

Renewable Ammonia as an Energy Fuel for Ocean Exploration and Transportation

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Introduction

In the United States, ocean wave energy is available to most areas near coastlines. The technically recoverable wave power resource is estimated to be 1170 TWh/year, which is approximately 30% of the annual electricity consumption of the United States (EIA, 2020b; Jacobson et al., 2011; Lehmann et al., 2017). However, because of numerous challenges including high structural loading and irregular output, there have been few commercial demonstrations of high-technology, readiness-level wave energy converters (WECs) connected to the grid for electricity generation (Sheng, 2019). Consequently, the focus is shifting to using wave energy for nongrid applications (i.e., those at sea or near remote coastal communities) where barriers to entry, including the cost of energy, are lower (LiVecchi et al., 2019). Potential ocean-based applications include providing power for

ABSTRACT

Renewable power generated from ocean wave energy has faced technological and cost barriers that have hindered its penetration into utility-scale electricity markets. As an alternative, the production of chemical fuels—for example, ammonia (NH₃), which has high energy density (11.5 MJ/L) and facile storage properties—may open wave energy to new markets including ocean exploration and transportation. Electrochemical synthesis of NH₃ from air and water at ambient conditions has been studied and documented in the literature. Based on recent reports, it is possible to achieve an overall conversion efficiency of 10% from wave energy to NH₃ by electrochemically reacting air and water. If all the 1170-TWh/year recoverable wave energy in the United States were used to produce renewable NH₃ fuel as a replacement for hydrocarbon fuels, more than 250 million tons of CO₂ emissions every year would be eliminated without accounting for the small amount of CO₂ emission from the conversion of NH₃. Several potential at-sea application scenarios have been proposed for renewable NH₃ fuel including production and storage for marine shipping and seasonal energy storage for Arctic exploration. Liquefied NH₃ has much higher energy density, both gravimetrically and volumetrically, than a variety of batteries; however, the energy efficiency of NH₃ is lower than that of commonly used batteries such as Li-ion batteries. The levelized cost of storing NH₃ prepared using electricity can be less than \$0.2/kWh, and the storage time can exceed 10,000 h, which indicates that NH₃ could be a promising energy-storage solution that makes use of abundant wave energy. However, safety and environmental concerns involved in the use of NH₃ at sea exist and are identified and discussed in this paper. Also discussed are challenges regarding the electrocatalyst used for NH₃ synthesis and how molecular simulation may help to screen electrocatalysts with high efficiency and selectivity.

Keywords: wave energy, NH₃, alternative fuel, energy storage, electrocatalyst

ocean observation systems and underwater vehicles. The latter application presents the challenge of storage and transmission of the harvested energy, especially if the location of the wave energy device is fixed. Storage using batteries is a direct approach, but the potential benefits of generating energy-dense liquids with this power warrant consideration. Ammonia (NH₃) is a promising candidate for wave energy storage because it can be used as a fuel that does not gener-

ate carbon dioxide (CO₂). The energy density of liquid NH₃ is 11.5 MJ/L, which is higher than that of liquid hydrogen (H₂) (8.491 MJ/L) and compressed H₂ (4.5 MJ/L) at 690 bars. Ammonia is known as a good H₂ carrier, and each NH₃ molecule contains about 48% more H₂ by volume than liquefied H₂ (Lan et al., 2012). The equilibrium conversion of NH₃ to H₂ and nitrogen (N₂) is over 98% at 425°C with a catalyst (Klerke et al., 2008; Lan et al., 2012). Compared

to H_2 , NH_3 is easier to liquify and transport. Ammonia can be pumped to an end user more quickly than a Li-ion battery can be fully charged, and it is much more energy efficient and cost efficient to store and deliver liquid NH_3 than compressed and/or cryogenic H_2 (Lan & Tao, 2014).

In addition to being a H_2 carrier, NH_3 can be used as a fuel in fuel cells, combustion engines, and gas turbines to recover the stored energy (Rollinson et al., 2011; Zamfirescu & Dincer, 2008). Although the use of the electricity generated by a WEC is still limited, the need for energy at sea is increasing especially in the area of powering marine shipping and underwater vehicles and seasonal energy storage for Arctic exploration (Ageev, 2002; Giordano & Raymond, 2019; Kesime et al., 2019). In this paper, we provide an assessment of using NH_3 as an energy storage mechanism and fuel for ocean exploration and transportation, briefly review electrochemical routes to synthesize NH_3 from air and seawater, discuss the role that molecular simulation can play in the development of better electrocatalysts for its production, and offer some perspective on the advantages and limitations of using it as an alternative fuel.

