because the commodity price of alumina remains unchanged.
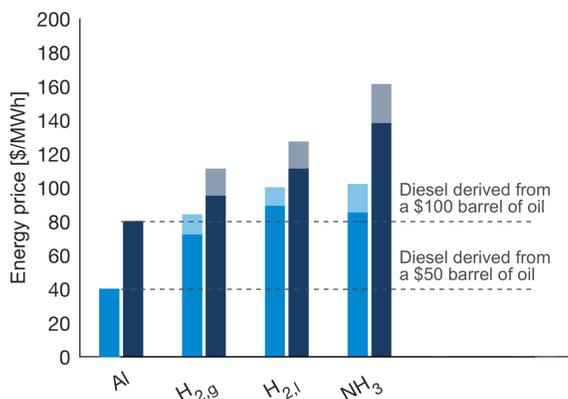
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Figure 6: Energy price for low-carbon energy carriers. The bars show the price of energy derived from low-carbon energy carriers, if the input electricity price were set to $36/MWh (dark blue) or $26/MWh (light blue). The pale region at the top of each bar represents the uncertainty related to the required inputs. The lower price for aluminum, when compared to hydrogen and ammonia, is due to the value of the oxide produced by the fuel. Hydrogen gas is compressed to 700 bar.

This analysis assumes the direct combustion route wherein all the energy of the fuel is released as heat. If the water-oxidation route is used, then it is assumed that both the thermal energy and the chemical energy (hydrogen) of the aluminum-water reaction are used for power. However, if only the hydrogen of the water-oxidation mode is desired, the energy-cycle efficiency drops by half.

Based on an aluminum price of $1247/tonne, the cost of hydrogen produced by the reaction would be $11223/tonne (approximately $287/MWh). The water-oxidation route would also produce 16.2 tonnes of alumina per tonne of hydrogen. If the oxides were sold at the commodity price of $330/tonne [71], the net cost of this hydrogen would be $5346/tonne (approximately $137/MWh). Hydrogen produced via solar thermal electrolysis ranges from $5 780/tonne and $23 270/tonne (approximately $148–$597/MWh) [72].

Another option for excess renewable electricity priced at $36/MWh is to produce hydrogen directly, rather than rather than through an aluminum-water reaction. Hydrogen production *via* electrolysis is 60–71% efficient, depending on the type of electrolyser and operating conditions [67, 68]. To produce 43 kg of hydrogen, the amount of hydrogen required to match the energetic contents of a barrel of oil, would cost $86–$102 in electricity alone. Electricity represents approximately 59% [73] of the cost of producing hydrogen gas therefore, the cost of 43 kg of hydrogen would be fall between $147 and $173.

Compression or liquefaction are required for any storage or transportation of hydrogen, processes which consume between 10% and 30%, respectively, of the energy content of hydrogen [68]. If the hydrogen were compressed to 700 bars, the cost would increase to $161–$187 ($95–$111/MWh); the price would further increase to $190–$216 ($111–$127/MWh) if the hydrogen were liquified. If the electricity cost was dropped to $26/MWh, the cost of hydrogen to match the energy content of a barrel of diesel would be $122–$142 ($72–$84/MWh) for 43 kg of compressed hydrogen and $151–$171 ($89–$100/MWh) for liquified hydrogen.

Although each technology used to produce AWRE ammonia are well understood, there are still many variables associated with the process which prevent a meaningful estimation

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of its cost [18]. However, a minimum price of AWRE ammonia can be estimated if just the cost of electricity needed to produce the required ammonia is considered. Each tonne of AWRE ammonia would require an energy input of 10–12 MWh [18]. Therefore, 3.2–3.8 MWh of electricity would be required to produce 322 kg of AWRE ammonia, the amount of ammonia required to carry 1.7 MWh of energy. The electricity alone to produce this amount of ammonia would cost \$138–\$161. If it is assumed, like hydrogen, that electricity represents 59% of the cost of AWRE ammonia production, ammonia would carry a commodity price of between \$234 and \$273 (\$138–\$161/MWh) to match the energy content of a barrel of oil. The commodity price for this same amount of energy would be \$144–\$173 (\$85–\$102/MWh) if the electricity price were \$26/MWh.

7 Conclusion

The need to transition away from carbon-based energy carriers is evident. For a complete progression of the global energy system to renewable energy, sustainable, recyclable energy carriers are needed. Now that electricity from wind, water and solar resources is more economical than electricity made from fossil fuels, it is prudent to produce energy carriers using renewable electricity. Such energy carriers would allow for the commodification and global trade of clean energy.

Aluminum is a viable option for an energy carrier because of its abundance, energy density, and high specific energy. When produced using renewable electricity priced at \$26/MWh, the resulting aluminum is cost competitive with diesel obtained from a \$50 barrel of oil. Furthermore, aluminum is safe to store and transport and the technology to produce and recycle it without emitting greenhouse gasses is in the process of being rolled out. Scaling aluminum fuel production to 1 TW capacity is feasible in terms of the availability of bauxite ore but several challenges need to be addressed. To have this capacity in place by 2050 would require an average annual growth rate of 25% over the first 15 years as well as a roll out of appropriate burners, aluminum-water reactors and equipment to retrofit existing engines.

8 Funding

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