EMERGING BATTERY TECHNOLOGIES IN THE MARITIME INDUSTRY

NOVEMBER 2021

ABS

TABLE OF CONTENTS

INTRODUCTION

Interest in shipboard battery systems has seen a rise in recent years. The possibility for reducing energy costs and environmental impact makes battery technology valuable for maritime use. Batteries can be used in a wide variety of applications, like peak-shaving in hybrid systems to help engines work at optimal loading and increase efficiency. They can be used to run motors or as a backup power source to reduce generator load. This could lead to reduced fuel costs for both propulsion and electric power generation. Battery systems work well with discontinuous renewable energy sources such as solar or wind energy, allowing their energy to be converted and stored for use at times when electric power generation is not available.

The International Maritime Organization's (IMO's) decarbonization targets make battery systems even more valuable. Reducing fuel consumption through the use of hybrid systems can aid greatly in reducing emissions to meet environmental requirements. For hybrid systems to be effective, there is a need for efficient and sustainable battery technologies that can provide the power needed for such a system. Improved batteries also allow for renewable energy to be further implemented, potentially reducing emissions. As emphasis continues to increase on reducing environmental impact, this may be an essential technology for an eventual shift to more hybrid or even all-electric vessels. ABS has published an advisory exploring the advantages and challenges that come with hybrid systems on vessels, looking at technologies like solar energy and fuel cells that may be useful in such a system [1]. This paper looks specifically at battery technologies and their potential impact on the maritime industry.

Lithium-ion (Li-ion) batteries are currently the most prominent battery technology in maritime applications. They have been shown to be useful for electrical energy storage and electricity distribution on vessels. Li-ion batteries are made of positive and negative electrodes (called the cathode and anode, respectively), an electrolyte and a separator. Despite many advantages over older battery technologies, Li-ion batteries have their own limitations. Li-ion systems require complex monitoring systems to keep them within the proper operating range for temperature and voltage. They are susceptible to thermal runaway, where a temperature rise can cause a self-sustaining chemical reaction and further increase in temperature. This can lead to battery failure and potential ignition of the electrolyte separator and electrodes, causing a fire in the battery system. Battery management systems and fire protection systems must be in place to prevent this from happening and prevent further damage in the event of thermal runaway. Some research indicates Li-ion batteries have very nearly reached their theoretical limit in energy and power density. This limits their potential for maritime applications where higher power and energy levels are needed, as more space is needed for a larger battery system to accommodate increased electrical load requirements.

The safety risks and energy limitations surrounding Li-ion batteries have sparked interest in other battery technologies both existing and being researched now that could be used as alternatives. A few of these technologies are metal-air batteries, REDOX flow batteries, ammonia batteries and solid state batteries. These potential alternatives to Li-ion batteries are in different stages of research, but they may show promise for battery systems to become more practical and widespread in maritime applications in the future.


© saroj mornparn/Shutterstock

METAL-AIR BATTERIES

OVERVIEW

Metal-air batteries (MABs) have the same general structure as Li-ion batteries but use air as a cathode and have a metal anode, with zinc, aluminum and lithium being among the leading metals researched currently. Because the cathode uses oxygen in the air instead of a typical lithium oxide cathode, the theoretical specific energy capacity is only limited by the capacity of the metal anode. This specific energy can be up to 10 times higher than that of a Li-ion battery depending on the MAB type. While many different anodes can be used in MABs, this paper will focus on lithium, zinc and aluminum.

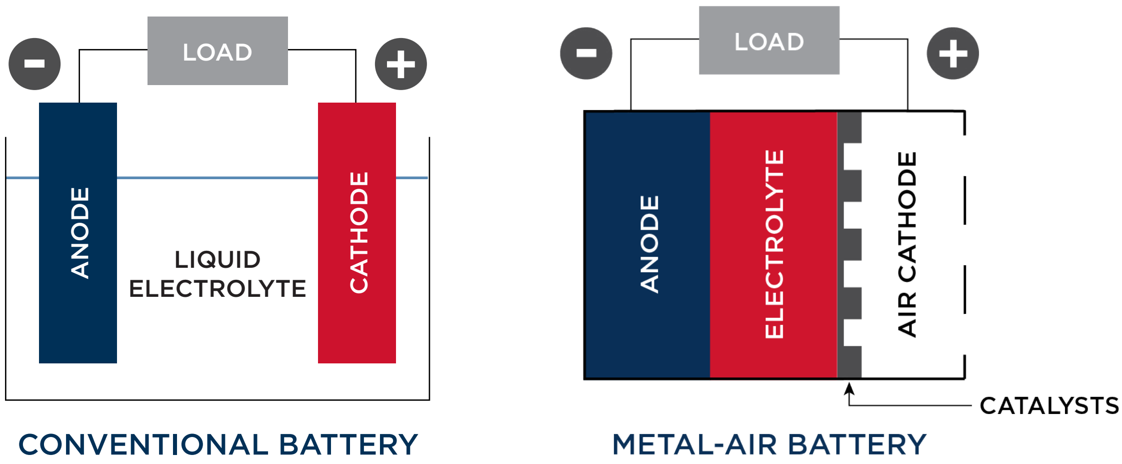

Figure 1: Conventional Battery vs Metal-Air Battery

MABs are widely sought after due to their very high energy density, however, several problems need to be addressed before they become widely available. Electrolytes and electrodes for MABs are generally unstable, limiting the cycle life of MABs significantly. The charge and discharge rates of MABs are limited by electrode reactions, typically reduction reactions at the air cathode. Reactions with air are generally slow, and so it is important that a catalyst be used on the cathode to increase the rate of reaction with air. Increasing the reaction rate increases the polarization performance of the MAB, which in turn increases the maximum power density of the battery [4].

Dendrite formation is also a common issue with MABs. Dendrites are growths of metal through the electrolyte that occur through poorly controlled deposition/gradient at the electrode interface, accelerated by high current density. They can lead to short circuit conditions if they grow large enough and are a common problem in many battery types. Different approaches exist for preventing dendrite formation in MABs, including replacing anode materials with ones with less dendrite formation. This however reduces the specific energy of batteries. Using a coating on the anode, however, helps prevent dendrites without reducing specific energy. This also increases the coulombic efficiency of MABs. Coulombic efficiency compares the discharge capacity to the charge capacity for each cycle of the battery. As with most equipment, efficiency is expected to decrease with time. Batteries with a low initial coulombic efficiency often have a poor cycle life as well. This is another issue with MABs, as their low coulombic efficiency limits their ability to be recharged and reused for long life applications [4]. Solid state electrolytes are also being considered as a means of increasing the stability and preventing dendrites, although the high internal resistance associated with solid state electrolytes means this is still a developing technology. However, more research towards solid state electrolytes could lead to an increase in energy density further in addition to reducing the thermal runaway risks associated with Lithium-air batteries.