Renewable NH_3 Production

Synthesis of NH_3 is generally accomplished by using the Haber-Bosch process in which N_2 and H_2 react at high temperature and pressure with an iron catalyst to produce NH_3 (see Figure 1a) (Klerke et al., 2008). The energy requirement for making 1 kg of NH_3 using this process is approximately 39 MJ/kg, and world-

wide, NH_3 synthesis contributed 1% of global CO_2 emissions and used 2% of global primary energy, which amounts to 270 million tons of oil (Erismann et al., 2008; Smil, 2001). Large amounts of nonrenewable energy are consumed in the production of NH_3 so the conventional Haber-Bosch process cannot be considered to be “green,” although the price for NH_3 produced from this process is about \$500 per ton, which is cheaper than common liquid fuels in most places in the world (Pfromm, 2017).

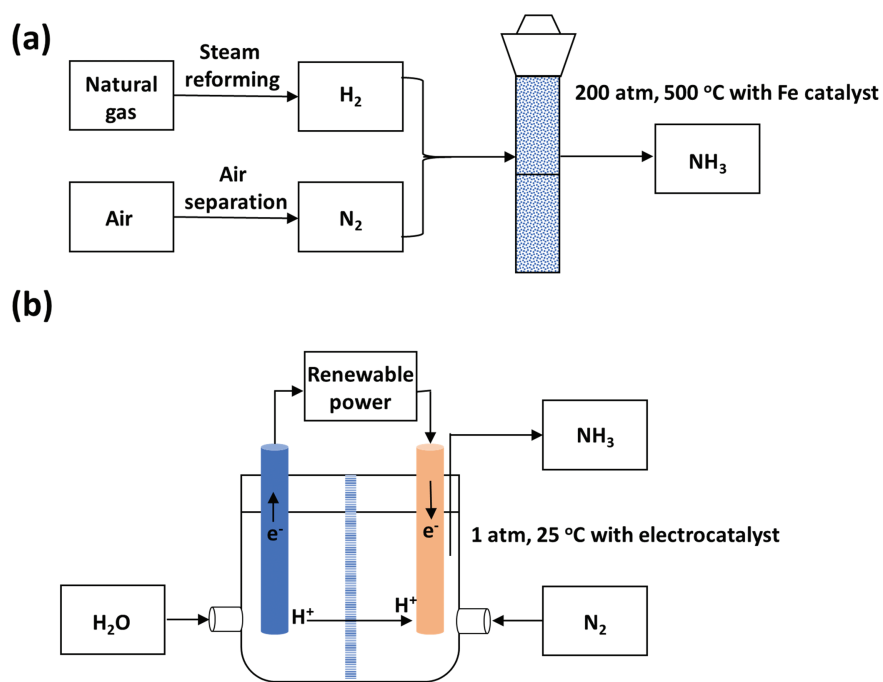
On the other hand, renewable NH_3 can be synthesized electrochemically as shown in Figure 1b. Reverse fuel cells are an environmentally friendly technology that use electricity to make NH_3 from air and water through the N_2 reduction reaction (NRR) under ambient conditions. Nitrogen is reduced to dissociated N

atoms on the cathode that are reacted with protons diffused from the anode to form NH_3 molecules.

The main challenges of electrochemically synthesizing NH_3 are the slow kinetics of N_2 adsorption, N triple bond ($N\equiv N$) cleavage, and the competing H_2 evolution reaction occurring in a similar potential range to the NRR (Jiao & Xu, 2019). Precious metals (e.g., platinum, gold, and rhenium) have been studied as appealing electrocatalysts for the NRR, but precious metal catalysts favor the competing H_2 evolution reaction, leaving insufficient catalytic sites for N_2 reduction to occur (Lan et al., 2013). Therefore, the Faraday efficiency (FE) of this reaction is very low (<1%), which means the percentage of the electrons used to produce NH_3 is very low. Electrocatalysts that can achieve a high FE are needed to make the electrochemical synthesis

FIGURE 1

Ammonia production processes. (a) Haber-Bosch method used in industry. (b) Reversible fuel cell reaction (gentler reaction) powered by renewable energy.



of NH_3 from seawater and air more economically viable.

Recently, interest in developing NRR electrocatalysts that are based on naturally abundant materials has increased (Cui et al., 2018; Guo et al., 2018; Jiao & Xu, 2019), but most of the catalysts investigated in laboratory environments are not efficient or selective enough for practical applications of NRR. Because of low efficiency and low selectivity, the amount of NH_3 produced in the experiments has been limited. This makes measuring the products difficult so a rigorous protocol that is not readily available in many laboratories is needed (Andersen et al., 2019; Tang & Qiao, 2019). Therefore, a primary task in this field is to develop more accessible and reliable methods for efficiently screening catalysts (Tang & Qiao, 2019).

