The Future of Batteries in the Marine Sector: What Lies Beyond the Horizon?

MV Hallaig in the Inner Hebrides (Tschuch, CC BY-SA 4.0)

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2 EXECUTIVE SUMMARY

The age of electric vehicles has arrived, with lithium ion battery cost falling fast and the UK Government committing to ending sales of petrol and diesel cars this decade. However, while the target of a fast-charging electric vehicle with a 500 km range and a dense network of charging points is a reasonable replacement for today's cars, pushing a boat hull through water requires a lot of energy, and commercial journeys may cover up to thousands of kilometres across the open ocean. Which boats, and which journeys, can be conducted under full electric propulsion is therefore a nuanced question. Even the much vaunted and long-awaited lithium air battery is likely to offer only four times the specific energy of today's lithium ion cells at 950 Wh kg^{-1}, compared to heavy fuel oil at 6000 Wh kg^{-1} (based on a 55% efficiency diesel engine). However, using a battery as part of a hybrid power system has clear advantages, by allowing more efficient operation of the main engines.

For the majority of propulsion requirements in any kind of vehicle, some kind of lithium battery will almost certainly be the preferred solution up until 2050. Lithium due to its low density and its position on the Periodic Table is unmatched as a charge carrier. It is small, light, and has the highest electrochemical potential of any element. Over the last ten years general consensus has shifted to the position that there is enough lithium to meet the exponential growth of electric propulsion, due to the growing exploitation of mineral deposits around the world. Furthermore, manufacturing experience is rapidly making lithium batteries cheaper, even against rising lithium price. It is likely that by 2030 even the majority of grid storage requirements, a market previously thought to be fertile ground for cheaper batteries with lower outright performance, will be most economically met by lithium batteries.

Prinsesse Benedikte Hybrid Ferry (JøMa, CC0 1.0)

Battery-electric ro-ro ferries for shorter routes (so far, up to 36 km between charges) are appearing across the world. New electric ferries also require high power shore-side electricity connections - a cost comparable to the battery itself. Pure electric propulsion has a wide range of benefits: less maintenance, significantly simplified drive train, faster power response, and no need to keep an engine in spinning reserve. There are also fully electric workboats and tugs, largely limited to harbour operation, and with duty cycles that allow for regular recharging**.**

For longer journeys, hybrids have proven benefits. A hybrid still uses an electric motor to turn the propeller, but the power is drawn from both batteries and diesel engines. In the future, fuel cells might also replace the diesel engines. What fuel cells and diesel engines have in common is that they are sluggish to respond to changes in power requirement and have poor efficiency when run away from their optimum operating condition. Motors and batteries retain their efficiency over a much broader range of speeds and loads and therefore a diesel engine/fuel cell can be used for base loads while the battery provides for fluctuating loads i.e. dynamic positioning, cranes, periods of high-speed operation, and hotel loads. Furthermore, a hybrid ship can be run on battery power in port or in protected areas, allowing emission-free operation in port or protected areas. Finally, plug-in hybrids with large battery capacity can reduce fuel consumption by sailing further under battery power obtained from the grid.

The existing fleet of hybrid ferries, workboats, tugs and offshore vessels have consistently demonstrated 15-30% fuel savings over comparable diesel boats. It is likely that the largest merchant vessels, powered by very large two stroke engines using direct drive, have the least to gain from hybrid power systems. They run their engines very close to optimum load for long periods with little fluctuating load. However, a relatively small battery is still likely to become common on these boats to improve hotel load management. Therefore, hybrid propulsion can be expected to become the new normal for all boats that cannot be made battery-electric, as the payoff time in terms of cost is generally less than ten years. Regardless of which future fuels are used to decarbonise shipping, hybrids will play a role, because diesel engines, fuel cells, and combined cycle gas turbines all share a loss of efficiency when operating at part load.

The question of which battery to use remains. Lithium-ion batteries are a work in progress characterised mainly by cathode choice. The most popular cathode in marine and automotive applications is nickel manganese cobalt (NMC) which provides reasonable safety combined with very good cell specific energy (see Figure 1). However, NMC has intrinsic issues with thermal stability, and depends on cobalt, which is scarce, expensive, and has ethical issues with its supply chain. All of the current lithium ion batteries use flammable organic electrolytes, and NMC in particular is vulnerable to thermal runaway, where cell temperature increases rapidly and leads to fires that are very difficult to extinguish. Since an uncontrolled fire onboard is not an option in marine applications, comprehensive fire extinguishing systems are required, as well as continuous cooling during normal operation. Even so, fire control relies on limiting the thermal runaway to a small number of cells, and so the cells are contained in waterproof metal cases and arranged in racks that are separated by a significant air gap. These design factors cause the fully installed energy density of lithium NMC battery packs to be around half of that for automotive battery packs – 86 Wh kg^{-1} for the Ellen E-ferry *vs*. 160 Wh kg^{-1} for a Tesla Model 3.

Seven Viking (TonjeR, CC BY-SA 4.0)

Because lithium NMC marine battery installations requires so much compromise to be made safe, there is a significant scope to use a lower performance but safer chemistry to achieve similar or better overall performance. A good example is lithium iron phosphate (LFP), which has around 65% of the specific energy of NMC but is far safer and replaces expensive and problematic nickel and cobalt with highly abundant iron and phosphorous. The increased safety means the next generation of Chinese electric vehicles will feature lithium iron phosphate packs with specific energy only 12.5% less than Tesla/Panasonic's lithium nickel cobalt aluminium (NCA) packs, which are themselves more energy dense than NMC. Because the safety requirements are even more onerous for marine applications, it is likely that LFP offers near parity specific energy to NMC, though this could not be confirmed from the literature. With more uptake of the technology for marine applications, LFP price should eventually drop markedly below that of NMC. LFP has already been approved for marine use and is currently in use on boats.

The widespread deployment of solid-state lithium batteries will almost certainly be the next significant advancement in energy storage, and this is expected within 5 years, with a second generation of solid-state batteries offering closer to their theoretical performance available within 10 years (see Figure 1). A solid-state electrolyte prevents the risk of dendrites shorting the battery and facilitates the use of a lithium metal anode – the 'holy grail', with the highest specific energy of any anode. Solid-state batteries could offer up to 75% better specific energy of the best lithium ion batteries today. However, the safety impact might be even greater: with the fire risk and even the cooling requirement all but eliminated, marine battery packs might triple in specific energy overall within 10 years (see Figure 2), with similar increases in achievable range.

The next 10 years are also expected to see a series of incremental advancements in cathode materials, including high nickel (for example, NMC811, shown in Figure 1) and lithium-rich, both of which offer higher voltages and capacities than today's cathodes. There is a trade-off in terms of cathode stability, but this might be sufficiently mitigated by the inherent safety of a solid electrolyte. The trend is to reduce or eliminate cobalt while raising specific energy and voltage. One cathode that seems unlikely to feature in marine applications is lithium sulphur. Despite having double the specific energy of today's lithium ion batteries, it cannot improve on the volumetric energy density of lithium NMC. It also has cycle life issues that are unlikely to be completely resolved, and subsequently is considered a suitable battery for aeronautical applications i.e. drones where weight is critical.

Sodium is touted as a potential alternative to lithium due to its abundance (in seawater), with lots of crossovers from lithium ion in terms of manufacture, electrode and electrolyte technology, but in reality, it is a larger, heavier ion with a lower electrochemical potential. Apart from decreased specific energy, the cycle life is shortened by the shuttling of larger ions into the electrodes. Other alternatives tend to fall around the lead acid performance level at under 50 Wh kg^{-1}, including flow batteries (which have been commercialised for grid storage) and aluminium batteries (which remain in the laboratory). These are discussed in some detail in this report but from a practical standpoint can be largely discounted from future marine applications up until 2050.

Finally, lithium-air (or other metal-air batteries) may appear in the 15-20 year timeframe (see Figures 1 and 2). While the theoretical specific energy of lithium-air is 3500 Wh kg^{-1}, 950 Wh kg^{-1} has been stated as a realistic maximum in practice. Metal-air batteries may still suffer the same problems as fuel cells with slow oxygen reactions and might also need the support of a high-power battery type. However, while this battery type remains in the laboratory with little evidence of an impending breakthrough, the elimination of the cathode and the quadrupling of the specific energy of today's battery cells make lithium-air an important potential contributor to future transport energy storage. The cell level specific energy of the different battery types discussed is shown in Figure 1 along with the expected timeframe for their arrival.

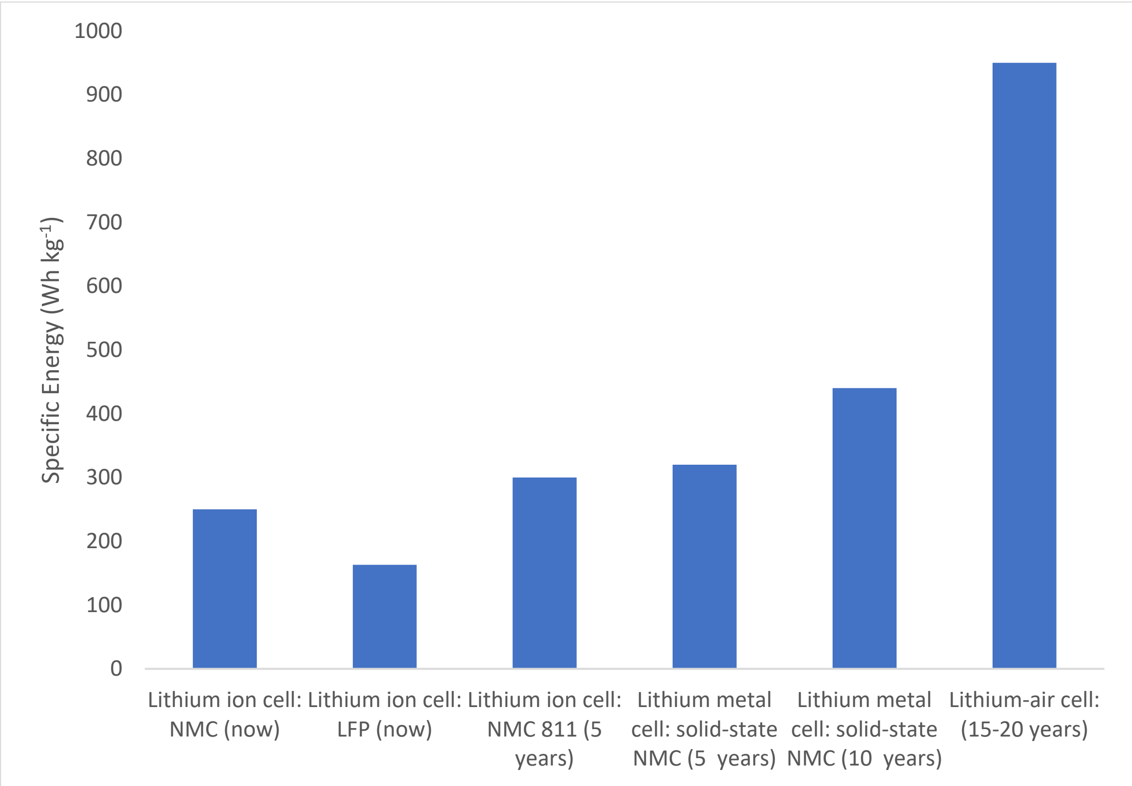

Figure 1 - Specific energy of cell chemistries expected to be used in marine over the next 5-20 years

Unexpectedly, there is one super capacitor ferry in operation, a river ferry in France with a 7-minute journey time and a 4-minute recharge time. Super capacitors have a specific energy of only around 15 Wh kg^{-1} but last tens of thousands, rather than thousands of cycles, and can undergo charge and discharge rates many times higher than batteries. This illustrates that the diversity of marine cycles calls unusual solutions, in very specific circumstances.