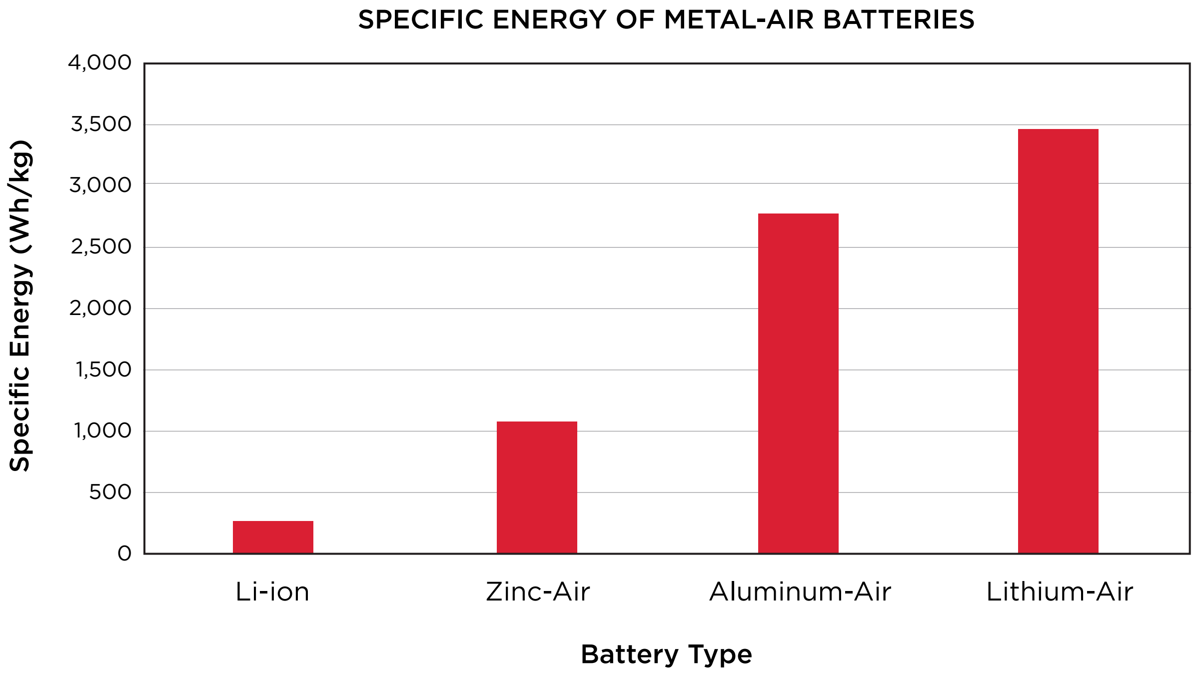

Figure 2: Specific Energy of Metal-Air Batteries

LITHIUM-AIR

PROS

Lithium-air batteries (LABs) are MABs whose anode is made of lithium. LABs have many potential benefits, as lithium is low density and has a very high theoretical specific energy. LABs have a theoretical specific energy of 3,463 Wh/kg, more than 10 times the specific energy of Li-ion batteries, which is around 265 Wh/kg [5]. Improvements to the catalysts used at the air cathode have also increased the power density of LABs, allowing for faster charge and discharge [4]. This gives them great potential as a high energy density, high power density means of storing energy.

CONS

In general, lithium batteries suffer from dendrite formation through the non-aqueous electrolyte which must be addressed to prevent harm to battery operation, or even safety concerns if dendrites were to puncture the separator within the electrolyte and cause a short circuit. Dendrite formation can be reduced through lithium coatings. This also helps reduce the negative effects of humidity and the atmosphere on LABs as they are very sensitive to water, carbon dioxide and nitrogen gas that can come in through the air cathode. Increasing the stability of LABs in air and reducing dendrite formation increases their cycle life, allowing for longer operation without the need for maintenance or replacement. In addition to being sensitive to air, LABs also have the thermal runaway risks associated with Li-ion batteries since the internal chemistry is similar with the exception of the air cathode. This means LABs, like Li-ion batteries, must be carefully monitored with battery monitoring and control systems to ensure their temperature does not rise and cause thermal runaway.

CURRENT STATE

LABs have also seen some development with solid state electrolytes, such as gel polymer and ceramic electrolytes. The use of a solid state electrolyte would increase the energy density of MABs, and in the case of ceramic electrolytes their mechanical strength helps further prevent dendrite formation [4]. Solid state electrolytes are also not prone to thermal runaway, which would make them especially useful for LABs where that is a concern. They do however suffer from poor ionic conductivity, can be unstable with lithium, and the contact between the electrode and electrolyte is often not very good. The stability and contact can be improved through using protective layers between the electrolytes and electrodes, limiting unwanted chemical reactions and improving contact and reducing internal resistance. Even with a protective layer, the stability of the electrolyte remains relatively low, leading to a poor cycle life. This makes current solid state LABs not yet ready for widespread practical application, but if improved, could lead to a safer, very high power and energy battery.

ZINC-AIR

PROS

Zinc-air batteries (ZABs) are similar to LABs, but they use zinc as the metal anode and have an aqueous electrolyte rather than a non-aqueous electrolyte like LABs generally have. The specific energy is lower than that of LABs, 1,085 Wh/kg compared to 3,463 Wh/kg for LABs [5], but the materials for ZABs are generally less expensive, making them a potentially economical alternative.

CONS

ZABs also suffer from instability with electrolytes and dendrite growth. Zinc migration is a common issue, where zinc irreversibly moves from the anode, reducing battery capacity and lowers the effectiveness of oxygen catalysts. ZAB batteries have already seen commercial success as small batteries for use in applications like hearing aid batteries, but these stability issues mean the current technology is not yet rechargeable.

CURRENT STATE

Research is being conducted to allow this already established technology to be rechargeable and therefore be used in a wider range of applications. Like LABs, protective coatings and different electrode materials have been shown to reduce dendrite formation. Separator technology that limits zinc migration helps prevent losses in coulombic efficiency and power density. Electrolyte additives have also shown some success in increasing stability, and the possibility of gel polymer solid state electrolytes is also being explored [4]. This helps to greatly increase cycle life of ZABs, making them more suitable for practical use.

ALUMINUM-AIR

PROS

Rechargeable aluminum-air batteries (AABs) are in extremely early stages of research. They show a high theoretical specific energy of 2,791 Wh/kg which is comparable to that of LABs [5]. The possibility of a battery with specific energy comparable to LABs while using materials that are much cheaper gives AABs a lot of potential benefit.