Computational Approaches to Study Electrocatalysts for NH_3 Synthesis

NH_3 synthesis from its constituent parts— N_2 and H_2 —is an energy-intensive transformation because it requires the activation and dissociation of the very stable $\text{N}\equiv\text{N}$ bond (~ 9.8 eV) (Pauling, 1960). As a result, efficient catalysts are required to activate and dissociate N_2 at low temperatures. Electrocatalytic NH_3 synthesis offers an alternative green way using catalysts that accommodate stable electron-donating environments (Abghoui & Skúlason, 2017). Recent progress in NH_3 synthesis shows that electrocatalytic reduction of N_2 to NH_3 is an attractive approach, which allows NH_3 synthesis to operate under benign conditions in a distributed manner with an electrolysis cell powered

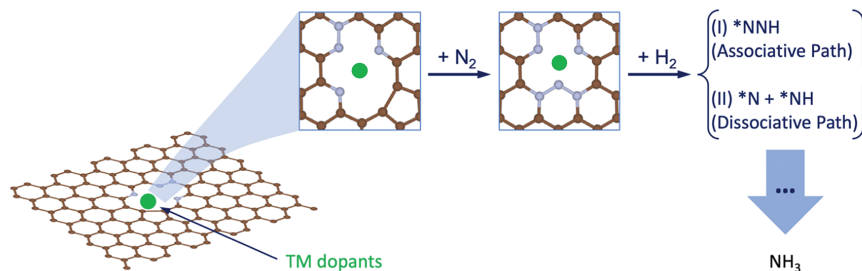
by electricity (Qing et al., 2020). Still, a key component of electrochemical NH_3 synthesis is the use of appropriate catalysts. Besides conventional bulk-like materials such as hematite (Licht et al., 2014), ultra-thin electrocatalysts such as doped graphene (Yu et al., 2018) have been used. Hattori et al. (2020) recently reported a novel heterogeneous catalyst based on a solid solution of CaH_2 and CaF_2 formed at low temperatures. The catalytic performance is attributed to weak ionic bonds between Ca^{2+} and H^- ions. They also emphasized that understanding the atomistic details of electrocatalytic systems can help develop energy-efficient and environmentally benign approaches to efficiently cleave the strong N_2 bond and provide a facile stream of H and electrons. Graphene is used widely in catalysis (Machado & Serp, 2012) where it is used either as a support to immobilize active sites or as a metal-free catalyst. Normally, graphene is chemically inert; however, its catalytic capacity can easily be modified and enhanced by functionalization or doping (Machado & Serp, 2012). Recent studies have demon-

strated that graphene doped with Br (Yu et al., 2018) or N (Mukherjee et al., 2018) provides an effective new way to design new catalysts for electrochemical synthesis of NH_3 . In this study, we built large computational models to elucidate the mechanistic steps of N_2 activation and subsequent electro-reduction. Here, based on a recent N-doped graphene catalyst model (Mukherjee et al., 2018), we examined the effect of defected N-doped (N_4 -defect) graphene (see Figure 2). The N_2 molecules are electrochemically reduced to NH_3 molecules via two possible pathways: 1) an associative pathway in which N_2 is adsorbed and then reduced by H-addition ($^*\text{NNH}$) and 2) a dissociative pathway in which N_2 is dissociated to $^*\text{N}$ species that are adsorbed and further hydrogenated.

For the reaction $\text{N}_2 + 6(\text{H}^+ + \text{e}^-) \rightarrow 2 \text{NH}_3$ (*), the free energy of a proton-coupled electron transfer electrochemical reaction needs to be computed. This can be done if the free energy of $\text{R} + (\text{H}^+ + \text{e}^-) \rightarrow \text{RH}$ is computed as (Nørskov et al., 2004): $\Delta G = E(\text{RH}) - E(\text{R}) - \mu(\text{H}^+ + \text{e}^-)$, where E is the energy of a system and μ is the chemical potential. Here, the

FIGURE 2

Theoretical models used to evaluate novel materials for the electrocatalytic NH_3 production. Defected graphene assists in N_2 adsorption, while doping with select transition metals may further facilitate N_2 activation and reduction at lower potential (carbon: brown; N_2 : blue; transition metal: green).



chemical potential μ of $(\text{H}^+ + \text{e}^-)$ is related to that of $\frac{1}{2} \text{H}_2$ and e^- as $\mu(\text{H}^+ + \text{e}^-) = \frac{1}{2} E(\text{H}_2) + \mu(\text{e}^-)$, where $\mu(\text{e}^-) = eU$ and U is an applied bias against the standard H_2 electrode. There are several proton-coupled electron transfer steps in the overall reaction (*), and this approach will allow catalysts to be screened for a particular electrocatalytic process efficiently and consistently (Cantu et al., 2018; Qing et al., 2020; Skúlason et al., 2012). It also has been used to study the electrochemical reduction of N_2 to NH_3 (Nguyen et al., 2015; Qing et al., 2020; Skúlason et al., 2012). Both pathways need to be investigated using the same approach to determine the mechanistic details and catalyst effects. Detailed results of the study on electrocatalyst using molecular simulation will be published in another paper.