An estimation of the maximum range of battery-electric boats is provided. Today's lithium NMC technology has allowed battery-electric boats with a range up to about 50 km, which in the case of Ellen have already substituted all of their ballast for batteries. Solid-state batteries, when mature in around 10 years' time, may triple specific energy (at the pack level, mostly through improved safety) and allow a range up to 150 km. Finally, lithium-air might double this specific energy again, taking range to 300 km. Therefore, it can be said, even with a large margin of error, that battery-electric boats are unlikely to significantly exceed a 500 km range and will probably never sail further than 1000 km. On longer journeys than this, a hybrid solution will be required. Figure 2 shows the relative specific energy of marine fuels compared to today's battery packs, those predicted for solid-state lithium in 10 years' time, and for lithium air in 15-20 years' time, showing clearly why fuel is required on longer journeys. The conversion efficiencies of motors *vs*. diesel engines and CCGTs are accounted for.

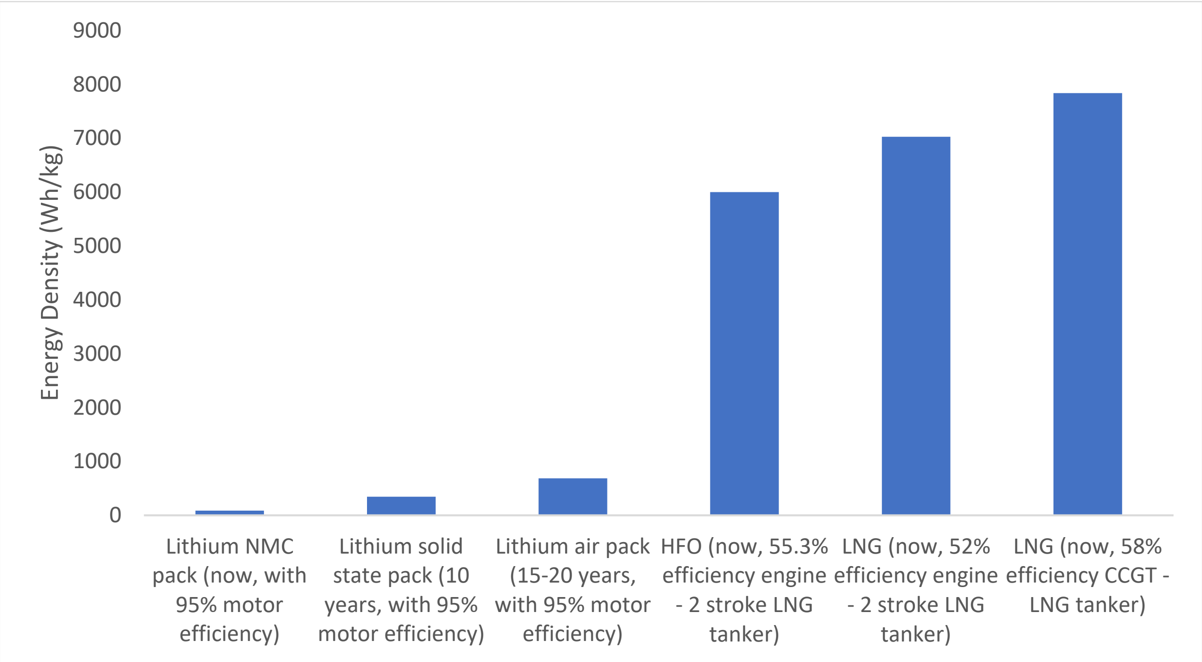

Figure 2 - Estimated pack level specific energy of different battery types vs. *HFO and LNG*

3 INTRODUCTION

This report sets out firstly to review current progress in the use of batteries on boats, in all commercial boat classes, both battery-electric and hybrid (battery-electric is the term used in this report to refer to a boat that gains all of its power from batteries and has no other power source on board). In doing so it also briefly touches upon the progress made by the classification societies, the particular considerations of marine applications in terms of fire safety and battery pack design, the battery management system, the future cost of today's lithium-ion batteries, life cycle considerations and resource issues. Fuel cells, alternative fuels, and supercapacitors are also briefly discussed. Then a discussion is made of as many case studies as could be found where batteries have already been used in boats.

From this current context the report then looks to the future and reviews the most promising battery chemistries that are currently expected to make their way from research to commercialisation or are already partway through that journey, including the most promising variants of lithium, sodium, potassium, multivalent metal batteries, metal-air batteries, nickel metal hydride and flow batteries. Throughout the report, the terms specific energy and energy density are used to refer to the amount of energy stored per unit mass (Wh kg^{-1}) and the amount of energy stored per unit volume (Wh l^{-1}) respectively.

MV Hallaig sailing in the Inner Hebrides (Tschuch, CC BY-SA 4.0)

4 CLASSIFICATION OF BATTERY SYSTEMS FOR MARINE APPLICATIONS

Several of the world's classification organisations and regulatory authorities have already started to produce guidance on the use of batteries on boats and provide type approval for battery systems for marine applications.

The Maritime and Coastguard Agency (MCA) have produced guidance for the safe design, installation and operation of lithium-ion batteries. This covers various elements of marine battery system design, from conception through to storage, transportation, installation, maintenance and safety procedures, and decommissioning/recycling [1].

DNV-GL is a Norwegian classification society. Unsurprisingly considering Norway's leading efforts on the electrification of boats, they have carried out significant research and trials and are currently awarding certification to all kinds of electric and hybrid craft. This includes fire safety systems [2] and class-type approvals [3], along with services ranging from design to testing. Boats that DNV-GL have approved include Viking Lady, Ampere, Edda Ferd, Edda Freya and Island Crusader.

Lloyd's Register Foundation, the UK-based classification society, have issued guidance on large battery installations. They take the view that the rapid progress in cell chemistries makes a prescriptive safety standard unfeasible. The document provides general guidance regarding the various elements of the battery installation. Rather than assess a new battery installation against a set of rules, LRF prefers to take an integrated approach, being involved from the concept design phase to avoid issues resulting from changes later on [4].

There are no current international standards for marine battery installations although two are being developed by the International Electrotechnical Commission (IEC) – 62619 and 62620 [4].

Bureau Veritas, the French classification society, has released notations and rules suitable for electric ships [5], and has approved BC Ferries' Damen and two Cemre offshore wind farm service vessels [6], as well as at least two lithium ion battery systems suitable for boats [7, 8]. They have also released guidance on the various battery system elements such as the BMS [9].

5 CURRENT AND FUTURE FUELS, FUEL CELLS AND SUPERCAPACITORS

Any comment on the use of batteries on boats in the future must be set in context of alternative fuels. Batteries are unlikely ever to be able to store all of the energy required for journeys longer than 500-1000 km [10, 11]. Therefore, while battery technology remains relevant to longer journeys as part of hybrid propulsion systems, there is still a need to replace a huge consumption of bunker fuel with something immediately less carbon-intensive with the scope to eventually be made carbon-neutral. This is particularly critical due to the fact that the proportion of boats that can ever be made battery-electric accounts for a very small part of global shipping. Heavy fuel oil accounts for 77% of total marine fuel use, and 90% of marine fuel is used by cargo-carrying ships; only 10% goes to passenger ships, fishing boats, tug boats, navies, and others [12]. While some of these cargo-carrying ships have short journeys and could be made battery-electric, the majority are not.

Of the available fuels, liquified natural gas (LNG) is widely considered to be capable of meeting future shipping requirements [11], although it is important to note that bunker fuels are not going anywhere soon due to the lifespan of existing ships. LNG is already available in many large ports due to existing large-scale trade [10, 11]. The most modern LNG tankers already use two- or four-stroke dual-fuel engines that can make efficient use of diesel or LNG, and some others even burn LNG in a highly efficient combined cycle gas turbine (CCGT) to generate power. LNG is far less polluting than traditional bunker fuels, lacking the sulphur and nitrogen content and the particulate emissions, and emits less carbon per unit energy. In fact, LNG engines can meet the stringent Tier III exhaust gas requirements with no exhaust treatment, the cost and energy savings of which are a major factor now incentivising its rapid adoption. LNG is already produced abundantly enough to fuel shipping for the foreseeable future, and supplies will last long enough to allow the development of renewable LNG production [11]. One very serious issue with LNG currently is the emission of unburnt methane to the atmosphere, measured to be as much as 36 g per kg LNG burnt at part load from one LNG-powered ferry. Methane has a much more powerful global warming effect than CO_2, and eliminating emissions of it is critical if LNG is to be considered a green technology [13].

To progress from fossil-fuel LNG, methane can be generated from biomass (including waste) and given that natural gas is largely composed of methane, liquefied bio-methane is suitable for LNG-powered ships. Methane can also be produced by the Fischer-Tropsch process using hydrogen and carbon dioxide as the feedstock, powered by renewable energy, referred to as synthetic LNG. Furthermore, methane can be turned into methanol, which makes it a liquid at room temperature, and decreases its carbon content at the point of use, however this additional step represents an increase in cost which makes methanol overall less appealing than liquefied methane/LNG [11]. However methanol has the significant advantage of being able to be used in a fuel cell [14], whereas direct methane conversion in solid oxide fuel cells remains a lab-scale technology [15]. Major engine manufacturer Wärtsilä also endorses the view that the path away from bunker fuels is through LNG and since the introduction of dual-fuel engines to the market in 2002 about 65% of new LNG tankers have been fitted with them [16].

Fuel cells are another appealing option for future propulsion. With an ability to convert fuel to electricity with about 50% efficiency (though higher values of overall efficiency can be reached if waste heat recovery is implemented), they offer the potential to carry a proportionally reduced amount of fuel for the same journey. However, fuel cells remain very expensive due to the membrane and catalyst components. Fuel cells can be run directly on hydrogen, methanol, or ammonia. Hydrogen storage requires very large volumes, even at 700 bar or when liquefied, and is challenging for long distance voyages as a result, but methanol or ammonia are both energy dense fuels and can be stored in liquid form at or near ambient temperature, though ammonia forms a toxic gas if released to the atmosphere [10].

Viking Lady at LNG Terminal (Skangass AS, CC BY 3.0)

The comparative space required for different fuels is illustrated by a recent modelling study which found that compared to heavy fuel oil, the required storage volume for the same amount of energy (adjusted for different operating efficiencies) would be 12 times larger for lithium batteries, four times larger for hydrogen at 700 bar, 1.2 times larger for ammonia and 1.01 times larger for LNG [10].

Hydrogen is a challenging prospect for long journeys due to its high volume and requirement for very cold storage temperatures in liquid form, but is still being seriously considered [10]. However, it is quite an appealing option for boats travelling shorter distances, including workboats and harbour tugs. Much of this is to do with the fact that producing hydrogen requires only an electrolyser, a power supply and a water supply. Therefore, it is possible to install an electrolyser in harbours. Fuel cell vehicles must have room for the hydrogen storage tanks, and due to the losses in electrolysis have poor energy efficiency, only about half the grid-to-wheel/propeller efficiency of electric vehicles. The relative benefit of hydrogen is the speed with which the boat can be refuelled (similar to diesel) [17]. Hydrogen is being taken forward by some parties: the city of Hamburg is building a 100 MW electrolyser, the world's largest, at its port, in line with the wider focus of Germany on hydrogen as a future energy vector [18].

What all of these non-battery energy systems have in common is that they operate most efficiently at a given power rating. This is true of all combustion engines, CCGTs, and even fuel cells. Academic studies and real world experience agree that a small high-power battery is a necessary companion to a fuel cell in cars and buses [19], a fact that is also demonstrated by the fuel cell/battery/LNG hybrid boat Viking Lady, with a relatively small battery providing the sudden bursts of power and kinetic energy recovery capability required for crane operation [20]. This means that the use of batteries as part of a hybrid system is equally applicable no matter what the future fuel or main power source for long voyages will be. In every case, a hybrid system can allow the main power generation system to operate closer to its peak operating efficiency throughout the voyage [11].

It should be noted that wind power is also making a resurgence with increasing ‘fuel-saving’ technologies being developed. It is a supplementary technology that could save significant fuel over long voyages by taking advantage of favourable winds [11].