CONS

Current AABs are generally non-rechargeable due to them being unstable with electrolytes. These non-rechargeable AABs have seen production and are available for commercial use as an alternative to Li-ion batteries. Although not rechargeable, the aluminum anodes and electrolyte can be replaced easily, allowing for the AABs to be reused without total replacement.

CURRENT STATE

Attempts to create rechargeable AABs using this technology have been met with limited success, as they have poor cycle life and lose capacity very quickly [4]. Electrolyte additives that help prevent corrosion have been experimented with and could lead to increased stability in AABs. The stability issues suggest that AABs will continue to see use as high capacity non-rechargeable batteries but will require more research to be a candidate for rechargeable MAB systems.

MATURITY COMPARED TO LITHIUM ION

Rechargeable MABs are still in very early stages of development. While commercial MAB technologies do exist, it may be several years before rechargeable MABs are developed and introduced for practical use, especially in the case of LABs. The potential for a high power, high energy battery makes them a very valuable topic of research, especially in applications such as electric vehicles. Advancement of this technology could lead to all-electric applications becoming more widespread, but there are several challenges to overcome before that can be possible. The electrolytes used in MABs are unstable with both the metal anodes used and the air cathodes. Dendrite formation is a common issue that must be mitigated through some form of protection, and sensitivity to moisture and gases like carbon dioxide further reduces electrolyte stability.

While advances show promise in increasing stability, current MABs have a very short cycle life. Inability charge and discharge for many cycles without a big loss in capacity means MABs are not yet suited for long life applications, which is why current ZABs are used as non-rechargeable batteries. AAB technology is in a similar state, where it is developed to be used for commercial applications but cannot be recharged yet, instead requiring electrolyte and anode replacement. The reactions at the air cathode also happen very slowly, and as such are usually the limiting factor when it comes to power and current density. However, promising advances in catalyst technology have led to high power densities being shown, specifically with ZABs [4]. This would improve charge and discharge rates to be comparable to current Li-ion battery technology.

MARITIME APPLICATION OUTLOOK

CHALLENGES

MABs currently are limited in application by the sluggish reactions with air, and they also have issues common to Li-ion batteries, like dendrite formation. A more difficult problem to resolve is their poor cycle life which makes them non-rechargeable. This non-rechargeability is a big topic of research, since increasing cycle life to allow for charging would greatly increase their usefulness. Potential for thermal runaway in LABs also raises concerns, requiring them to be carefully monitored to ensure safe operation.

POSSIBILITIES

The high energy density of MABs makes them potentially useful in maritime applications. While already used in non-rechargeable applications like hearing aids with ZABs, the rechargeability of this technology is still in development. Since they are similar in operation to Li-ion batteries, they might be used as a plug-in replacement for them with increased energy density if made rechargeable. In this case, the system could be used for load leveling or storing energy from discontinuous renewable sources. Their increased energy density would also increase the range of hybrid or all-electric vessels. Non-rechargeable high energy density AAB systems have been developed for maritime use that provide another source of energy. While non-rechargeable, the system is easily reusable with the replacement of only the electrolyte and aluminum anodes.

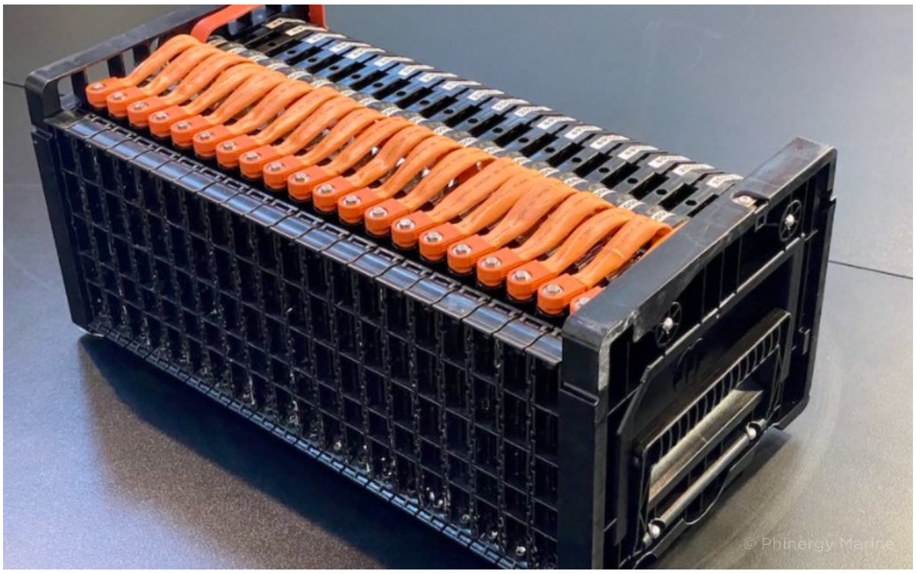

Figure 3: Aluminum-Air Batteries

REDOX FLOW BATTERIES

OVERVIEW

REDOX flow batteries (RFBs) are batteries whose operation is based on a chemical reduction and oxidation (REDOX) reaction between two liquid electrolytes in the battery cell. These electrolytes are stored in tanks and pumped into the cell as needed, reacting across an ion-selective membrane so the electrolytes are not mixed together. The electrolytes are redox pairs, being able to reversibly react with each other to charge and discharge depending on the battery's needs.