Renewable NH_3 for Ocean Activities

NH_3 Production Scale and Impact

Water is the most abundant source for H_2 , and sea water is abundant. In the most desirable scenario, NH_3 would be directly synthesized from air and water without producing H_2 . Bacteria and some plants can synthesize NH_3 from air and water at ambient temperature and pressure (Lan et al., 2013). However, at practical scales, an electrocatalyst is needed to artificially synthesize NH_3 from air and seawater without N_2 separation and H_2 production.

In early research, the precious metal platinum was used as the electrode and electrocatalyst to generate NH_3 at 20°C and 1.6 V at a rate of $2.78 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$. A 2-M potassium hydroxide solution was the

electrolyte, and the FE of this electrochemical reaction is less than 1% (Kordali et al., 2000). The low FE, which is mainly due to the competing H_2 evolution reaction, can be increased with enhanced selectivity of the NRR. In the literature, an FE of 10% was achieved with a current density of 0.17 mA/cm^2 when an N-doped porous carbon was used as the NRR catalyst for NH_3 preparation under ambient conditions (Mukherjee et al., 2018). The production rate of NH_3 can be estimated to be $1.0 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ using Equations (1) and (2).

$$\text{FE} = \frac{3 * F * [\text{NH}_3] * V}{17 * Q} \quad (1)$$

$$[\text{NH}_3] * V = R_{[\text{NH}_3]} * t * A \quad (2)$$

where F is the Faraday constant $96,485.3 \text{ C/mol}$, $[\text{NH}_3]$ (mol L^{-1}) is the concentration of NH_3 in the electrolyte, V the volume of the electrolyte, Q is the total charge passed through the electrodes during the reaction, t is the reaction time, A is the surface area of the working electrode, and $R_{[\text{NH}_3]}$ is the production rate of NH_3 . Assuming 10% FE and $1.0 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ as the production rate of NH_3 , the energy conversion efficiency of this electrochemical synthesis of NH_3 is about 20% given the energy density of liquefied NH_3 (4.32 kWh/L). Using this value, a marine energy device averaging 20-kW power output can generate up to 1 barrel (an oil barrel is approximately 159 L) of liquefied NH_3 in a week. This 20% energy conversion efficiency for the electrochemical synthesis will be used later in our analysis.

The hydrodynamic power efficiency of a WEC is the ratio of

the power captured to that of the power available within the width of the primary interacting part of the device. The efficiency depends on the type of WEC, and the reported values in the literature ranged from less than 5% to over 70%. We selected 50% power efficiency for our assessment based on a sea trial result in which a pitching type WEC was used (Aderinto & Li, 2019). This is a conservative fixed value assumption compared to the power efficiency calculated later in this paper for a utility-scale WEC, and it is used throughout the calculations in this paper except in the passenger vessel example for which the power efficiency is related to the dimension of the WEC device.

The total NH_3 production of the United States in 2019 was approximately 14 million metric tons (Garside, 2020). If 84% of all the technically recoverable wave energy in the United States (1170 TWh/year) could be converted to the cost-effective clean fuel NH_3 through the marine and hydrokinetic (MHK) energy technology, it would produce as much NH_3 as the total current U.S. NH_3 production. This NH_3 could be used to fuel more than 56 million cars and eliminate 256 million tons of CO_2 emissions every year. In the meantime, the CO_2 emission from the conversion process of NH_3 was estimated to be 3–4 orders of magnitude lower and can be neglected here (Parker et al., 2007).

Potential NH_3 Usage at Sea

Alternative Fuel for Marine Shipping

The potential for wave energy to produce liquid NH_3 fuel for shipping is presented here as a hypothetical use case. Ammonia is under consideration