5.1 Energy density of fuels

In order to understand the performance of batteries relative to fuels, the specific energy of various fuels is calculated. The lower heating value (which accounts for the energy obtained by burning the fuel, minus the amount of energy required to vaporise the water content of the fuel) is used. The lower heating values of four fuels are shown below [21]:

Diesel fuel – 42630 kJ/kg, 0.85 kg/l

Heavy fuel oil – 39000 kJ/kg, 0.98 kg/l

Marine gas oil - 42800 kJ/kg, 0.86 kg/l

LNG – 48600 kJ/kg, 0.428 kg/l

In 2014, work began on two new large, 180,000 CBM LNG carriers by the Samsung Heavy Industries (SHI) in Korea on behalf of a collaboration between SK Shipping and Marubeni. The chosen engines were 6-cylinder Wärtsilä X62DF 2-stroke dual-fuel engines, the first large LNG carriers featuring Wärtsilä’s 2-stroke dual-fuel technology [22]. The specifications for this engine, which has a diesel-only equivalent, allow comparison of HFO and LNG power outputs and efficiencies. The diesel-only variant of the engine is used for HFO calculations as it gives better fuel efficiency than the dual-fuel variant. Using the max continuous (R1) rating, the consumption of HFO is 167.0 g kWh^{-1} and of LNG is 142.5 g kWh^{-1} [23]. These numbers produce efficiencies of 55.3% efficiency for HFO and 52.0% efficiency for LNG for the X62-DF two-stroke main engine suitable for LNG tankers. In a dual-fuel engine that lacks spark plugs, LNG also requires less than 1% pilot fuel (i.e. marine gas oil) in order to prepare the fuel for combustion, which then ignites the entire mixture when compression reaches suitable levels. This is negated in the comparison. Overall, this gives a useful specific energy of the two fuels as 21115 MJ m^{-3} for HFO and 10812 MJ m^{-3} for LNG, and 21.6 MJ kg^{-1} for HFO, and 25.3 MJ kg^{-1} for LNG [21], which is 7028 Wh kg^{-1} for LNG and 6000 Wh kg^{-1} for HFO. Finally, some LNG tankers use CCGTs with efficiency up to 58% [10], pushing the specific energy for LNG up to 7839 Wh kg^{-1}.

MV Hallaig (Abbott, CC BY-SA 3.0)

6 SUPERCAPACITORS

Supercapacitors are a technology with a specific energy of <20 Wh kg^{-1} but up to 30 kW kg^{-1} specific power. They store energy via the separation of charge (which avoids a rate-limiting chemical reaction); this occurs in the electrolyte and on the surface of the electrodes and does not involve any insertion of ions into the electrodes. They last for tens of thousands of cycles [24]. There is in fact a boat in operation, the Ar Vag Tredan in France, which is entirely powered by supercapacitors. The boat recharges entirely in just 4 minutes of boarding time between 7-minute crossings and sails 28 times a day. This means the supercapacitors are cycled around 7000 times a year, which would exhaust a battery very quickly. The supercapacitors are expected to last for 15-20 years. This goes to show that the diversity of marine duty cycles means that a variety of energy storage solutions are likely to feature as more and more boats convert to electrical power [25].

While supercapacitor/battery hybrids have been proposed, in order to combine large amounts of energy storage using batteries with the ability to generate rapid bursts of power suitable for crane operation [26], no such examples could be found in the real world. It is possible that when batteries are employed on boats, the lithium NMC/iron phosphate chemistries currently in use are able to produce enough power by themselves. Future solid-state batteries might have slightly lower power due to the solid electrolyte having lower ionic conductivity (although this is not certain). Furthermore, any future metal-air battery may have poor specific power due to the inherent sluggishness of the oxygen reaction, so supercapacitor/battery hybrids may become popular in the future.

7 Hybrid Systems

While the range of battery-electric boats may be forever limited to less than 1000 km, batteries still have a major role to play on almost every future vessel as part of a hybrid system. For commercial boats of any kind, fuel costs tend to dominate through-life operating costs, and therefore any technology offering savings has a good chance to save money overall as well as reducing emissions [27]. Discussing the design and layout of a hybrid power system is beyond the scope of this report since it is a complex, multi-variate optimisation exercise [27, 28]. However, the types of boats that have been hybridised, the role of the battery pack, and the savings achieved are discussed.

Sten Odin (van Beem)

The fuel saving achieved by hybridisation is very simple: whether the power source is an internal combustion engine, a CCGT or a fuel cell, there is an optimal point of operation for maximum efficiency and the efficiency falls off rapidly away from this point. This means that where the duty cycle involves spending the majority of time very near the point of maximum efficiency, i.e. long-distance shipping, there is less to gain from hybridisation than in an application where the propulsion or hotel loads fluctuate significantly, i.e. fishing vessels, offshore vessels, cruise ships, tug boats, workboats, and tour boats. The battery and motor system, which is efficient across a wide range of loads, handles the fluctuating loads while the engines run at constant speed servicing the base (average) electrical load. Furthermore, when fluctuating loads are reduced on the engines, service life is extended, further decreasing operating costs and downtime [29].

The range of fluctuating loads that the battery can handle is extensive. Dynamic positioning, crane operations (where kinetic energy recovery can save much of the energy used), and hotel loads are just a few. Meanwhile, the battery can be used to allow the boat to sail without emissions in port or in protected areas such as the Norwegian fjords (the so-called 'Hour of Power' concept). On board, the services provided by the battery include peak shaving, load-levelling and backup power – the same services energy storage systems can provide on the mainland electrical grid [20].

Hybrids that do not take power from the mainland electrical grid offer fuel savings consistently between 15-30%. The Scandlines ferries, which have a predictable load cycle that intuitively has less to gain from hybridisation still achieve 15% savings [30] while the Roald Amundsen tourist expedition boat is expected to save 20% [31]. The Normand Server and Normand Supporter offshore vessels see savings of 15-20% [32]. Tugs, which spend around only 2% of their duty cycle operating at maximum power, are a particularly good target for hybridisation, and the Carolyn Dorothy and the Campbell Foss achieve 20-30% fuel savings [33], while the RT Adriaan achieves 20% savings [34]. The Aurora Spirit chemical tanker saves 30% of fuel [35] and a Korean research vessel built by STX offshore also saves 30% [36]. The hybrid ferry Victoria of Wight saves 17% [37].

If a hybrid boat plugs into the grid, which many of them already do, then the savings can be greater, because electricity can be used as a direct substitute for fuel, and the amount of fuel saved is directly linked to the capacity of the battery. Some 'hybrids' for example are intended to run predominantly on battery power and feature diesel engines only as a backup [38, 39]. Others, such as the chemical tankers Sten Tor and Sten Odin, feature plug-in connections but operate mainly as conventional hybrids, with 22% fuel savings [40]. Future offshore wind service vessels may also be able to take advantage of recharging from the windfarms [41]. Indeed, the UK has just bought two hybrid-electric wind farm service vessels powered by Danfoss-Editron hybrid systems [42].

The size of the battery required to make these savings is small compared to the size of battery incorporated on battery-electric boats. For example, the hybrid offshore vessels are typically more than 100 m long yet feature battery packs of 546 kWh (Edda Ferd) [43], 560 kWh (Normand Server and Normand Supporter) [32] or 1 356 kWh (Seven Viking) [44]. This is compared to 4 300 kWh for Ellen, which is a 60 m battery electric ferry [45].

Because a hybrid battery pack is smaller than that of a battery-electric vehicle, the power requirement per cell increases. This means that the battery type specified may be different from battery-electric boats. For example, high power lithium-ion batteries have more porous, thinner electrodes to allow faster ion diffusion, sacrificing specific energy in the process. The power requirement may also mean that hybrid vessels are slower to adopt potentially less powerful technologies like solid-state lithium (the solid electrolyte may slow ion diffusion) or lithium-air (the oxygen reaction is inherently sluggish).

LNG-powered vessels are unlikely to run on battery-electric in port, because emissions concerns are driven by particulates and NO_X rather than CO_2. However, there are still fuel savings to be made from load levelling and peak shaving of hotel loads and consequently even the biggest tankers and containerships are in future likely to have (relatively small) batteries on board.

Despite the more complicated power system and the reduced fuel saving of a hybrid system, expected payback time for Viking Lady is still less than 5 years [46] and this will be similar for others.

Color Hybrid (Tørrissen, CC BY-SA 4.0)

8 FORECAST COST OF LITHIUM ION BATTERIES

The price per kWh of lithium ion batteries has dropped dramatically in the last decade. This is crucial context for understanding the likelihood that any competing technology will enter the market. Figure 3 shows the representative cost of a 4.065 MWh marine battery installation (the initial cost in 2015, and then the cost for replacing the battery if it becomes exhausted at various points from 2020 onwards) from the electric ferry Ellen which operates in Denmark [45].

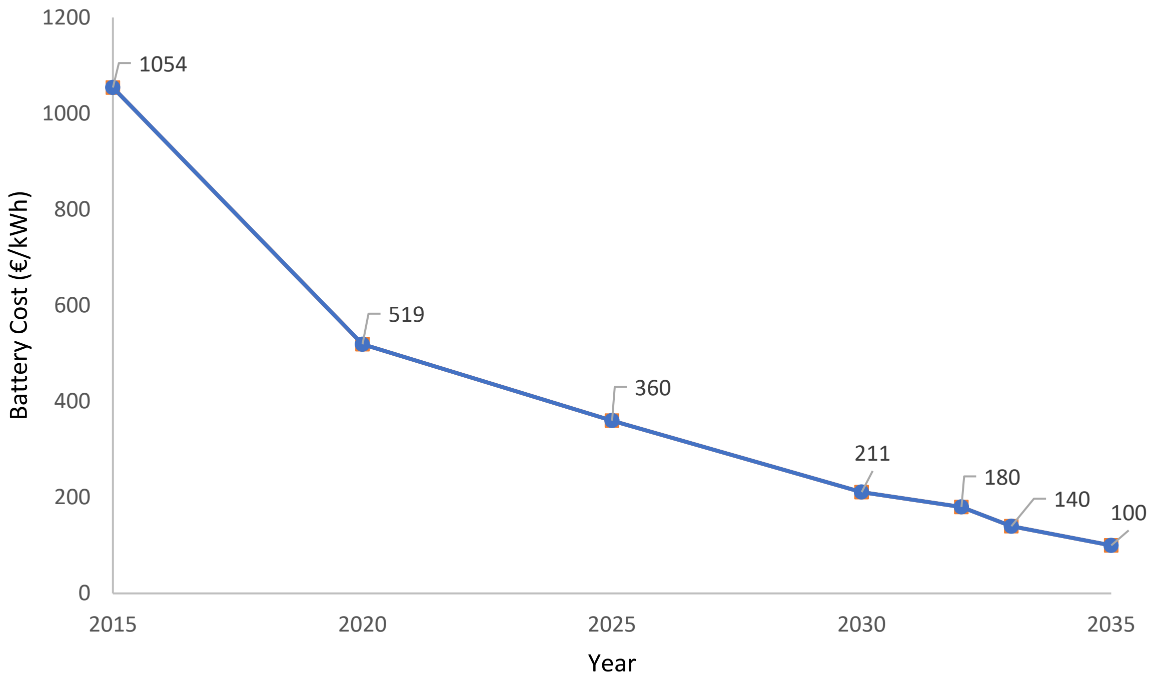

Figure 3 - Battery cost trends until 2035, based on Ellen E-Ferry (4.065 MWh battery). Based on real and estimated prices from Leclanché, assembled by Marstal Navigationsskole, adapted from [45]

This is despite the rising cost of lithium (see Figure 4). Notably, post-2018 prices are not included: it is assumed that following the Covid-19 pandemic, EV sales will pick up and drive the lithium price higher at a similar rate to pre-2018. The reason for the reduced cost of lithium ion batteries is entirely due to intense focus on efficient mass manufacture for the automotive industry, in facilities such as the giga-factories.