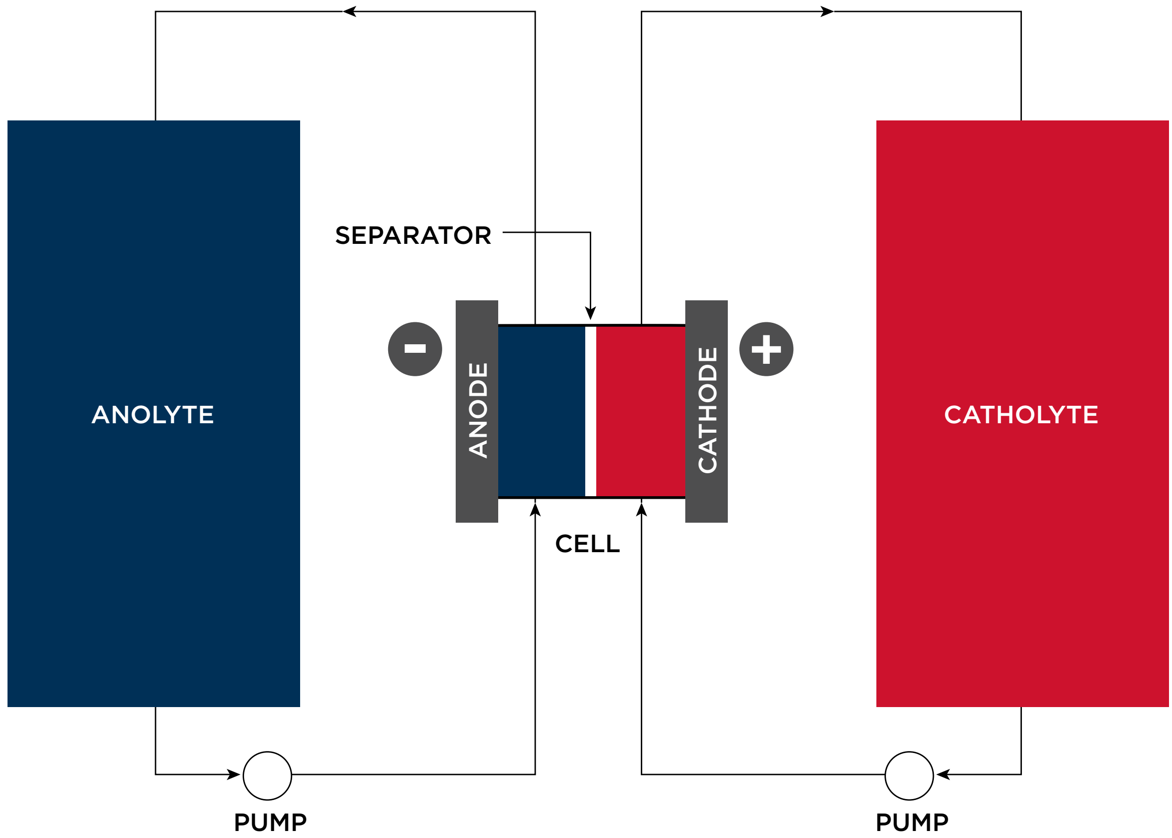

Figure 4: Redox Flow Battery

The positive and negative electrolytes are sometimes called the catholyte and anolyte, respectively. There are two types of RFBs called true RFBs and hybrid RFBs. In true RFBs, the chemical agents that store the battery's energy are fully dissolved in the electrolyte all the time. In hybrid RFBs, at least one chemical is plated as a solid inside of the cells when the battery is charging. Common true RFBs include vanadium-vanadium and iron-chromium systems, while hybrids include zinc-bromine and zinc-chlorine systems. Vanadium as a liquid electrolyte is typically used in REDOX flow batteries. While other electrolytes exist, this paper focuses on vanadium and iron-chromium. The recharging process of RFBs requires electrolyte replacement, typically stored in "refilling fuel tanks".

PROS

RFBs have a unique advantage in that the amount of energy they can store is determined by the amount of electrolyte stored in the tanks. This means that theoretically, a RFB can be designed to store as much energy as needed for an application [6]. True RFBs also have complete separation of energy rating and power rating since the energy stored in the tanks is independent from the power in the cells. This allows energy to be determined by tank size and power to be determined by cell design and connections. Hybrid RFBs do not have this separation since energy storage is dependent on the metal plating inside the cell during charging. This means energy storage depends both on tank size and cell design.

RFBs offer great customizability in energy and power requirements and are easily scalable to meet said requirements. Multiple cells can be run from one set of electrolyte tanks and the cells can be connected in series or parallel, or most often a combination of the two, to meet power and voltage requirements. Since cells can share electrolytes, those cells are always at the same state of charge as each other, making battery management and monitoring systems simpler [6]. These advantages help make RFB systems modular so they can meet a project's specific needs relatively easily.

RFB systems are very stable. Not only do the electrolytes used in RFB systems have low flammability, but they can be used to help manage battery heating to help reduce the need for external cooling systems. This limits potential for thermal runaway, greatly increasing battery safety. RFB systems also have low rates of self-discharge when idle, which is even lower when the system is shut down since the two chemicals can't react with each other. This makes RFBs suitable for applications where long periods of energy storage are needed. Overcharging and full discharges also cause little damage to the batteries, allowing for a more stable operation.

CONS

One of the biggest disadvantages of RFBs is their low energy density. The chemistry of the battery along with the external tanks and other equipment required means these battery systems take up a lot of space, lowering the energy density [7]. This can be a problem when space is limited, making current RFB systems generally more suited to large scale energy storage applications where space is available and the major concern is being able to store a lot of energy.

VANADIUM REDOX FLOW BATTERIES

PROS

Vanadium REDOX flow batteries (VRFBs) are true RFBs whose electrolytes use Vanadium ion REDOX reactions to generate energy. VRFBs have a good cell voltage and are suitable for high power systems if scaled as necessary. VRFBs generally have low rates of self-discharge as well, allowing for longer storage of energy. VRFB systems have been designed and produced successfully with commercial systems having been utilized in onshore applications around the world [8].

CONS

Despite the success seen in the application of VRFBs, they have drawbacks that must be addressed. VRFB materials can be expensive due to vanadium's cost and the many parts of the system such as the cell, electrolyte tanks, battery management system and pumps. However, the lack of a need for a fire suppression system and their low maintenance costs with long lifetimes can offset the initial costs over the length of their use, which can be up to 20 years or more. Vanadium also has limited solubility and stability in the electrolytes used in VRFB systems, which limits the energy density of the system. These stability issues make VRFBs somewhat temperature sensitive, operating between 10 and 40 °C. The use of electrolyte additives and other methods largely mitigate stability issues; however the energy density remains low, and the temperature must still be monitored. The power density is also limited by polarization within the battery system, which also decreases energy efficiency [8].

IRON-CHROMIUM FLOW BATTERIES

PROS

Iron-chromium flow batteries (ICBs) utilize iron and chromium as the active elements in the electrolytes for the REDOX reaction. As a true RFB, they have separated power and energy ratings which helps greatly in designing for specific system needs. A benefit of ICBs is that they have lower material costs as iron and chromium are more abundant than vanadium, allowing for a potentially cheaper alternative to VRFBs.

CONS

ICBs do have some drawbacks compared to VRFBs. Their cell voltages are slightly lower and must operate at a lower current density for optimal efficiency. The thermal management system may be more important as well, since the operating temperature is around 65 °C. The cycle life of ICBs is also lower than that of VRFBs [9]. The other operating parameters however are comparable to VRFBs, making them still a viable alternative.

Table 1: Vanadium and Iron-Chromium Comparison

Electrolyte	Cell Voltage	Energy Efficiency	Voltage Efficiency
Vanadium	1.25 V	80.30%	93.7%
Iron-Chromium	0.94 V	78.40%	93.3%

MATURITY COMPARED TO LITHIUM ION

The high energy storage and easily scalable power makes RFBs a potentially rewarding technology, but with some design drawbacks. The high energy capacity makes RFBs a great option for renewable energy systems that do not generate continuous energy. VRFBs and ICBs have both already seen commercial use, notably in renewable energy but with other applications as well. VRFBs have been used to store energy for wind farms in Japan, and in California, ICBs were used to store solar power as just two examples [10, 11]. The ability for discontinuous renewable energy sources like solar panels or wind turbines to have their energy stored for later use is likely a requirement if they are ever to be considered for practical use, and RFBs have the capacity to hold that energy for later use when it is needed.