as a carbon-free alternative to existing fuels such as heavy fuel oil and diesel fuel for ships of the future and is considered by some to be the most promising alternative (DNV-GL, 2019). It has been reported that NH_3 can be directly used as a single fuel or in mixtures with other fuels in a conventional diesel engine. When NH_3 is used alone, researchers have proposed to raise the in-cylinder temperature and pressure through pre-combustion process to overcome high auto-ignition temperature of NH_3 (Lee & Song, 2018). The MAN Energy Solutions company plans to introduce a retrofit package to convert its MAN B&W engines to NH_3 -powered engines by 2025. In term of costs, the expected extra investment for the NH_3 -fueled engine conversion is around 30% (MAN Energy Solutions, 2019). The corresponding CO_2 emission generated from the conversion of the engine is negligible comparing to the reduction of CO_2 emission throughout the lifetime of the NH_3 engine. According to the U.S. Energy Information Administration, ocean-going vessels in the United States consume approximately 375,000 barrels of fuel oil equivalent per day. This total includes approximately 250,000 barrels that may be high-sulfur-content fuel oil (EIA, 2018). If all the recoverable wave energy in the United States were used to produce liquefied NH_3 as an alternative carbon and sulfur-free fuel for marine shipping, 45,856 metric tons of NH_3 could be produced every day based on the previous analysis. The energy density of heavy fuel oil is about 1700 kWh/barrel, and the energy density of the liquified NH_3 is estimated to be 6329 kWh/metric ton (Vogel & Kalb, 2010). If we consider the kilowatt-hour equivalent value, more than 68% of

the sulfur-bearing heavy fuel oil currently used for marine shipping can be replaced by NH_3 , resulting in a significant reduction in CO_2 emissions and complete elimination of sulfur emissions.

Fuel Generation and Storage Station

Given the potential to produce NH_3 from sea water, the option of ocean-based generation and refueling stations is possible. The following scenario of such a station near a high-latitude port is considered. In many high-latitude coastal locations, which are projected to suffer some of the largest effects of climate change, the cost of energy is a key factor in assessing impacts (Day & Rybczyk, 2019). Fuels generated locally for marine transportation and industry (e.g., ferries and fishing fleets) would immediately offer resiliency benefits and potentially offer cost benefits. Shipping costs may decrease, as fuel for the voyage could be sourced near ports in places without access to petroleum fuel supply chains.

Size and power requirements for an appropriately scaled WEC-powered NH_3 fuel generation platform can be estimated by considering the wave resource, the projected power conversion efficiency of a WEC, and energy cost per liter of generated NH_3 . We select a use case of powering marine transportation for the Alaskan island port city of Sitka because of the frequent stops by large ferries and cruise ships and relatively high cost of electricity of 20 cents/kWh, which is 70% higher than the national average (EIA, 2020a). A passenger vessel (MV *Matanuska*) running a voyage between Bellingham, WA, and Sitka along the mainline of the Alaska Marine

Highway System is used as an example. The voyage takes approximately 4 days each way including about 65 h underway at an average diesel fuel consumption rate of 886 L/h, which amounts to a total of 57,590 L of fuel. Using a volumetric energy density of 38 MJ/L for diesel fuel, this is energetically equivalent to 190,297 L of NH_3 . Assuming a similar fuel-to-propulsion conversion efficiency, over the 192-h window between arrivals, an average of 991 L of NH_3 per hour would need to be generated and stored by the fueling station to replace spent fuel for a return voyage. We used wave data from nearby National Oceanic and Atmospheric Administration coastal weather buoy 46084 (NDBC, 2020) and Equation (3) to calculate a wave energy resource intensity in units of watts per meter:

$$J = \rho g^2 \frac{T_E H_S^2}{64\pi} \quad (3)$$

where T_E is the energy period, H_S is the significant wave height, ρ is the density of water, and g is gravitational acceleration. The calculation resulted in an average of 32 kW/m, with significantly higher power available during winter months. Assuming a capture width ratio (i.e., the mechanical energy conversion efficiency per length of the WEC) for a point-absorber WEC consistent with historical examples of the type, a first-order estimate of practical power generation (P_W) neglecting device hydrodynamics is calculated using Equation (4):

$$P_W = \eta(B) * B * J \quad (4)$$

where B is the characteristic dimension of the device (diameter in this case) and

$\eta(B)$ is an empirical efficiency as a function of size (Babarit, 2015):

$$\eta = 1.3B + 5.6 \quad (5)$$

Given the high volume of fuel required, an array of utility-scale WECs rated at 3 MW each will be considered for this application. Individual device dimensions can be adjusted to achieve a high capacity factor (i.e., ratio of average to rated power) of around 30%, resulting in machines that are 50 m in diameter at this site. Power output for such a WEC over a typical year at this location is shown in Figure 3. Combined with an energy-to-NH₃ conversion factor of 21.6 kWh/L (as described above), we then simulate the cumulative production and net stored volume of NH₃ over a typical year (see Figure 4). If starting from no supply, an array of 30 WECs would be required to produce enough fuel for each voyage over

the course of the year, with an excess supply for 17 additional trips because of the seasonality of the resource. Larger arrays of WECs pumping to a centralized storage and fueling platform may meet the needs of multiple large ships servicing Sitka.