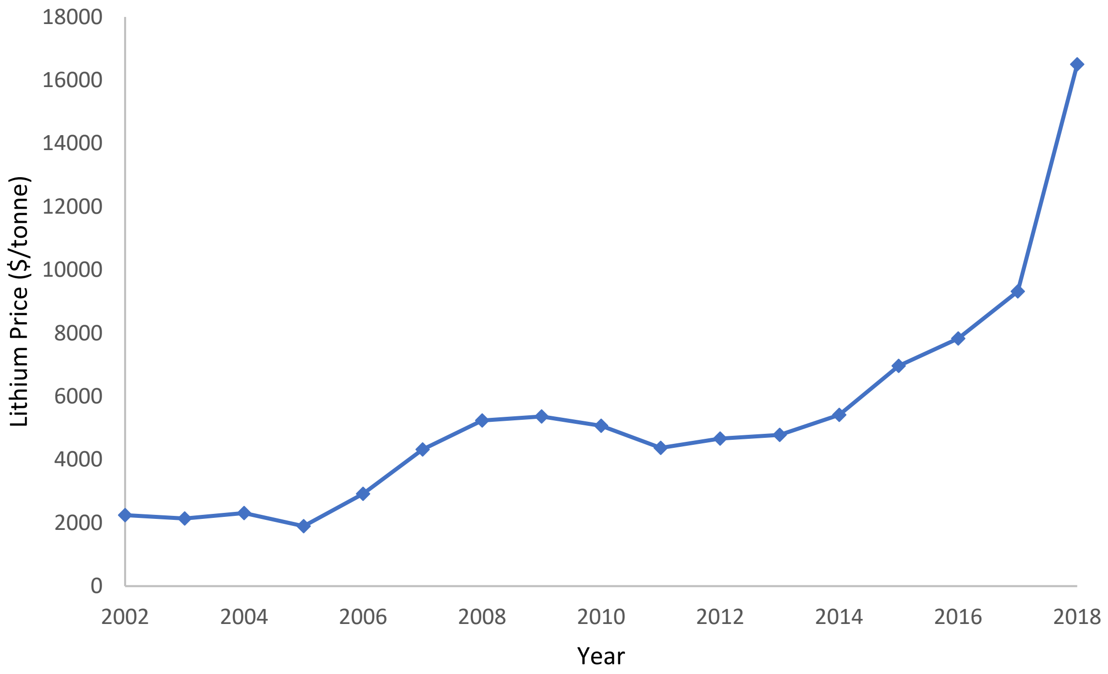

Figure 4 - lithium price history, data from [47]

The impact on competing chemistries cannot be understated. Per total kWh stored over the lifetime of the battery (termed levelized cost of energy storage), lithium ion is already competitive for many grid-based applications and by 2030 is expected to be the most economically viable option for grid storage performing almost any function (versus pumped hydroelectricity, vanadium redox flow batteries, flywheels and others) [48]. This is particularly relevant because grid-based energy storage has long been seen as the realm of battery technologies with less performance than lithium but better environmental credentials and lower material cost – a trade that might intuitively also be acceptable in marine applications. With this sector dominated also by lithium-ion, research of alternate chemistries is largely dependent on funding from governments and other players who wish to create independence from the supply chains of lithium, nickel or cobalt.

It is a common perception that lithium supplies are limited and may soon be exhausted. This is based on the fact that around half of the world's lithium is sourced from just a few countries in South America (Argentina, Chile and Bolivia), where lithium is found in salt lakes below the surface. This lithium is obtained by pumping the brine to lakes on the surface, where the sun evaporates the brine. This is a slow process (12-18 months) that cannot respond quickly to changes in demand. However, lithium is found all over the world in more conventional mineral deposits, and as demand increases, mining of mineral deposits is becoming economic in more places. While lithium price has increased steadily over the past decade, experience gained from lithium mining may eventually stabilise price, particularly when the proportion gained from cheaper brines becomes minimal [49].

Batteries are very much driving the increasing demand for lithium, and in 2020 were already consuming 65% of the world's supply, whereas in 2015 only 31% was used for batteries. Despite this trend, it is now generally believed the rapid growth of the EV market will not exceed the lithium reserves [50].

The more significant resource issue is with cobalt, which is why manufacturers are trying to drive down the cobalt content in their batteries. The Democratic Republic of the Congo supplies about two thirds of the global supply, of which batteries consume around half. Many manufacturers cannot guarantee their supply chains are free from cobalt mined by children; this is because artisanal miners provide about 20% of the DRC's output and are not regulated [50].

Batteries are also placing high demand on the nickel supply chain, consuming about half of the world's production in 2017, with a projected 10x increase in demand by 2025. This is not however thought to be an issue. The marine sector is in a favourable position because it could relatively easily swap to lithium iron phosphate and achieve similar performance, with no use of nickel or cobalt at all [50].

Because there are lithium chemistries such as lithium iron phosphate that avoid the use of cobalt and nickel and still outperform any non-lithium type of battery chemistry, and because lithium prices may be expected to stabilise due to the increased mining of mineral deposits over the next decade [51], it is unlikely that sodium or others will replace lithium for transport applications in the foreseeable future. It is reasonably certain that for marine applications, some form of lithium battery will remain the economically favourable option for at least the next two decades.

Conventional lithium ion battery electrolyte is not subject to any resource constraints and the world has plenty of spare manufacturing capacity [50].

Aurora (van Beem)

9 STRUCTURE OF BATTERY PACKS/MODULES FOR MARINE APPLICATIONS

Modern marine battery packs use the same lithium-ion chemistries as cars, but while cars have their battery cells arranged in the tightest possible configuration to minimise the size of the battery pack, marine batteries are arranged more like a stationary battery pack on the grid, in racks with space in between. Currently, due to the unique design of each boat, marine battery systems are more expensive per kWh than either automotive or grid battery installations, though this gap should narrow with experience [20]. A key reason for the difference in layout is safety. In the event of an automotive battery fire, the vehicle can be abandoned at the side of the road and left to the emergency services. A battery fire on a boat however must be extinguishable by the boat's own fire suppression systems, and the batteries are so large that a whole battery fire and the accompanying explosion risk would be impossible to control. Space must be left between the racks to allow access by the fire extinguishing media and to prevent propagation from one rack to another. This is discussed in more detail in the Cooling and Fire Safety Systems section.

For a lithium-ion battery pack, a careful trade-off is required between power and energy. For example, porous electrodes with high surface area and good access by the electrolyte are good for power. In contrast, dense, thick electrodes are better for energy density. As the intended discharge time gets longer this problem tends to go away because there are more cells to split the load between, but for smaller batteries, particularly those functioning as part of a hybrid drivetrain, the power requirements can be strenuous enough to affect the battery cell design.

In practice, it is hard to find accurate numbers for the specific energy of complete battery systems in boats. However, the 4.3 MWh system on the Ellen E-ferry is reported to have a total battery module mass of 50 tonnes, which gives a specific energy of 86 Wh kg^{-1} [45] for a lithium ion NMC battery system, which can be taken as a state-of-the-art number for marine applications at the time of this report publication. It is suggested that when first assessing the feasibility of placing battery systems on boats, this figure is used unless a more detailed engineering design can be carried out, certainly instead of the common 250 Wh kg^{-1} number that applies to individual lithium ion cells. Also, this figure does not include the fire extinguishing system, and making a comment on the energy density (volumetric) of the system is even harder. In comparison, the Tesla Model 3 battery pack is reported to have a specific energy of 160 Wh kg^{-1}, nearly double that of the Ellen ferry [52].

As an example of marine best practice, the Ellen E-ferry splits the modules into 20 individual units, each of which has its own power converter, so if it suffers a failure it will only lose 5% of its available energy and power. In order to reduce power conversion losses on board, the entire boat operates on DC power with the AC/DC converters needed to convert shore-side power to DC power contained in the shore side infrastructure to save weight on the boat. The only exceptions are the power converters to drive AC to the main propulsion motors and thrusters; modern power electronics mean these converters are the size of shoeboxes [45].

Figure 5 - Ellen E-Ferry battery room (Ærø Kommune and Henrik Hagbarth Mikkelsen) [45]

10 The Battery Management System

The battery management system is the ‘brains’ of the battery pack and has the complex task of optimising its performance. Each cell is a complicated electrochemical system that the BMS can only assess through very limited external parameters such as outside cell temperature, voltage and current [53]. It has several key goals. The first and most obvious is to calculate the state of charge. This information must be calculated to inform the user (or the computer controlling an autonomous boat) of the remaining energy available. The three main ways of calculating state of charge are conventional (now obsolete), model-based (most common) and machine learning (the future). The model-based approach uses mathematical models carefully constructed from extensive experiments and tests, which is time-consuming and expensive. The machine-learning approach is trained by feeding a learning algorithm with many examples of cells at different states of charge and with the associated data, from which it learns to predict the state of charge. This approach has the advantage of being quick (providing data is available), taking advantage of modern algorithms and abundant computing power to avoid the human effort required for the model-based approach [54].

The second goal is to balance the battery cells. The inevitable small variations between battery cells means that if no intervention was made, then as the battery was cycled, differences in the individual cell charge levels would start to accrue. If left unaddressed, this would mean that charging of the whole pack would have to stop when the lowest capacity cell had reached full charge, leaving significant empty charge capacity. Therefore, passive and active balancing systems have been designed. Passive systems detect and discharge the more fully charged cells through a resistor, which is obviously disadvantageous in terms of discarding electricity that has already been used to charge the battery, creating waste heat, and causing increased cell cycling. Active systems use capacitors, DC/DC converters or switch systems to move energy from cells with higher state of charge to those with lower state of charge, or simply disconnect those cells with higher charge levels. Active systems are more expensive to implement [53], but the added performance is worth it for larger packs in frequent use, and battery packs on boats are well above the size threshold to benefit.

An equally critical role played by the BMS is fault detection and management. It is a general requirement that for lithium ion batteries, the BMS must be able to detect voltage and temperature abnormalities in every single cell in the battery pack and shut down the affected string of cells in response [9]. Furthermore, if the temperature continues to rise, the BMS should initiate the fire extinguishing system. Any unusual cell voltage fluctuations can also indicate a short circuit.

Finally, the BMS also calculates the state of health, which is how much total life remains in the battery compared to when it was new. It normally achieves this by measuring the total capacity of the battery and the change in internal resistance. While there is not a complete consensus on what exactly constitutes state of health, it is normally taken as total battery capacity relative to when the pack was new. Given the fact that battery behaviour is dependent on so many factors, it is likely that the future trend in BMS design will be towards learning algorithms that can use increasingly large amounts of data gathered from many similar battery packs. Although AI requires data from many thousands of cells to develop a model, the model once established can be simplified to a set of parameters and implemented at the BMS level. At the moment, state of health estimation algorithms are unique to lithium ion and would need to be completely reinvented to suit the failure mechanisms of any alternative chemistry [55-57]. However, it is likely that the temperature and voltage sensing architecture would remain the same. Because, especially for large battery installations, this introduces a lot of wiring and complication, future battery sensors may be wireless, which will make replacement of damaged battery modules much easier [58]. Furthermore, in order to gain better knowledge of the inside of the battery cells, sensors and chips may be integrated into individual cells to provide a range of state of health parameters at the chemistry level, providing an entirely new level of insight into individual cell health with major benefits for gaining the maximal performance from the battery pack [59].

Ampere (Wikimalte, CC BY-SA 4.0)

11 Fire Safety and Cooling Systems

While the BMS is responsible for controlling the cooling and fire safety systems, the engineering of the fire safety system is worth discussing. The cooling need is directly related to the efficiency of the battery, as any inefficiency turns into waste heat during charge or discharge. Lithium ion battery life is shortened considerably when operated at higher temperatures [20], and this relates to the temperature in the electrodes, not the surface cell temperature. Therefore, cooling must be effective at removing heat from the core of the battery itself. One of the key things to note is that the fire safety system will vary depending on multiple factors, for example whether or not the battery pack is in a specialised room (is it acceptable to flood the room?), how big it is, and what chemistry the battery employs.

The lithium ion battery with NMC cathode is the most dangerous lithium ion battery type currently used on boats. Tests show that it is easy to provoke a NMC cell to thermal runaway. When a NMC battery fire occurs, a combination of flammable solvent and alcohol vapours are produced, along with oxygen, carbon monoxide, carbon dioxide, and small quantities of highly toxic gases such as hydrogen chloride, hydrogen cyanide and hydrogen fluoride [2]. The main risk of gas evolution is explosion, and for this reason aggressive ventilation is essential in the event of a battery fire to prevent a dangerous build-up of gases [20]. Carbon monoxide is a useful indicator of thermal runaway and sensors should be provided to detect for it. However, the benefits of ventilation are limited if a large pack is totally engulfed – even one hundred air changes per hour would not prevent an explosion powerful to damage the bulkheads in a 4000 Ah battery fire. A further problem is that if the fire engulfs the entire battery, fire extinguishing will almost certainly be impossible due to the extreme amounts of heat being released [2].