RFBs are very easily scalable to meet the requirements of whatever system they are needed for. They are also safer in comparison to Li-ion batteries, as thermal runaway is not possible for RFBs. In the event of overheating, RFBs can simply be shut down and will naturally cool down to safe levels. RFBs can have high initial costs, but low maintenance and long-term storage capabilities reduce their cost over their lifetime. ICBs can lower the initial costs with the drawback of lower cycle life. Additionally, RFBs in general have poor energy density, taking up a lot of volume with their tanks and supporting equipment for a relatively small amount of energy. While not as widely used as Li-ion technology due to space requirements, RFBs have seen commercial use and provide a good alternative for applications that require high amounts of energy storage and have the space required.

MARITIME APPLICATION OUTLOOK

CHALLENGES

A big challenge in using RFB technology in maritime applications is the low energy density. The space requirements for these systems could be a concern in an onboard environment where space and weight must be managed carefully. This must be considered carefully when determining maritime use for these batteries, although research on improving the electrolytes used may increase the energy density, making this less of a concern.

POSSIBILITIES

RFB batteries are a proven technology onshore and have seen many applications. Their energy storage capabilities are high and can easily be scaled to meet given requirements for a vessel. They are also generally considered in the industry to be safe with easy shutdown procedures, with little to no self-discharge while shut down. Their cost over the lifetime is also a benefit, as the high initial costs are offset by long lifetimes and less maintenance requirements. Their applications are similar to those of Li-ion batteries, so they could be considered as a replacement system. The low self-discharge of RFBs could make them very useful for long-term energy storage in addition to standard applications like load leveling. Testing of VRFBs is being done to determine if the technology could be used on vessels despite their low energy density [12].

AMMONIA BATTERIES

OVERVIEW

Ammonia as a source of environmentally friendly energy is a big topic of research because of its potential to emit almost zero carbon. Ammonia has been used as fuel and as a reactant in fuel cells. In addition to being used directly for energy, ammonia can be used as a means of transporting hydrogen for use in hydrogen fuel cells. Hydrogen is very difficult to liquefy and transport, requiring extremely low temperatures. Ammonia can be liquefied at much higher temperatures, making it more suitable for transport and storage. It could then be used as a fuel or be converted to hydrogen. The standard process for ammonia production has carbon emissions, but a new process using reverse fuel cell technology has been developed which can produce ammonia with no emissions, albeit at a slower rate [13]. This shows promise for ammonia potentially becoming a leading source of clean energy. Ammonia batteries are in extremely early stages of research as ammonia has been mostly considered as a fuel for combustion or fuel cell reactions, or as a means of transporting hydrogen for use as fuel. The main application for ammonia in batteries is in thermally regenerative ammonia batteries (TRABs).

THERMALLY REGENERATIVE AMMONIA BATTERIES

OVERVIEW

TRABs are batteries which use an electrolyte with added ammonia and electrodes in a standard cell configuration. The battery discharges normally, producing energy through chemical reactions. However, instead of recharging through an external source of electricity, TRABs use thermal energy to refresh the ammonia electrolyte and recharge. The thermal energy vaporizes the ammonia, moving it through a condenser where it can recharge and move back to its liquid state. The catholyte and anolyte swap sides while discharging and go back to their initial positions when heat is applied, where it becomes charged again. A major benefit is the potential ability for TRABs to operate with low temperature, low grade waste heat. This allows for waste heat normally not suitable for other energy recapturing methods to be used as a source of electricity.

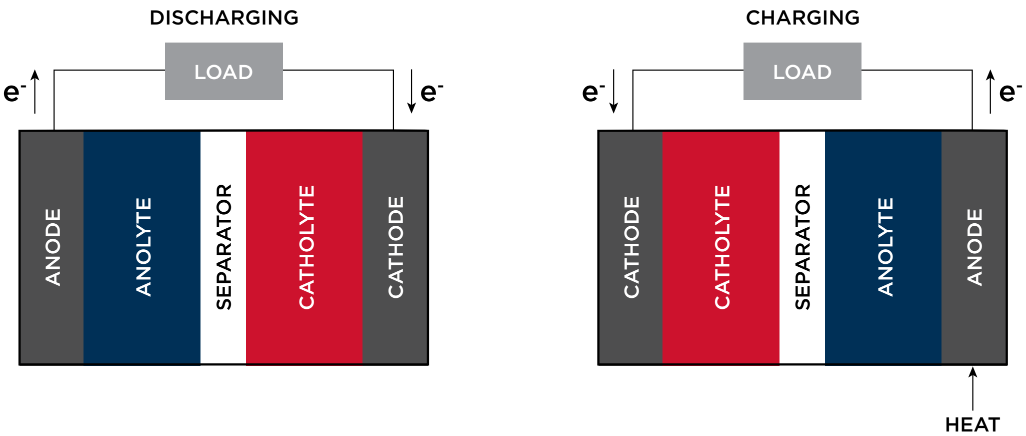

Figure 5: Thermally Regenerative Ammonia Battery

CHALLENGES

While TRABs could potentially produce energy through the use of waste heat, challenges must be overcome first. The first is the very low efficiency of the current TRAB chemical reaction, with a Carnot efficiency of about 13 percent [14]. While it is beneficial that waste heat would be utilized at all, for TRABs to be worth using the efficiency must reach higher levels. Means of improving this efficiency include changing the chemistry of the anode and cathode to allow for increased current density.

More important than improving efficiency is improving the cycle life of TRABs. Current research on TRABs mostly relies on replacing the electrolytes often to ensure proper testing. This makes TRAB technology not truly regenerative, as the system cannot recover the original charge even when sufficient thermal energy is supplied, with regeneration not possible at temperatures below 90 °C. Research shows promise in increasing cycle life through altering the regeneration process, although this still requires higher temperatures [14]. Until this is rectified, TRABs will not be suitable for practical applications as they would require near constant maintenance to ensure proper operation, and they would only be operable above a specific temperature threshold.

AMMONIA FLOW BATTERIES

TRABs have been designed using standard battery geometry, with an ammonia electrolyte and electrodes. However, ammonia flow batteries (AFBs) have been designed and researched as an alternative to standard TRABs. AFBs combine the thermal regenerative properties of TRABs with the design of RFBs, allowing the catholyte and anolyte to be stored in large quantities in external tanks and pumped through the AFB as needed. In the AFB, ammonia is added to the anolyte to produce a potential difference between the anolyte and catholyte, allowing for the production of electricity through chemical reactions.