Liquefied NH₃ also can be used to power autonomous underwater vehicles (AUVs) through technologies such as a direct NH₃ fuel cell. Liquefied NH₃ used to replace the lead-acid battery currently typically used in an AUV can provide 100 times more energy with the same volume, which can greatly extend the working time and expand the working area for the AUV. Compared to a typical Li-ion battery, liquefied NH₃ still can provide 10 times more energy, and there is no fire hazard when using NH₃. Also, there will be minimal impact on the performance of the AUV from the external water pressure change when the AUV is submerged (Hasvold et al., 2006).

Seasonal Energy Storage for Arctic Exploration

Over most of the ice-covered seas in the Arctic, winter temperatures average between about -30°C and -20°C (-22°F and -4°F) (DMI, 2019). Under these temperature conditions, many batteries including Li-ion batteries and even lead-acid batteries cannot function (i.e., charge and recharge) properly (Gandhi et al., 2009; Goodenough & Park, 2013). The severe snowy weather and lack of sunlight during the winter season make solar photovoltaic panels poorly suited to support scientific activities in the Arctic. An on-site modular NH₃ generator using wave energy at an Arctic station is an ideal solution for the production and storage of NH₃ year-round, particularly during the winter season. The modular system could be installed in the sea under the ice and could produce liquefied NH₃ continuously. For example, a modular NH₃ generator powered by a 20 kW MHK device could produce more than 8,000 L of liquid NH₃ in a year, assuming a 10% FE for the NRR process (Mukherjee et al., 2018). Based on the energy density of NH₃ (4.32 kWh/L), the accumulated NH₃ would contain energy equivalent to approximately 34 560-kWh electrical energy, which is enough to supply a research station in the Arctic during the winter season when transportation of fuel is very difficult or not possible (Soloveichik, 2014).

Safety and Emission Concern

NH₃ can be burned in internal combustion engines or used in a NH₃ alkali membrane fuel cell or a solid oxide fuel cell; however, NO_x emissions are a concern (Duyndlaeher et al., 2010). This can be mitigated by using the available selective

FIGURE 3

Power output for a single 3-MW WEC over a typical year.

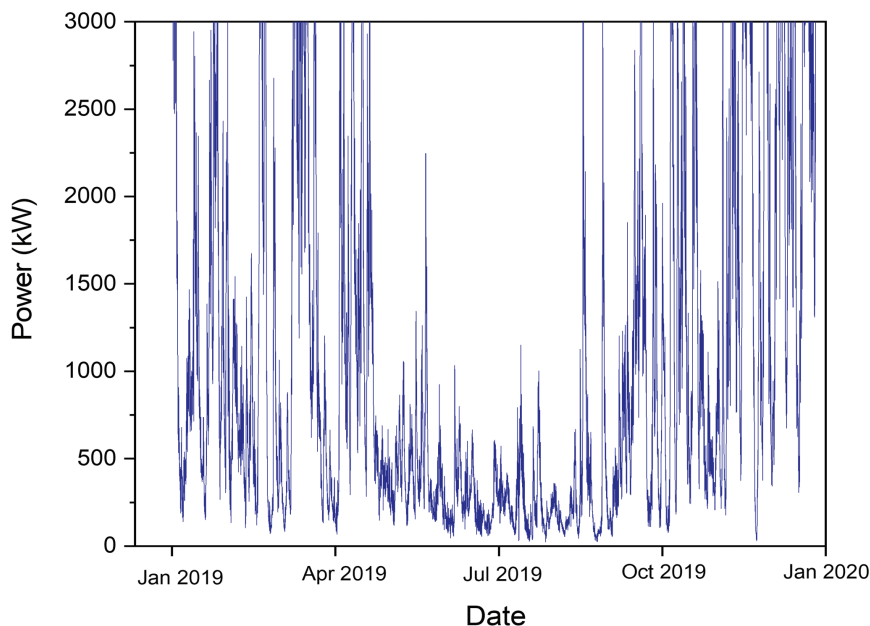
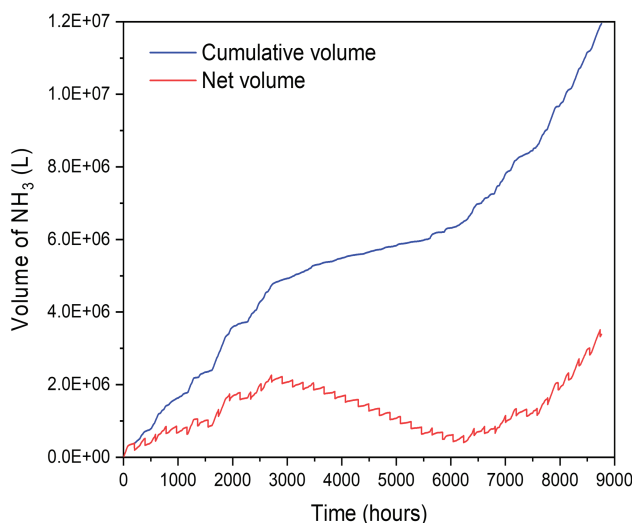


FIGURE 4

Estimated cumulative and net NH_3 production for a 90-MW array powering a long-haul passenger ferry over a typical year.



catalytic reduction technology in which the NO_x is reduced by NH_3 on metal oxide and zeolite catalysts to form N_2 and H_2O (Han et al., 2019). Another route is to convert NH_3 to H_2 so the only emission would be N_2 during generation of H_2 (Lan et al., 2012; Rollinson et al., 2011). In this manner, NH_3 plays the role of an intermediate product to facilitate the collection and transportation of the chemical energy from renewable electricity.