Although oxygen evolution is only enough to fuel the fire within the cell, it still makes NMC battery fires very hard to extinguish, since most fire extinguishers work on the principle of denying oxygen to the fire. This is in addition to the fact that a cell core is inaccessible and combines chemical and metal fires. A key factor is preventing the thermal runaway from propagating to adjacent cells, and therefore the extinguishing medium’s other key role is cooling. Furthermore, other high risk equipment should be excluded from the battery room, which itself should be fireproof [2, 20].

A trial conducted by DNV-GL on lithium ion NMC cells compared the extinguishing effects of direct foam injection (FIFI4MarinCAFS), high pressure water mist, NOVEC™ foam, and sprinklers. Direct foam injection showed the best heat absorbing performance, high pressure water mist was very good for heat absorption and also was good at absorbing evolved gases and lowering their temperature, while NOVEC extinguished flames but was less good at absorbing heat and was not compatible with ventilation. Sprinklers performed similarly to high pressure water mist but introduce the risk of explosive gas pockets being formed and were the only system not able to extinguish visible flames due to the inability to get water where it was required. Foam and direct injection water, with the ability to flood into the modules, did a better job of reducing the main battery fire temperature, however water injection is not recommended due to conduction risk. As a last resort the entire battery room can be flooded with seawater, which is effective despite the high conductivity of seawater, but this will destroy the battery system. Deionised water is normally used for sprinkler or mist systems, reducing the conductivity and consequent damage. A further consideration is whether to encase the battery modules in IP44 protection, protecting them against flooding, and containing the waste products which would otherwise make the extinguishing water extremely alkaline. The fire suppression system should be suitable for multiple events, addressing the possibility of a reignition hours or even days later [2].

Putting this into practise, the Ellen E-ferry, which is DNV-GL type approved, has both cold foam and high-pressure water mist systems on board, and also a hot gas evacuation system. Each battery is encased in an IP65 metal containment system to help prevent battery fires from propagating [45].

Even for the relatively high risk NMC batteries in use today, there is still not enough data to conclude whether battery systems are actually higher risk than diesel propulsion systems. As safer battery systems are produced over the next decades, the risk of transport fires should decrease due to the elimination of fuel, at least in the case of battery-electric propulsion systems [2].

12 SHORE-SIDE INFRASTRUCTURE AND CHARGING SYSTEMS

When considering an electric or hybrid boat, one might assume that the batteries will dominate the cost of the project. This is not true. Experience with the Ellen E-Ferry shows that even during the project period, battery costs fell by half, and the EU report on the project states that shore-side infrastructure and power electronics are likely to be the dominant cost driver on future projects. For this reason, Ellen has shore-side infrastructure at only one of her two ports. Compared to a new diesel ferry, Ellen herself cost an additional €3 661 848 while the shore side infrastructure and connection cost €2 451 660, a split of approximately 60:40. The shore side infrastructure cost €1 068 503 while the connection cost more at €1 383 157. Of all of the costs, the connection cost is likely to be the one that changes the least in the future. The battery itself cost €4 283 277 [45].

A detailed investigation of shore-side infrastructure is beyond the scope of this report, but this point is important to highlight, as it further sets in context one of the key messages: the price of lithium ion batteries is rapidly fading as a barrier, and when costing is done for a future project, the infrastructure is absolutely key. The costs of laying new power lines and installing safe, automated recharging systems is much more of a stable cost, and given the decreased price of batteries, it may be that installing shore-side battery systems that can charge slowly before fast-charging a boat when required is more economically feasible than fast charging a boat directly from the electricity grid.

13 LIFECYCLE CONSIDERATIONS: SECOND LIFE AND RECYCLING

The impact of batteries on the environment is a common discussion point, with many asking whether the significant environmental costs of producing lithium ion batteries are actually offset in practice. Even in privately owned cars, which are far more lightly used than commercial vehicles, the full-life GHG emissions for electric vehicles are between 15 to 30% lower than for conventional vehicles, based on a representative European electricity mix including fossil fuels. (In this analysis, more than half the lifetime GHG emissions were from electricity generation, so going to 100% renewables dramatically increased the benefit) [60]. In boats, the benefits of battery operation are even greater due to the significantly increased duty cycle of commercial boats. Taking the Ellen E-ferry as an example, the GHG emissions created by the manufacture of the battery pack were equivalent to just three months of operation by a new diesel-electric ferry on the same route [45]. A lifecycle meta-analysis concluded that lithium ion battery cells required 328 Wh to produce 1 Wh of storage capacity, and 110 g of CO_2 equivalent (not including recycling) [61]. Currently it takes more energy to extract lithium from mineral deposits than from brines, and as the world production of lithium grows and naturally shifts towards mineral deposits, it will increase the GHG emissions and energy requirements of lithium [50]. As well as CO_2 emissions, lithium ion battery production is linked to ozone layer depletion, acidification of fresh and saltwater, and pollution of the ground [50].

The use of cobalt in most lithium ion batteries is an ethical, environmental and supply security issue, because cobalt is by far the most expensive and least abundant element used, and lithium ion batteries already consume over 50% of the world's production. The Democratic Republic of the Congo produces 66% of the global supply, and many battery manufacturers cannot guarantee their products are free from contributions from child labour [62]. Other types of lithium ion battery, notably lithium iron phosphate, avoid these difficulties by eliminating cobalt. Iron and phosphorous are both comparatively abundant and have no ethical issues in the supply chain, and involve less energy in their production from extraction through to battery production [50]. Other types of battery altogether are also less environmentally damaging to make. While sodium ion batteries require the same controlled environment as lithium for manufacture, sodium is many times cheaper and faces no abundance issues, since it can be extracted from seawater.

Because the battery itself does not cause any emissions while in operation, the next impact it has is at decommissioning. Discarding lithium ion batteries to landfill carries the risk of leaching the various chemicals into the ground and possibly the water supply and represents a complete loss of the raw materials that went into the original production of the battery system. The risk associated with the leaching of raw materials is moderate but will clearly get worse as the volume of disposed batteries continues to grow; at the moment, some countries allow lithium ion batteries to enter landfill and others do not. The best way to treat a lithium ion battery that has been retired from a vehicle is to re-use it in a new context. Batteries are generally considered to be exhausted for transport use when they reach 80% of their life, but for less demanding applications such as grid storage, they still have ample capacity. This approach avoids the inherent risk of cell disassembly. In this respect lithium ion batteries are more dangerous than other commercialised technologies such as nickel metal hydride or lead acid, and the accidental entry of a lithium ion cell into a recycling facility not equipped for it has resulted in several fires [63]. The risk severity is clearly higher for a specialised lithium ion recycling facility with a very high number of lithium ion cells stored in one place [64].

Future Oldendorff bulk carriers will feature ABB kinetic energy recovery cranes for self-unloading (Mernissi, CC BY-SA 4.0)

This approach of taking cells and re-using them directly is referred to as ‘cascaded use’ or ‘second-life’. However, this has issues as well, one of which is who takes responsibility for the safety and performance of the second-life battery. This issue is simplified if the original manufacturer recovers the battery pack and decides what to do with it, and this model is likely to be the one adopted by the automotive industry. Furthermore, the state of health is an average value across the pack and varies between cells to the point where some cells are virtually as new. Taking healthy cells from a used battery pack and including them in an otherwise new battery pack is termed remanufacturing. Some automotive companies such as Nissan are already using both cascaded approaches for their stationary home storage and remanufacturing for new automotive batteries [60]. Other companies such as Lithium Australia are trying to take control of every aspect of the lifecycle of a lithium ion battery, from the mining of the materials to the eventual recycling of the cells [50].

Recycling of lithium ion batteries is the next best option after re-use. Because of the dangers involved and the difficulty of separating the elements, recycling of lithium ion batteries is still very much a work in progress, with some pilot-level start-ups conducting recycling, but none yet able to economically recover all of the useful materials in the battery [65]. There are four main recycling processes for lithium ion batteries. Pyrolysis melts and reduces the waste battery to extract the metals. The toxic solvents are safely burnt to provide the process energy, and the cobalt, nickel and copper are efficiently extracted. However, lithium remains in the slag. Pyrometallurgy processes the metal oxides to metals in a smelter, creating an alloy to be processed for new batteries. Lithium is also trapped in the waste. Hydrometallurgy uses lithium brine to shred the cells. This recovers all the solid elements including plastics with lithium as lithium brine. Hydrothermal processes are preceded by mechanical separation of the battery, followed by crushing of the cathode materials, before dissolving the binder in solvent so the aluminium foil can be recovered [60]. Current levels of lithium ion recycling are very low, with only 1% of rare earth elements recycled at all, due to their low concentration in recycling products [66], despite the fact that cobalt, nickel and even graphite are considered extremely critical by the EU [67]. Future predictions are optimistic with a 2018 study estimating that one third of global cobalt supply would be met by recycling by 2021 [60]. While recycling always sounds appealing, it is possible that sometimes recycling can be more environmentally costly than primary production [61].

Ease of recycling is a key attraction of alternative battery chemistries. Examples already exist: up to 98% of a lead acid battery can be recycled using the dominant pyrometallurgical process, and battery recycling provides 85% of the recycled lead available on the market, as well as polypropylene from the battery cases and gypsum from the captured flue gas content [68]. However the smelting process consumes a lot of energy, and other research is ongoing into lower energy processes such as those using environmentally safe solvents or via electrowinning [68, 69]. Nickel metal hydride (NiMH) batteries are already efficiently recycled via pyrometallurgical processes (SNAM and Inmetco) or molten salt electrolysis (Honda) [70]. Lithium iron phosphate also has a relatively simple theoretical recycling procedure that requires only room temperature operation, where the recycled products can be manufactured back into a new electrode [71].

Because conducting a lifecycle analysis is beyond the scope of this report, the reader is directed to the Ellen E-ferry case study [45] and DNV-GL’s ‘Life Cycle Analysis of Batteries in the Marine Sector’ [72] for a deeper coverage of this topic.

Aditya, India's first solar ferry (Samarjitbharat, CC BY-SA 4.0)

14 Classes of boats and case studies of electrification or hybridisation

The various classes of boat, and the progress that has been made towards their electrification, are discussed in this section. However, the conclusions are summarised here first.

Passenger boats have already seen considerable electrification, particularly in Scandinavia. The current class-leading roll-on roll-off (ro-ro) ferry is the Ellen E-ferry which undertakes a 36 km round trip 7 times a day, partly recharging between each round trip. It is fully electric and has a 4.3 MWh lithium NMC battery. At the moment, this is the longest ferry route serviced by a fully electric boat. Meanwhile many ferries travelling longer routes have been hybridised, either as new boats or as retrofits. This typically saves around 15% fuel and allows zero emission operation in harbour.

Once solid-state lithium batteries are commercialised, the range of all-electric ferries will be extended. It is highly uncertain how far exactly, because it is not at all clear that today's ferries actually push the upper limit of range, and instead appear to be conservative in design, with a focus on environmental operation, safety, public acceptance and a short payback of CAPEX by reduced OPEX. That said, the batteries in Ellen were designed to entirely replace conventional ballast, and in fact the front battery room was heavier than expected, requiring some additional ballast at the aft end [45]. Solid-state batteries will increase safety as well as specific energy at the cell level, resulting in a battery pack with far less empty space and safety features (waterproof cases, cooling, fire safety systems) than before. The added safety may also increase the willingness to use larger batteries on boats. Therefore, solid-state lithium might allow battery-electric ferry ranges up to 150 km and lithium-air might allow up to 300 km.