Using a zero gap AFB design has shown high power densities at low temperatures which increase as temperature increases [15]. Carnot efficiencies have also increased with AFBs, reaching 37.9 percent. The RFB design also allows for the AFB to store a large amount of energy in the external catholyte and anolyte tanks. While cycle life problems remain to be solved, this shows promise for AFBs as a high power density, high energy storage means of capturing low grade waste heat to generate electricity.

MATURITY COMPARED TO LITHIUM ION

TRABs are still in the very early stages of research, and it will likely be many years before they can be commercialized. They show promise in possessing a high power density and being able to run off low temperature waste heat. This could lead to system energy efficiencies increasing because previously unusable waste heat can now be used for electricity generation. However, for this to be realized, a system with greater cycle life must be developed and the efficiency must be increased. TRABs currently quickly lose function when the electrolyte is reused instead of fresh electrolyte being added to the system. This makes current TRABs unsuitable for practical applications, as it is not reasonable to replace the electrolyte very frequently. Since TRABs are so new, there is still much room for potential improvement which may lead to an effective energy storage system.

While AFBs also suffer from poor cycle life, they do show promise with a higher power density and lower temperatures for energy generation. The potential for a high power density and energy storage capabilities makes AFBs another option for recapturing low grade waste heat. RFBs in general are a more developed battery technology however, suggesting that AFBs may be faster in their development compared to TRABs with a traditional battery structure. AFBs maintain the advantages of RFBs being easily scalable and having separation of power and energy rating, giving them further benefits if their limitations can be overcome. AFBs are very early in research stages, and as such are not ready for practical applications.

MARITIME APPLICATION OUTLOOK

CHALLENGES

TRAB technology is in the very early stages of research. The limited cycle life of these batteries indicates that they are not yet useful outside of lab settings where the electrolytes can be manually refreshed. Even when able to cycle, the batteries require high temperatures and additional equipment for complete regeneration. As such, it will likely be several years before these batteries see any kind of production or commercial use.

POSSIBILITIES

The ability to use low grade waste heat for power generation could be very valuable for maritime applications. The possibility for low grade waste heat to be recovered and used for electricity generation could lead to an overall improvement to efficiency. Improving cycle life would make AFBs a great option in general for waste heat recovery due to the high energy storage potential and high power density. The RFB structure would allow for the separation of power and energy ratings, making the system more customizable for specific applications if needed. This does also come with the downsides of RFB systems, namely the lower energy densities. Ammonia is also a renewable resource, making these batteries environmentally friendly.

It must also be considered that TRABs operate differently than Li-ion batteries by design and might not be suitable as a plug-in replacement for Li-ion batteries. Since they regain charge from thermal regeneration and not from an external electrical source, they might not be as well suited for applications like load leveling or storing energy from renewable sources. If such an application were needed, it seems likely that a different type of battery would work better, like a Li-ion battery. As such, it is possible instead that TRABs could be considered as an additional source of electricity generation and storage from heat, and a separate battery system of a different type could be used for storing energy generated by other electrical sources.

SOLID STATE BATTERIES

OVERVIEW

PROS

Solid state batteries (SSBs) are batteries whose electrolytes are solid, unlike the liquid electrolytes found in current Li-ion batteries. SSBs work under the same operating principles as Li-ion batteries, with the electrolyte being the only major design difference. Using a solid electrolyte allows the battery to be more compact and is lighter than liquid electrolyte, potentially increasing the energy density and decreasing weight when compared to Li-ion batteries. The use of a solid electrolyte also makes SSBs safer since solid electrolytes are not prone to thermal runaway like the flammable liquid electrolytes in Li-ion batteries. Solid state batteries are being tested with several different electrode and electrolyte materials, with lithium being a popular anode due to its high energy density.

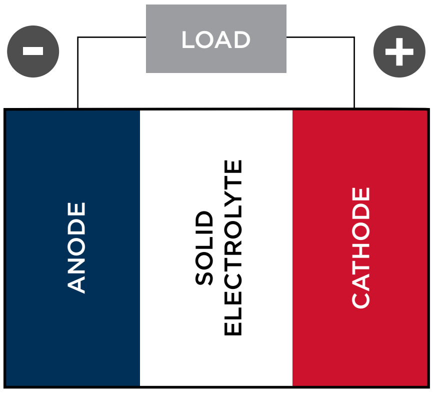

Figure 6: Solid State Battery

CONS

There are many advantages for SSBs over their Li-ion counterparts, but some design issues have yet to be resolved. Volume changes during operation of the cathode, anode and electrolyte lead to poor contact between said components, which causes many issues for battery operation. Since the electrolyte is not contacting the entirety of the cathode or anode, internal resistances at those boundaries are very high, leading to poor conduction. This reduces the power of the SSB, decreasing charge and discharge rates. Poor conduction also leads to rapid deterioration of battery health, giving SSBs a poor cycle life. SSBs are also sensitive to the environment, as exposure to atmospheric gases can change interface chemistry [16]. Solid electrolytes generally have lower room temperature conductivity than liquid electrolytes, so for best operation SSBs must be operated at higher temperatures than Li-ion batteries [17]. The need for a temperature control system in addition to the high material and development cost can make SSBs expensive to research and produce.

As previously stated, the poor contact between cathode-electrolyte and anode-electrolyte interfaces causes high internal resistance and reduced conductivity. This contact issue is further worsened by dendrite and void formation at said interfaces. Voids are gaps formed when stripping Li metal from the anode during discharge. This further decreases the contact area between the anode and electrolyte, increasing current density in the areas where contact still remains. During battery charging, Li metal is plated back onto the anode. However, when current densities are too high, charging can also cause dendrite formation. Void formation often leads to local current densities high enough to cause dendrite formation, even when the current density of the overall battery is below the critical current density that would normally lead to dendrite formation. Until this issue is resolved, SSBs must operate at low current densities to avoid voids and dendrites, limiting their power rating [17]. Research on different electrolytes and ways to improve interface conductivity is being conducted to help mitigate the many negative effects that stem from SSB interfaces.

ELECTROLYTES AND INTERFACE MATERIALS

Inorganic lithium-ion conductive ceramic materials are the leading solid state electrolyte being researched. Garnet as an electrolyte is one option. Garnet has a high ionic conductivity at room temperature which is beneficial for the operation of the battery in general. The leading benefit for garnet comes from its stability with Li metal. This would allow for Li metal anodes to be used, increasing energy density of SSBs. However, garnet has poor contact with Li metal, increasing resistance at the interface. This can be mitigated by using an intermediary liquid electrolyte or alloy material between the Li and garnet, greatly reducing boundary resistance [18].