In addition to being a potential pollutant, NH_3 is toxic. If the application scenario is on land, NH_3 is lighter than air so it tends to disperse in the atmosphere. Also, the human nose can detect even 1-ppm NH_3 so it would be as safe as the use of gasoline as a transportation fuel (Reich et al., 2001). However, if NH_3 is produced and stored on the sea, leaked NH_3 could dissolve quickly in the sea water and impact the pH of the water and the living animals. Development of sensing technology and efficient emergency

mitigation measures are needed to safely generate/use NH_3 as a fuel in ocean exploration and transportation activities.

Comparison With Other Energy-Storage Technologies Energy Density and Efficiency

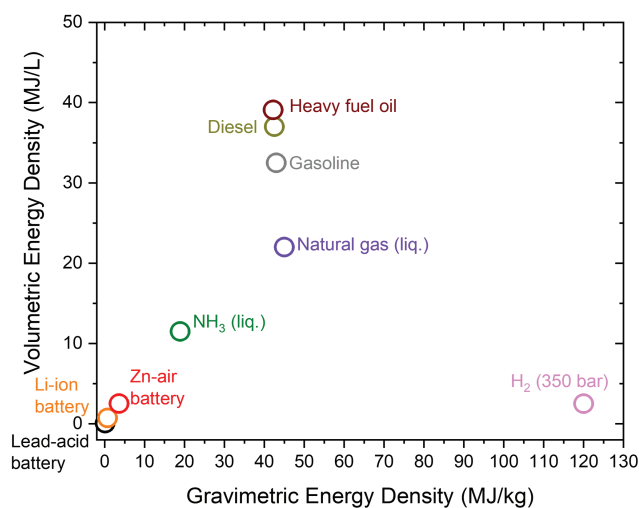
The energy densities of common energy sources for transportation together with liquefied NH_3 are summarized and compared in Figure 5 in terms of both mass and volume base (Davis et al., 2018; Zuttel et al., 2010). Lead-acid batteries have low energy densities in both the gravimetric and volumetric bases. The energy densities of Li-ion and zinc-air batteries are much higher than those of traditional lead-acid batteries. Liquefied NH_3 has a much higher energy density than any battery, which indicates its advantages in applications where volume is a limiting factor for energy storage such as in AUVs.

Compressed H_2 has substantial advantages compared to liquefied NH_3 in mass-basis energy density. However, liquefied NH_3 has more than twice the volumetric energy density than compressed H_2 at 350 bars. Liquefied H_2 has comparable volumetric energy density to liquefied NH_3 , although it is much more difficult to liquefy H_2 than NH_3 . All commonly used hydrocarbon fuels, including diesel fuel, gasoline, liquefied natural gas, and heavy fuel oil, have significantly higher energy densities than liquefied NH_3 . However, hydrocarbon fuels are not renewable, and their use generates greenhouse gas emissions. Some hydrocarbon fuels such as heavy fuel oil currently used for marine shipping emit sulfur oxide compounds, which is an environmental issue (EIA, 2018). Therefore, liquefied NH_3 is a good candidate as a renewable fuel for applications where high volumetric energy density is desired.

Energy efficiency refers to a method of reducing energy consumption by using less energy to attain the same amount of useful output. The total energy efficiency for a Li-ion battery can be as high as 96% because irreversible heat generation is low during the charge and discharge of the battery (Farhad & Nazari, 2019; Zhang et al., 2013). On the other hand, the efficiencies of end-use applications of NH_3 in an internal combustion engine, polymer electrolyte membrane fuel cell, and solid oxide fuel cell range from 20% to 50% (Giddey et al., 2017), which are much lower compared to Li-ion batteries. However, high energy efficiency is not a priority at sea. High energy densities, versatile application scenarios, and the ability to be stored for extended

FIGURE 5

Gravimetric and volumetric energy densities of energy sources for transportation.



time periods endow liquefied NH₃ with unique advantages in applications such as an at-sea fuel station and seasonal at-sea energy storage.