Without suitable in-depth case studies, it is impossible to estimate the range of a fully electric workboat, particularly seeing that different workboats will have different duty cycles, different amounts of equipment required on board, different access to onshore refuelling/recharging infrastructure, and will be different sizes. However, a Chinese workboat operating on the Miyun reservoir has a 50km battery-electric range, a range that is quite similar to Ellen [38]. What can be said with certainty is that hybridisation offers more significant fuel savings for a complex duty cycle. As time goes on hybridisation can be expected to be seen on all workboats that are not suitable for battery-electric propulsion, and plug-in hybrids will allow a greater proportion of the duty cycle to be completed under electric power. For example, an offshore support vessel supporting a windfarm has a predictable duty cycle that involves charging opportunity at port, and potentially at the wind farm, taking power directly from renewable energy. Whereas existing wind farm service vessels use diesel engines to power Dynamic Positioning (DP), a future plug-in hybrid could perform this duty using renewable electricity without the round-trip losses through the battery system – while also recharging the battery to power as much of the trip back to port as possible, particularly in harbour, to reduce emissions in port [41]. For vessels with cranes, kinetic energy recovery systems can be used to regenerate electricity during load lowering. The same discussion applies to research vessels.

Whether cargo-carrying vessels can be made battery-electric or not depends entirely on their range requirements. While these boats are large and potentially have significant capacity for installing battery packs without much constraint on the form factor of the installations, maximum possible ranges will still be in the same order of magnitude as those achievable for ro-ro ferries. There are many cargo-carrying vessels in the world sailing regular routes of less than 300 km, and these may eventually be targets for electrification, providing there is enough time to charge them. However, above this range, synthetic fuel cell operation or synthetic fuel in internal combustion engines or CCGTs will eventually dominate (in the zero-carbon scenario), with hybridisation to improve efficiency, allow operation at peak efficiency of fuel cells, internal combustion engines, or CCGTs, and ensure environmental compliance in port. Container ships have the potential for longer range; their layout is ideal for battery implementation and their operating speeds are typically less than 10 knots, improving efficiency. The battery-electric Birkeland container ship is now sailing around the coast of Norway, with a maximum distance of 56 km between ports, again similar to the range achieved in workboats and ferries [73].

Beffen, by Torbjørn Wilhelmsen (CC BY-SA 4.0)

14.1 Passenger

14.1.1 Ferries

14.1.1.1 Beffen

Beffen means ‘Bergen electric ferry’ – a small harbour ferry in Bergen, Beffen began operating in 2015 [20].

14.1.1.2 Scandlines: Prinsesse Benedikte, Deutschland, Prins Richard, Schleswig-Holstein, Berline, Copenhagen

2.7 MWh of lithium polymer batteries were retrofitted as part of a hybrid solution to a previously diesel-electric ferry, Scandline’s Prinsesse Benedicte, which operates between Rødby in Denmark and Puttgarden in Germany. She operates fully electric in harbour, eliminating emissions in port, and the lifespan of the diesel engines has been tripled. Payback time on the Corvus Energy battery systems was predicted to be less than 5 years [20, 74]. The similarly hybridized Deutschland, Prins Richard, Schleswig-Holstein went into service in 2014. Hybridizing these four ferries saves about 15% CO_2 emissions compared with the original diesel-electric propulsion systems. In 2016 the Berlin and Copenhagen, each 1500 passenger ferries with capacity for 480 cars and a 1.5 MWh Corvus Energy battery, went into service. The CO_2 emissions are reduced by operating the diesel engines at optimal loading, more of the time [30].

Scandlines have stated their ambition is to be fully electric within a few years, but this is a challenge as the Rødby-Puttgarden route is 18.5 km, and there is currently only a 15 minute wait at each port during which to conduct fast charging [75].

14.1.1.3 Gee’s Bend ferry

HMS Ferries operate the US’ first all-electric ferry, Gee’s Bend. It runs a 1.45 nm route in Alabama, and has charging points on both sides. It has two battery rooms for redundancy and a ventilation system in case of a thermal event. Key benefits for the operator are the reduced maintenance over time compared to diesel [76].

14.1.1.4 Clyde and Hebrides Ferry Service: MV Hallaig, MV Lochinvar, MV Catriona

MV Hallaig was claimed to be the first diesel-lithium ion hybrid ferry in the world when it was launched in 2011. Owned by Caledonian Maritime Assets Limited, these three ferries resulted from Scottish Government and EU investment and were built on the Clyde by Ferguson Marine Engineering Ltd. 38% reduction in fuel consumption is claimed for the hybrids compared to conventionally powered boats of the same size. The boats have 700 kWh batteries, carry 150 passengers and 23 cars. MV Catriona was the last of the three to enter service, in 2016 [77].

14.1.1.5 Wightlink: Victoria of Wight

Victoria of Wight entered service in August 2018 and is a hybrid vessel running the Fishbourne-Portsmouth route. She can carry 1170 passengers and 178 vehicles, and uses 17% less fuel than a smaller ship running the same route [37].

14.1.1.6 Color Hybrid

Built by Ulstein Verft and run by Color Line, the Color Hybrid is a plug-in hybrid servicing Sandefjord-Strömstad since 2019. It has a 5 MWh lithium ion battery pack that is charged in port, enabling emission-free operation in the fjord of Sandefjord. It carries 2000 passengers and 500 cars [78].

14.1.1.7 India to build ferries for Oslo fjord

Demonstrating the synergies between autonomous operation and battery electric propulsion, in 2020 Norway's ASKO Maritime commissioned India's Cochin Shipyard Limited (CLS) to build two electric ferries operating on the Oslo fjord, each carrying 16 trailer units and powered by an 1846 kWh battery [79].

14.1.1.8 E-Ferry Ellen

A 31-car ferry operating between Ærø and Als in Southern Denmark, Ellen is an excellent case study for several reasons. Firstly, it is still the longest battery-only ferry route at 22 nautical miles (36 km) roundtrip (she has charging infrastructure at only one of her two ports) [80], and secondly, it was an EU Horizon 2020 project and consequently a huge amount of data has been made available. It has a 4.3 MWh battery of which 3.8 MWh is used over the full course of a day, with each return journey consuming 1.6 MWh. It is powered by a 4 MW fast charger, and the ferry takes advantage of operating at higher speed (13.5 knots) to gain 20-40 minutes of recharging opportunity between return journeys. Because of these short recharging opportunities, it only regains 1.1 to 1.3 MWh, and so the battery state of charge decreases steadily over its seven daily voyages, and is recovered overnight. The regular trips during the day mean that wind effects are largely negated [45].

Ellen E-ferry (Ærø Kommune and Henrik Hagbarth Mikkelsen) [45]

Passenger feedback has highlighted the increased comfort due to reduced noise and vibration from fully electric operation. The E-ferry has an 85% grid-to-propeller efficiency, more than twice as high as the tank-to-propeller efficiency for an equivalent diesel (Wärtsilä 16V14 diesel engines assumed running on <0.1% sulphur diesel). This high efficiency means that the reduction in GHG emissions are significant even if not running on fully renewable electricity: a new build diesel would have emitted 2520 tons of CO_2 over 2019, while Ellen running on a conventional Danish electricity mix would have emitted only 510 tons over the same period. PM_{10} emission for the conventional electricity mix is also only 34 kg relative to 542 kg for the new build diesel [45].

The battery balances itself overnight, rather than trying to move significant amounts of energy between cells during the day. It charges up at full speed to 65%, a little slower to 80%, and then at half speed to 90%. It does not use the top 10% of capacity to extend the life of the pack. The report highlights that the initial task of balancing such a large battery is a significant project in itself taking several months. Ellen always operates with a baseline of capacity in reserve (2x 400 kWh). The batteries are split between a forward and aft battery room for redundancy and balance [45].

The report also provides detailed information on the breakdown of efficiencies within the system. The ship-to-shore charging cables run at a 1.5% loss (this can be higher if the cables are not laid properly due to induction and other effects), and the losses inside the battery during charging are also about 1.5%. This leads to an efficiency of 92% from the grid to stored energy in the battery, and a 92% efficiency from the batteries to the propeller [45].

While much has been made of the use of lightweight materials in electric cars to offset the increased mass of the battery, this is not something that has happened in Ellen, and her construction is not significantly different from a conventionally powered equivalent. A significant saving can also be made on manpower due to the reliability of all-electric propulsion: about 12% compared to a new build diesel, with a crew of 3-4 rather than 4-5. Maintenance costs over the year are reduced by 37%. Overall, the lifecycle analysis indicated that providing the ferry ran on renewable electricity, the only downside for the environment was the mineral scarcity involved in the batteries [45].

The project highlighted that the regulatory environment needs to keep up in order for the creation of jobs and services around the marine battery industry to be maximal. While it is usual for the regulatory environment to lag behind innovation, authorities must adapt fast to create the most benefit. In total, Ellen has 980 kW of power, split between a 700 kW main motor, 250 kW of thrusters, and a 30 kW hotel load. DNV-GL were the classification society that approved Ellen [45].

14.1.1.9 Ar Vag Tredan

The Ar Vag Tredan is the world’s first electric ferry powered entirely by supercapacitors. It conducts 28 crossings per day with a charge time of 4 minutes and a journey time of 7 minutes. The supercapacitors are expected to last 15-20 years [25]. This demonstrates the feasibility in niche marine applications for using unexpected energy storage solutions.

14.1.1.10 Ampere

The first large-size all-electric battery car ferry is Norled’s Ampere, which started operating in 2015. This has a 1 MWh battery, achieves 10 mins charging between each crossing, and is fully charged overnight. It sails a 5.7 km route [81].

14.1.1.11 Aditya

Aditya is a 75-person solar-powered battery-electric ferry making 22 trips a day with a top-up battery charging cost of only $2.60 a day [82].

14.1.1.12 Aurora and Tycho Brahe

Aurora and Tycho Brahe are fully electric passenger ferries operating a 4 km route between Sweden and Denmark. Tycho Brahe is 238 m long and has a 4.1 MWh battery pack [83].

14.1.1.13 Elektra

Finland’s first hybrid electric ferry, operated by FinFerries, sails a 1.6 km route 25 times a day. Charging is completed in five and a half minutes with a complete charge overnight. It carries 90 cars and 375 people at 11 knots. The battery has a 1 MWh capacity and solar panels, saving 60% in operating costs compared to a similar diesel [84].

14.1.1.14 Junlyu
China's first electric ferry, running sightseeing trips in Wuhan. No specifics available [85].

14.1.1.15 Plymouth Electric Ferry – The Mermaid
A consortium is working to produce the e-Voyager, a retrofit of the existing ferry The Mermaid [86].

14.1.2 Cruise ships and tour boats

14.1.2.1 Niagara Falls: Nikola Tesla and James V Glynn
Nikola Tesla and James V Glynn are two catamaran tour boats that sail for *Maid of the Mist*, the tour boat company that operates at the foot of the Niagara Falls. The boats split a 316 kWh battery capacity between the two hulls, providing redundancy, and the batteries are supplied by ABB. The energy for the boats comes from hydroelectricity generated by the Niagara river itself. Business upsides are the significant reduction in OPEX which is rapidly paying off the increased CAPEX [76].

14.1.2.2 Vision of the Fjords, Legacy of the Fjords, Future of the Fjords
ABB has provided hybrid technology to the Vision of the Fjords sightseeing ferries. All three boats have now been converted. The Vision of the Fjords itself is a 400-person capacity boat, 40 metres long, with plug in charging at each port as well as diesel-electric power [87].

14.1.2.3 MS Roald Amundsen/MS Fridtjof Nansen
MS Roald Amundsen is the world's first hybrid expedition ship. Carrying 530 people, the hybrid system is expected to lower fuel consumption by 20% [31].

14.2 WORKBOATS

14.2.1 Offshore support vessels

14.2.1.1 Edda Ferd
The first new build offshore supply vessel with battery system installed was Edda Ferd in 2013 [20]. It is a 150 m offshore vessel equipped with 546 kWh from Corvus Energy. One job the boat has to do is power a 400-tonne capacity crane that is used to lower items to the sea floor; it is able to capture the energy released from lowering the load and absorb it into the batteries, the hotel load, and the propeller. The boat is reported to spend around 70% of its time in Dynamic Positioning [43].

14.2.1.2 SolstadFarstad – Normand Server and Normand Supporter
Normand Server and Normand Supporter have been converted to hybrid propulsion, each with 560 kWh batteries providing a 15-20% reduction in emissions [32].

14.2.1.3 Seven Viking
Seven Viking is a 107 m hybrid offshore support vessel with 1356 kWh of Corvus batteries. The battery provides load levelling, peak shaving and spinning reserve. The hybrid system is a retrofit [44].