Sulfide electrolytes also have good conduction for SSBs, making them another good option. Sulfide glass electrolytes are less rigid and can more easily be formed for better contact with electrodes. This increases the maximum charge and discharge rates, increasing the power of the SSB. Sulfide electrolytes can also be coated in composites to further improve the interface conductivity. Sulfide electrolytes do suffer from instability when exposed to the atmosphere, requiring either inert conditions or a change in chemical composition to make them more stable in air [19].

Another common problem in SSBs is the creation of an interphase layer between electrolytes and electrodes. The interphase layer is a layer of material formed through chemical reactions and atomic diffusion between electrolyte material and electrode material. This interphase can grow into the electrolyte and often impacts the performance of the battery due to the increase in interface resistance. This is an issue in non-solid state batteries as well, so the same approach is used to prevent interphase layers from forming. Coatings on electrolytes are often used to prevent or limit the growth of interphases, keeping interface resistance as low as possible [20]. Composite interphase layer additions are materials intentionally placed in the interfaces between electrolyte and electrodes. These composites have also seen success in suppressing dendrite formation in addition to reducing interface reactions and resistance across the interface.

Combining electrolytes and interface coatings has also seen some reported success. A Harvard University study claims that a multilayered system consisting of graphite, an electrolyte called LPSCI, and an electrolyte called LGPS can be used to create a SSB with high cycle life and high current density [21]. LPSCI is an electrolyte that is more stable with lithium, but easily allows dendrites to form within it. LGPS is an electrolyte that is unstable when with lithium but limits dendrite formation. The battery is structured with graphite coating the anode, a layer of LPSCI, then a layer of LGPS, LPSCI again, and finally the cathode. This design aims not to prevent dendrite formation, but to restrict it to the LPSCI layers and block it with the LGPS layer. The battery chemistry then allows the battery to fill in holes left by the dendrites forming. It also allows lithium to be used as the anode, which greatly increases the battery's energy density. This is a promising application of new electrolyte technology and shows that SSB research is working towards practical use.

MATURITY COMPARED TO LITHIUM ION

Solid state batteries are a promising alternative to current Li-ion battery technology, but they are still being heavily researched. This rate of research and the promising prototypes being developed may indicate that SSBs could soon see commercial development and application. SSBs offer the possibility for higher energy densities and specific energies than are possible in Li-ion batteries. This would allow for greater energy storage with the same footprint as current Li-ion batteries. They are a lower risk option than current Li-ion batteries, as no flammable liquid electrolyte means there is no possibility of a thermal overload causing a fire. However, contact between the solid electrolyte and electrodes at their interfaces is limited. This creates many operational issues for SSBs, including high internal resistance, low conductivity, low power, low cycle life, and void and dendrite formation. Improved electrolytes and means of improving the contact between electrolyte and electrodes are being developed to help resolve these limitations. If the issue of poor conduction is resolved, it seems possible that SSBs could become a widespread alternative to Li-ion batteries due to their safety and high energy density, assuming their cost does not outweigh their potential benefits.

MARITIME APPLICATION OUTLOOK

CHALLENGES

Most challenges with SSBs come from the interfaces between solid electrodes and the solid electrolyte. The high local current densities created when voids and dendrites form limit the current density allowable in the batteries. Poor contacting leads to higher internal resistance and low cycle life. Research into aspects like interface coatings and separators to stop dendrite formation shows promise in mitigating many of these issues, but it may be some time before they can be fully resolved and production of SSBs can begin.

POSSIBILITIES

Solid state batteries are still being researched and as such have flaws that must be overcome. However, their possibility for providing high energy capacity may make it possible for them to be used in maritime applications. Companies have already begun research toward development of SSBs for electric vehicle technology because of the much faster charging speeds that could come as a result. If research does end up improving the conductivity, power and cycle life of SSBs, they could be a big advancement in battery technology. Since SSBs would, after further research and development, be similar in practice to Li-ion batteries but with an increased energy density, it is possible that they may be implemented in vessel systems that already use Li-ion batteries as a plug-in replacement.

While SSBs must be operated in a specific temperature range, they do not have the possibility of going into thermal runaway due to the lack of a liquid electrolyte, posing less risk than Li-ion batteries. This combination of safety and high energy density indicates that SSBs could eventually become replacements for Li-ion batteries in maritime applications, such as auxiliary power systems or storing energy generated from non-continuous renewable sources.

Table 2: Battery Technology Data

Battery Type		Voltage (V)	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Cycle Life	Power Density (mW/cm^2)
Lithium Ion		3.7	265	670	High	**
Metal-Air Batteries	Lithium-Air Batteries	2.96	3,463*	2,004*	Low	**
	Zinc-Air Batteries	1.65	1,085*	1,670*	Low	479
	Aluminum-Air Batteries	2.71	2,791*	**	Low	**
Redox Flow Batteries	Vanadium Redox Flow Batteries	1.25	20	15-25	High	**
	Iron-Chromium Flow Batteries	0.94	**	**	High	70-100
Ammonia Batteries	Thermally Regenerative Ammonia Batteries	**	**	1.03	Very Low	3.7
	Ammonia Flow Batteries	**	**	**	Very Low	2.80 at 55 °C
Solid State Batteries		2.6	350	**	Medium	**

* indicates theoretical value
** indicates no established value

Table 3: Battery Rate of Charge Comparison

Battery Type	Lithium Ion	Metal-Air	Redox Flow	Ammonia	Solid State
Rate of Charge	Fast	*	Medium**	Slow	Fast

*Current metal-air batteries are recharged mechanically by replacing the anodes and electrolyte
**Redox flow batteries can also be recharged mechanically by replacing the electrolytes in addition to standard charging methods

CONCLUSIONS

Increasing environmental concerns necessitate advancements towards a cleaner maritime industry. As hybrid and all-electric vessels become more common as a means of reducing emissions, improved battery technology will be a requirement to ensure efficient and effective operation of environmentally safe systems. Current lithium-ion batteries are sufficient for maritime applications, but their limited energy capacity and safety concerns indicate the need for next generation batteries to allow for advancements in maritime battery systems. Higher capacity batteries would allow for more efficient hybrid vessels and could potentially make all-electric vessels more viable. Improved battery systems also allow for renewable energy sources to better have their energy captured and stored, especially for discontinuous energy like wind and solar that are not always available. With so many developing technologies relying on a high power, high energy source of electricity, it is imperative that new battery technologies are developed and implemented. A few emerging battery technologies and their potential for use in the maritime industry are compared in the table below.