Levelized Cost of Storage

In energy storage applications where renewable electric energy from wave energy is converted into liquefied NH₃ for future use, the levelized cost of storage (LCOS) is usually used in the techno-economic analysis of long-duration energy storage (i.e., more than 20 years). We used Equation (6) to calculate LCOS.

$$\text{LCOS} = \frac{\sum (\text{Capital}_t + \text{O\&M}_t + \text{Fuel}_t)(1+r)^{-t}}{\sum \text{Energy}_t(1+r)^{-t}} \quad (6)$$

where Capital_t is the total capital expenditures in year t , O\&M_t is the fixed operation and maintenance costs in year t , Fuel_t is the fuel cost in year t , Energy_t is the amount of energy released in megawatt-hour in year t , and r is the discount rate. Lazard Asset Management published an analysis of the costs of different energy storage technologies (Lazard, 2017). Based on the data in the Lazard report and a presentation from ARPA-e (Advanced Research Projects Agency–Energy) about NH₃ for energy storage and delivery (Soloveichik, 2016), Figure 6 shows the comparison between the LCOS of NH₃ compared with other energy storage options, including lead-acid batteries, Li-ion batteries, vanadium redox flow batteries, H₂, and compressed air.

Compared to a conventional lead-acid battery, the Li-ion battery and the vanadium redox flow battery have much lower LCOSs and longer storage durations, while compressed air and H₂ have lower LCOSs and longer storage durations than batteries. However, NH₃ has an even lower LCOS and longer storage duration than the other energy-storage technologies. This endows NH₃ an advantage for use in seasonal energy-storage applications such as in Arctic exploration, as discussed previously.

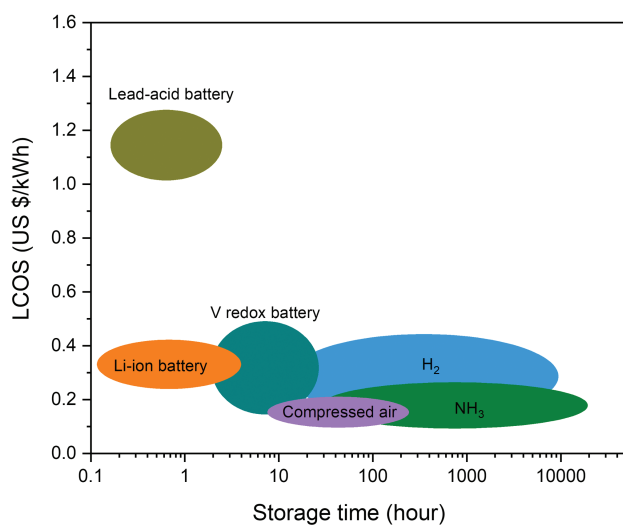
Conclusion and Perspective

Synthesis of NH₃ using renewable electricity from wave energy can help increase the accessibility and use of wave energy that is abundant in the United States. Ammonia can be liquefied easily, stored, and transported for use in ocean exploration and transportation activities. Liquefied NH₃ has higher gravimetric and volumetric energy densities (11.5 MJ/L and 18.6 MJ/kg, respectively) and a lower LCOS (<\$0.25 kWh) relative to currently available batteries, including Li-ion and vanadium redox flow batteries, which indicates a promising future of NH₃ as an alternative energy-storage solution. Based on current estimates of the efficiency of electrochemical synthesis of NH₃ from air and water and the efficiency of large wave energy devices, a large array at significant cost would be needed to generate enough NH₃ to support one ferry. Competing with the availability and much higher energy densities of hydrocarbon fuels for large-scale marine transportation would require an infrastructure effort similar in scope to utility-scale electricity generation. However, it is more reasonable in the near term to use a smaller (approximately 20 kW) MHK device to generate and accumulate enough NH₃ fuel to support the winter energy use of a typical Arctic base. Similarly, producing a smaller amount of fuel for an AUV also is viable if appropriate fuel cell technology is available.

Although NH₃ has great potential to provide seasonal energy storage for the Arctic region, safety and emission concerns need to be addressed. Also, the efficiency and selectivity of the electrocatalysts used in the process to reduce N₂ are still low. Potential fouling, scaling of electrodes, and

FIGURE 6

LCOS comparison between NH₃ and other energy storage technologies.



corrosion of the overall system in the seawater environment add further complexity to the deployment of the NH₃ generation system to marine energy devices at sea. Use of molecular simulation may help guide the development of the NRR electrocatalysts with improved efficiency. The performance of novel electrocatalysts and the electrochemical synthesis system will need to be tested and critically evaluated using real seawater in both laboratory-scale and meso-scale experiments. More reliable experimental methods still are needed to determine NH₃ productivity under realistic conditions. The durability of the system in a seawater environment should also be evaluated. The research described above would further the state of technologies and lead to the realization of renewable NH₃ from the ocean.

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