14.2.1.4 Viking Lady
Norway's FellowSHIP project has yielded the Viking Lady which has a fuel cell, battery system, and can run on LNG, diesel or even methanol. The fuel cell is a molten carbonate system running on LNG; it provides 320 kW power [88].

14.2.1.5 Ørsted Horsean Two offshore wind farm crew transfer vessels
Two hybrid crew transfer vessels scheduled for 2021, 35m long, with Danfoss Editron systems [89].

14.2.2 Tugboats

14.2.2.1 Carolyn Dorothy and Campbell Foss

Carolyn Dorothy was the first hybrid tug in the world, followed by the Campbell Foss. They are estimated to save 20-30% fuel [33].

14.2.2.2 RT Adriaan

RT Adriaan is a hybrid tug for longer range [90]. A late-stage conversion of an almost-ready conventional 'Rotor Tug', 32m long, with lithium polymer batteries, taking advantage of the fact that on conventional tugs, the necessarily powerful diesel engines only operate at maximum power for 2% of their life. The battery capacity is 78 kWh and saves 20% of fuel consumption [34].

14.2.2.3 Zeetug30

Zeetug is a battery-electric inner harbour tug that takes advantage of regular recharging opportunities [90]. It has a total storage capacity of 1 484 kWh for a 19m boat, the world's first battery-electric tug, and began sailing in 2019 [91].

RT Adriaan Tug (Torn, CC BY-SA 2.0)

14.2.3 Workboats

14.2.3.1 Estonia's hybrid patrol boat

A 45 m hybrid patrol vessel for search and rescue, firefighting, offshore patrol and pollution combat. It can sail at 27 knots at full power or 10 knots on electric power. Built by Baltic Workboats [92].

14.2.3.2 Two Workboats on Miyun Reservoir

The first workboat commissioned for the Miyun Reservoir and powered by Danfoss Editron is a batter-electric workboat, used for rescue, forest fire prevention and cleaning operations. The range is claimed to be 160 km but this appears to be a mistake because the other ship, which is only 15 t heavier at 90 t *vs.* 75 t, has a stated range of 50 km. The battery size is 960 kWh. The second is a hybrid workboat used for water quality monitoring with a range of 50 km, also making use of a 960 kWh battery, though it only uses the diesel generator as back up/a range extender [38].

14.3 Fishing boats

14.3.1.1 Karoline

Karoline is an 11m fishing boat with 195 kWh of lithium polymer energy storage. It has a small 50 kW auxiliary generator for back up and is intended to function battery-electric for a 10-hour working day [39].

14.4 Merchant Vessels

14.4.1 Tankers

14.4.1.1 Sten Tor and Sten Odin

Sten Tor and Sten Odin are two chemical tankers that operate in the Baltic and North Sea emission control areas. They are the first tankers to use a hybrid propulsion system and the batteries function as spinning reserve when manoeuvring in port, and are also plug-in, taking advantage of a 400 kW shore connection [35]. The batteries also perform load levelling and peak saving functions. Yearly fuel savings for Sten Tor is approximately 22%, from a battery size of only 181 kWh, demonstrating the savings that can be made on a 155m long vessel from a relatively small installation [40].

14.4.1.2 Aurora Spirit offshore shuttle tanker

The Aurora Spirit is an offshore shuttle tanker built by Samsung Heavy Industries, burning LNG, using batteries as part of a hybrid power system that performs functions such as peak load shaving. Total energy consumption saving is about 30%, from 110 GWh per year to 75 GWh [35].

Edda Ferd, (Jamieson, CC BY 2.0)

14.4.2 Container Ships

14.4.2.1 Birkeland – Norway's fully electric container ship

The Birkeland will be the first fully autonomous and fully electric containership, and completion is estimated for late 2020. It will carry up to 120 six metre containers. It will use a battery pack of between 7 and 9 MWh, and uses this instead of ballast. It will have a service speed of 6 knots and will sail up to 56 km between ports (the actual range could not be found) [73].

14.4.2.2 ReVOLT – concept autonomous electric container ship

The ReVOLT is a concept fully autonomous battery-electric container ship. By sailing at 6 kn, it would travel up to 185 km on a 5 422 kWh battery, carrying up to 100 six metre containers. It is estimated that payback time compared to a conventional diesel ship with crew would be less than 1 year due to operating costs 4.5 times lower than the diesel ship [20].

14.4.2.3 Port-Liner – Dutch fully electric autonomous container ship using vanadium redox flow batteries

Port Liner have identified inland container shipping on waterways as a good opportunity for the use of vanadium redox flow batteries, packaged in individual containers. They claim that four redox flow battery containers will allow a 100m ship with a 14x 6m container capacity to travel up to 230 km on inland waterways, fully autonomously [93]. Vanadium redox flow batteries have specific energy of up to 30 Wh kg^{-1} compared to the 86 Wh kg^{-1} (at pack level) achieved for the Ellen E-ferry using lithium NMC, so it will be interesting to see if these boats are successfully built and what range they demonstrate if so.

14.4.3 Cargo ships

14.4.3.1 Pearl River Electric Cargo Ship

This Chinese coal-carrying cargo ship is claimed to have a range of 80 km from its 2.4 MWh lithium ion battery and takes 2 hours to charge. The battery weights 26 tons and the ship is 70.5 metres long [94]. It sails at 7 knots [95].

14.5 Research Vessels

14.5.1.1 SeaRobotics/Torqeedo hybrid research boat

A small autonomous research vessel for subsea mapping and long-range hydrography with a 30.5 kW lithium ion battery and a 25 kW diesel generator. Sails for 10 hours on battery power between charges, particularly suitable for low-noise operation, and then recharges itself using the diesel engine, providing up to six days on station [96].

14.5.1.2 Korean research vessel by STX offshore

A 5 900 tonne research vessel, based in Korea, in operation since 2016, powered by a Danfoss hybrid power system and built by STX Offshore and Shipbuilding Co. Ltd, with stated 30% energy savings [36].

14.5.1.3 Peruvian Navy Research Vessel

The Peruvian Navy have commissioned a hybrid-electric research vessel powered by a GE hybrid system, with specific emphasis on silent operation for research in the Antarctic; it will have DNV-GL SILENT certification [97].

Scandlines Motor Ferry Tycho Brahe (Bjoertvedt, CC BY-SA 3.0)

15 Future Batteries

The key questions this report seeks to answer for the various battery types considered are the viability of the battery type and the timelines to commercialisation to the stage where a battery type becomes available for marine use. The list is not exhaustive and represents a best effort at covering the most likely chemistries to be discussed or implemented in transport applications.

In terms of specific energy, actual data or reasonable predictions of it are available at the cell level. However, accurate predictions of pack level energy density are far more difficult. There is a lot of complexity in marine design due to the many constraints including available space, safety, and weight distribution, to mention just a few. The prediction that solid-state lithium and lithium air will offer specific energy 3x and 6x higher respectively is a very rough estimation for indicative purposes.

The impact of the required fire safety system and related concerns over the maximum size of any particular battery room is significant. Of the considered batteries available today, NMC is the most dangerous and also has the highest energy density [2]. Future chemistries are likely to require significantly less fire safety system and may be able to be contained in a single battery room, or at least without the explosion-proof compartments and ventilation systems.

In terms of technology readiness level, TRLs 1-2 (laboratory research) are either very recent concepts, or are delayed by fundamental technology obstacles, such as metal air batteries. It is assumed that these batteries will be available at the earliest in 15 years, because although significant research may be underway, there is no guarantee that the hurdles can be overcome. TRLs 3-5 may be available in the 10 years: they have had the required fundamental breakthroughs but have yet to reach the maturity required for large-scale use, due to the need to prove successful manufacture and operation at large scale and develop the refinement in manufacturing and design required. TRLs 5-7 are batteries that have been proven at large scale pilot tests, but for which supply chains and factories have yet to be built and might be available in 5 years. Finally, TRLs 8-9 are batteries that are mature and reaching mass manufacture, such as lithium iron phosphate. The TRL scheme does not apply to batteries that are already widely used such as lithium NMC.

16 LITHIUM

With the exception of a very limited quantity of NiMH batteries used by Toyota, lithium ion batteries dominate the market for electromobility today. A combination of factors makes lithium extremely unlikely to be displaced. Firstly, it has the highest electrochemical potential of any element in the Periodic Table, which means that no other element can generate such a high battery voltage. Secondly, it is the lightest metal, which works with its voltage to give it the highest theoretical specific energy of any battery anode. Thirdly, it is now a mature technology that continues to benefit from the economies of mass production; the price of lithium ion battery storage has dropped significantly over the last ten years and continues to do so [50]. Fourthly, despite some highly publicised battery fires, public acceptance is generally good, which makes introducing new types of lithium ion battery much easier than introducing an entirely new kind of battery to the market.

Electric vehicles have rapidly grown to demand two-thirds of new lithium ion battery production in 2017. The number of electric vehicles globally was about 5 million in 2018, and is predicted to grow to 20-40 million vehicles by 2030; over the last few years it has increased about 60% per year [50].

The main types of lithium ion battery available today are lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminium (NCA). LCO has very high specific energy, and is popular for mobile devices, but is expensive [98], thermally unstable and has limited cycle life (<1000 cycles) [50], making it unsuitable for transport use, so it is not discussed further. LMO has a different characteristic, with very good thermal stability and fast charging capability, but again the cycle life is short. LMO batteries are either combined with NMC batteries to provide a blend of high power and high energy, or outright replaced by NMC, which already combines the benefits of nickel with manganese. Therefore, LMO is not further discussed either. The three current technologies that remain are discussed in their own sections below.

Future lithium ion batteries are discussed in detail below, but a quick summary of specific energies is provided here. A current lithium ion cell achieves about 250 Wh kg^{-1}, around ten times less than petrol. Replacing the graphite anode with pure lithium (by going to solid-state) allows an increase to 440 Wh kg^{-1}, based on a lithium transition metal oxide cathode. Lithium sulphur allows 650 Wh kg^{-1} while lithium air will allow 950 Wh kg^{-1}. Meanwhile, the energy density offers less scope for improvement, from 700 Wh l^{-1} for today's cells to over 1,100 Wh l^{-1} for lithium air (although this is high enough to rival petrol) [99].

At the moment, global lithium ion battery production is dominated by a few large companies, including Samsung, LGChem, Panasonic, CATL and Sony. About three quarters of global production is concentrated in China [50]. However, marine battery system suppliers manufacture their own cells in many cases, and these are distributed around the world.

The fire risk associated with lithium ion batteries is caused by a combination of volatile organic electrolytes, cathode materials that can release oxygen during thermic breakdown, and anodes on which lithium can plate, form dendrites, and short circuit the battery, creating a thermal event that can propagate throughout the battery pack and destroy the entire vehicle [100-102] . Many of the new materials being researched for these batteries attempt to solve the fire safety problem through different electrode materials and electrolytes.

The research pipeline for future lithium is more promising than for any other battery type. For these reasons, there is plenty of evidence on which to base the assertion that the most likely future type of battery to be found on a boat over the next few decades will be some kind of lithium battery.

Aurora (Oberger, CC BY-SA 4.0)

16.1 Operation
Lithium ion cells are assembled in their discharged state, with all the lithium required for battery operation contained in the cathode. When charged, this lithium travels to the anode. In the first few cycles, the solid electrolyte interphase layer (SEI) is formed by parasitic reactions between the lithium at the anode and the electrolyte, which prevents lithium from being absorbed in further side reactions.

16.2 Progress on anodes
Given the issues with multivalent metal batteries (see Section 20), there is a general agreement that lithium metal represents the ultimate anode, due to its unrivalled electrochemical potential (-3.040 V *vs.* standard hydrogen electrode) and low density giving high specific capacity (3860 mAh g^{-1}). However, lithium metal does not plate evenly, and rapidly forms dendrites during cycling. These dendrites are sharp protrusions that can easily pierce the separator in the battery, shorting out the battery and leading to thermal runaway. A previous attempt by Moli to commercialise lithium metal batteries in the 1980s ended in their withdrawal from the market due to repeated battery fires, and

since then the use of lithium metal with liquid electrolytes has remained firmly at TRL 1-2 [99]. The only viable solution to using a lithium metal anode is to use a solid electrolyte with enough strength to resist dendrite penetration, allowing carefree battery cycling without the risk of thermal runaway [99, 103]. Lithium batteries with solid electrolytes are close to large-scale commercialisation, and once achieved, other types of anode research will be largely obsolete. They are discussed in full in the next section.