Table 4: Battery Technology Comparison

Battery Type	Advantages	Disadvantages	Potential for Maritime Use
Metal-Air	High theoretical specific energy	Poor cycle life Unstable electrolytes Sensitive to moisture and atmospheric gases Lithium-air batteries still risk thermal runaway like Li-ion batteries	If a stable electrolyte can be found and the cycle life improved to allow for rechargeability, metal-air batteries show potential for use in maritime applications due to their extremely high specific energy
Redox Flow	Large amounts of energy storage Separation of energy and power ratings Low rate of self-discharge Easily scalable	Low energy density Expensive materials	The low energy density and specific energy mean the space and weight REDOX flow batteries take up must be carefully considered to determine if they could be useful in a maritime application
Ammonia	Recovery of low grade waste heat Environmentally friendly	Early in research Low efficiency	Ammonia batteries are very early in their research but may become useful for recapturing of low grade waste heat for additional energy
Solid State	High energy density and specific energy Safe against thermal runaway conditions	Poor interface contact High internal resistance Poor cycle life Expensive	Solid state batteries show promise in potentially providing a high energy density and safe alternative to current lithium-ion batteries if interface contact can be improved

REFERENCES

ABS Advisory on Hybrid Electric Power Systems – https://ww2.eagle.org/content/dam/eagle/advisories-and-debriefs/ABS_Hybrid_Advisory_17033.pdf

The Four Components of a Li-ion Battery – https://www.samsungsdi.com/column/technology/detail/55272.html?listType=gallery

How Does a Lithium-ion Battery Work? – https://www.energy.gov/eere/articles/how-does-lithium-ion-battery-work

Materials Design for Rechargeable Metal-Air Batteries – https://www.sciencedirect.com/science/article/pii/S2590238519300335

Recent progress in rechargeable alkali metal-air batteries – https://www.sciencedirect.com/science/article/pii/S246802571630019X

What is a Flow Battery? – https://flowbatteryforum.com/what-is-a-flow-battery/

Why Energy Storage – https://energystorage.org/why-energy-storage/technologies/solid-electrode-batteries/

The Next Generation Vanadium Flow Batteries With High Power Density – A Perspective – https://pubs.rsc.org/--/content/articlehtml/2018/cp/c7cp07456e

A Comparative Study of All-Vanadium and Iron-Chromium Redox Flow Batteries for Large Scale Energy Storage – https://www.sciencedirect.com/science/article/abs/pii/S0378775315303608

51 MWh Vanadium Flow Battery System Ordered for Wind Farm in Northern Japan – https://www.energy-storage.news/news/51mwh-vanadium-flow-battery-system-ordered-for-wind-farm-in-northern-japan

Iron-Chromium Flow Battery Aims to Replace Gas Plants – https://spectrum.ieee.org/energywise/energy/the-smarter-grid/new-flow-battery-aims-to-replace-gas-plants

Could Flow Battery Technology Help Shipping Decarbonize? – https://www.maritime-executive.com/article/could-flow-battery-technology-help-shipping-decarbonize

Ammonia - A Renewable Fuel Made from Sun, Air, and Water – Could Power the Globe without Carbon – https://www.sciencemag.org/news/2018/07/ammonia-renewable-fuel-made-sun-air-and-water-could-power-globe-without-carbon

On the Regeneration of Thermally Regenerative Ammonia Batteries – https://link.springer.com/article/10.1007/s10800-018-1240-0

High Power Thermally Regenerative Ammonia-Copper Redox Flow Battery Enabled by a Zero Gap Cell Design, Low-Resistant Membranes, an Electrode Coatings – https://pubs.acs.org/doi/10.1021/acsaem.0c00400

Promising All-Solid-State-Batteries for Future Electric Vehicles – https://pubs.acs.org/doi/10.1021/acsenergylett.0c01977

2020 Roadmap on Solid-State Batteries – https://iopscience.iop.org/article/10.1088/2515-7655/ab95f4

Toward Garnet Electrolyte-Based Li Metal Batteries: An Ultrathin, Highly Effective, Artificial Solid-State Electrolyte/Metallic Li Interface – https://advances.sciencemag.org/content/3/4/e1601659

Development of Sulfide Solid Electrolytes and Interface Formation Processes for Bulk-Type All-Solid-State Li and Na Batteries – https://www.frontiersin.org/articles/10.3389/fenrg.2016.00025/full

Review-Interfaces: Key Issue to Be Solved for All Solid-State Lithium Battery Technologies – https://iopscience.iop.org/article/10.1149/1945-7111/ab7f84

Battery Breakthrough for Electric Cars – https://news.harvard.edu/gazette/story/2021/05/researchers-design-long-lasting-solid-state-lithium-battery/

LIST OF ACRONYMS AND ABBREVIATIONS

AAB	Aluminum-Air Battery
ABS	American Bureau of Shipping
AFB	Ammonia Flow Battery
ICB	Iron Chromium Flow Battery
IMO	International Maritime Organization
LAB	Lithium-Air Battery
MAB	Metal-Air Battery
RFB	REDOX Flow Battery
SSB	Solid State Battery
TRAB	Thermally Regenerative Ammonia Battery
VRFB	Vanadium REDOX Flow Batteries
ZAB	Zinc-Air Battery

CONTACT INFORMATION

GLOBAL SUSTAINABILITY CENTER
1701 City Plaza Dr.
Spring, Texas 77389, USA
Tel: +1-281-877-6000
Email: Sustainability@eagle.org

NORTH AMERICA REGION
1701 City Plaza Dr.
Spring, Texas 77389, USA
Tel: +1-281-877-6000
Email: ABS-Amer@eagle.org

SOUTH AMERICA REGION
Rua Acre, n° 15 - 11° floor, Centro
Rio de Janeiro 20081-000, Brazil
Tel: +55 21 2276-3535
Email: ABSRio@eagle.org

EUROPE REGION
111 Old Broad Street
London EC2N 1AP, UK
Tel: +44-20-7247-3255
Email: ABS-Eur@eagle.org

AFRICA AND MIDDLE EAST REGION
Al Joud Center, 1st floor, Suite # 111
Sheikh Zayed Road
P.O. Box 24860, Dubai, UAE
Tel: +971 4 330 6000
Email: ABSDubai@eagle.org

GREATER CHINA REGION
World Trade Tower, 29F, Room 2906
500 Guangdong Road, Huangpu District,
Shanghai, China 200000
Tel: +86 21 23270888
Email: ABSGreaterChina@eagle.org

NORTH PACIFIC REGION
11th Floor, Kyobo Life Insurance Bldg.
7, Chungjang-daero, Jung-Gu
Busan 48939, Republic of Korea
Tel: +82 51 460 4197
Email: ABSNorthPacific@eagle.org

SOUTH PACIFIC REGION
438 Alexandra Road
#08-00 Alexandra Point, Singapore 119958
Tel: +65 6276 8700
Email: ABS-Pac@eagle.org

TX 11/21 21157