There are some clear trends in anodes for lithium batteries that can be summarized. Nanostructuring (which specifically means engineering the size, distribution, and coating of particles, as well as the grain size and distribution within particles) has led to such clear improvements that it can now be expected that all anodes in production have been nanostructured. As particle sizes get smaller, surface area increases and diffusion distances decrease, increasing power capability and decreasing resistance. Furthermore, the electrical and ionic conductivity of the anode can be precisely tailored by the combination of different component materials [104].

However, nanostructuring also brings about negative effects: an increased incidence of side reactions due to the increased surface area, and an increase in cost from increased processing [104]. Nanostructured materials may also be difficult to recycle due to the complex multi-material structures created.

Graphitic carbon remains the most commonly used anode used in lithium ion batteries, due to its very good conductivity, structural and chemical stability. It consists of layers of carbon which can hold at the most one lithium atom per six carbon atoms, giving it a maximum theoretical specific capacity of 372 mAh g^{-1}. Lithium intercalation into carbon occurs at very close to the Li/Li^+ potential, meaning that nearly the full discharge potential of a given cathode can be reached. Graphite electrodes are well understood, mass produced, mature, and close to their theoretical limit in terms of performance. They do not require complex processing, and graphite is an abundant and cheap by-product of the steelmaking industry [104]. However, it should be noted that due to the connection to steelmaking, China produces all of the graphite used in lithium ion batteries, causing the US and the EU to list it as a critical mineral [67]. Given the significant greenhouse gas emissions of steelmaking, it is also desirable to reduce the supply risk and the emissions by eliminating the need for graphite if possible.

A key disadvantage of graphite is the poor lithium diffusion rate. This (alongside poor diffusion in commonly used cathode materials) limits efforts to create batteries that can be satisfactorily fast charged. Fast charging results in unwanted additional solid electrolyte interphase growth and lithium formation on the electrode surface, leading to dendrites [105].

It is possible that some improvements in performance can be made through the use of carbon nanotubes or graphene. Graphene can theoretically achieve LiC_3, doubling the specific capacity of graphite at 744 mAh g^{-1}. However, graphene sheets and carbon nanotubes are very hard to produce at anything except for the smallest scales, and the technology is still at a low TRL level of 1-2 [104].

An alternative to carbonaceous materials is to use alloys of different metals. These store lithium via chemical reaction, leading to a phase change. While the theoretical specific capacity can be higher than for carbon (each alloy atom can potentially store more than one lithium atom), the phase changes lead to significant volumetric expansion, causing swelling, failure and detachment of the nanoparticles in the electrode. Additionally, electronic conductivity is often poor in these alloys, and the SEI layer is not stable but thickens over many cycles, absorbing active lithium. However, it is possible to create a mixture of active metals that store lithium (i.e. antimony) with inactive metals that provide a buffer against volumetric expansion (i.e. niobium) [104].

One way of avoiding the problem of lithium deposition on the surface of the anode is to raise its potential further above Li/Li^+, so that intercalation occurs at a safe margin above the potential necessary for lithium plating. However this reduces the discharge potential of the battery, lowering specific energy [104].

Transition metal oxides are another possibility, but remain firmly at TRL 1-2, suffering from low coulombic efficiency and high potential that reduces the discharge potential of the battery. They can also store lithium via insertion or conversion [104].

Finally, silicon is vaunted as offering the best storage capacity of lithium of any element. Each silicon atom can theoretically bond four lithium ions giving a specific capacity of 4200 mAh g^{-1}. However, the impact on the volume of the electrode for increasing its atom count by five times is huge (a 400% increase in volume), and nothing close to this is achievable in practice - a anode with a high quantity of silicon will swell and crack in a way that destroys first the SEI layer, and then the electrode itself in just a few cycles. Therefore, a small amount of silicon can be included in a carbon matrix with the capability to withstand and buffer the expansion caused by the lithium storage on silicon [104].

While silicon is already included in small quantities in some commercial carbon-based anodes, there is much debate over the best way to include it. It is accepted that only small amounts can be included, buffered by a mainly carbon construction to limit and absorb the expansion. It can be included as particles, as a thin film, or as nanowires. In every case the aim is to have the silicon very thin in at least one direction, so that it has a dimension in which it can expand where a fourfold volume expansion is not disruptive to the electrode structure. Strategies have been attempted such as encapsulating silicon within carbon nanotubes or mixing it with graphene to take advantage of the high strength of these materials. However, high processing cost and lack of ability to produce these materials at scale keeps these techniques at TRL 1-2 [104, 106].

Lithium titanate (LTO) is a mature anode that replaces graphite for applications where energy density is less important, and high power, outstanding cycle life (15 000 to 60 000 cycles) and safety are desired. The cycle life is provided for by the very low volume change of the electrode during cycling (<1%), while the safety is because the battery cuts off 1 V from the Li/Li^+ potential, giving a large safety margin against plating lithium onto the electrode, with the accompanying risk of dendrite formation. LTO has a spinel structure, making lithium ion diffusion rapid through the electrode structure, giving it its high rate capability. Additionally, an SEI layer is not formed on the lithium titanate electrode, contributing to its stability and high rate capability. However, LTO has relatively poor specific capacity (175 mAh g^{-1}), which combined with its restricted discharge potential gives a specific energy of <100 Wh kg^{-1} for LTO cells. It also has much better cold weather operation than graphite, down to -30°C [107, 108].

LTO has seen at least one marine application so far due its fast charging capability and safety, in the BB Green ferry in Riga, Latvia. It currently uses a 200 kWh LTO battery which can be discharged over a 30 minute journey, and recharged in 15 to 20 minutes at 4 C [109]. This is particularly suitable to this vessel because it is a high-speed air-supported vessel that uses a fan to create an air cushion under the boat, and then travel faster with less drag as a result. Therefore, the ability to deliver very high power can dramatically reduce the energy required to make a given voyage, suiting this particular vessel to a high power, low specific energy battery type. This illustrates the lack of a one-size-fits-all approach to marine applications, at least at the moment with the range of properties achievable from different battery types.

Elektra (LPfi, CC BY-SA 3.0)

16.3 Solid electrodes (solid-state batteries)

The current type of lithium ion battery electrolyte offers a range of benefits including good electrochemical stability (ability to withstand high voltages without breaking down) and good ionic conduction, essential for high efficiency and power operation. However, they are based on lithium salts dissolved in organic solvents, and these organic solvents are highly flammable and contribute significantly to any battery fire that occurs. For this reason, solid electrolytes have been explored [110]. However, the key benefit is really that a solid electrolyte is also a way to allow lithium to be used as a metal anode rather than storing it in graphite: it could feasibly be made strong enough to prevent dendrite growth or penetration.

Furthermore, there are types of cathode that offer even higher voltages than current lithium ion batteries and this is another clear way to increase the specific energy density of the battery. However, the voltages on offer (up to 5 V) are high enough to cause electrochemical breakdown of the current crop of electrolytes. Therefore, to make use of these new cathode materials, new electrolytes are needed.

The three types of solid-state electrolyte are polymer-, oxide-, and sulphide-based. Polymers (for example, polysiloxane or polycarbonate) have poor chemical stability and conductivity at lower temperatures, but good mechanical flexibility, while oxides (for example, $Li_{12}GeP_2S_{12}$) have very good chemical stability and strength, but are difficult to mass produce and are inflexible. Sulphides have the best ionic conductivity due to the low energy interaction of lithium and sulphur atoms, can be processed using conventional roll-to-roll methods, and have intermediate mechanical properties [50, 110-112]. Other promising variations demonstrating promising performance in the lab include polymer/oxide composites or cross-linked polymer networks, but it is not clear that these are close to commercialization [110, 113], while at TRL 1-2, too many options are being considered to discuss here, including electrolytes based on ionic liquids, metal organic frameworks, and cellulose [110].

Researchers at Samsung are among the first to claim a breakthrough, combining a lithium metal anode with a thin (5 µm) layer of silver-carbon nanocomposite layer pressed onto the anode, and a nickel-rich layered oxide cathode. This resulted in 900 Wh l^{-1} energy density, cycle life over 1000 cycles and coulombic efficiency of 99.8% [114, 115]. Meanwhile, Toyota had planned to reveal a solid-state battery vehicle at the Tokyo 2020 Olympics before the Covid-19 outbreak with a view to reaching the market in 2025, with a sulphur-based electrolyte [116]. Other companies also see promise in the sulphur-based route, with start-up Solid Power on the verge of commercializing solid-state lithium metal batteries using sulphide-based solid electrolytes. The solid electrolyte effectively removes the upper temperature limit of the batteries, meaning cooling systems may become completely unnecessary. However, pack heating will still be required especially for fast charging because the ideal operating temperature is higher than for conventional lithium-ion batteries [111]. These are claimed to be already mature for stationary applications, with only automotive approval standing in the way of use in electric vehicles by 2026, and are claimed to offer 320 Wh kg^{-1} in pouch cell format, significantly better than current lithium-ion batteries, with aspirations to exceed 400 Wh kg^{-1} in the future [117]. Meanwhile Volkswagen have partnered with QuantumScape with a total $300m investment to develop solid-state batteries, though no details are available [118].

In summary, solid-state batteries are clearly moving from TRL 5-6 and TRL 7-8, and should be available within 5-10 years [111, 114]. A solid-state electrolyte should be compatible with existing cathode materials, which means that a choice will remain over cathode materials ideally suited for marine applications. Given the very high safety of solid state batteries meaning that the battery racks in the module can be placed much closer together, combined with the increased specific energy and energy density at the cell level and the lack of mass and volume occupied by a cooling system, the impact could be a very significant increase in overall pack specific energy and energy density. Furthermore, cathode choice can still be made based on materials availability and cost. For example, either the highest performance attainable via a layered oxide cathode including all variants of NMC can be chosen for performance applications, or to attain supply security, lithium iron phosphate can be used instead to eliminate the rare metals cobalt and nickel [110]. However, the choice will then be about materials supply and lifecycle impacts alone as safety aspects should be significantly improved regardless of the choice of cathode.

Maid of the Mist Tour Boats, Niagara Falls

16.4 Liquid electrolytes

The conventional lithium electrolytes are $LiPF_6$ salt dissolved in some mixture of organics and esters including ethylene carbonate, propylene carbonate, dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethyl methyl carbonate [107]. These kinds of electrolyte have the benefits of forming a protective passivating layer on the aluminium cathode current collector, high ionic conductivity, low viscosity, and stable SEI layer formation. The exact proportions are crucial to the formation of a stable SEI layer formation, which forms from components of the electrolyte during the first few cycles. The process of SEI layer formation, critical for safe operation in lithium ion batteries with $LiPF_6$ electrolytes and graphite anodes, irreversibly consumes some of the lithium in the battery, and this represents an unavoidable loss of capacity for these batteries. The exact nature of the battery cycling for the first few cycles is also critically important to their performance over the rest of the cell life, and therefore commercial lithium ion cells are all cycled carefully as a final part of their manufacture [119].

These organic electrolyte components are all highly flammable and are a major part of the fire risk presented by today's lithium ion batteries. They are also limited in their electrochemical stability, prohibiting the use of very high potential cathodes that could increase the specific energy of lithium-ion batteries [120].

A non-toxic, very safe option is to use aqueous electrolytes instead (those based on water). These are non-flammable but have reduced electrochemical stability and produce batteries with low cycle life. Ionic liquids are also non-flammable and have electrochemical stability competitive with organic electrolytes. However ionic liquids are expensive and viscous, limiting their low temperature performance [50].

In summary, the conventional $LiPF_6$ salt in organic solvent liquid electrolytes currently represent a best-achievable compromise with no clear route to improvement (except for marginal improvements gained by additives, which are normally proprietary), and the most obvious way to improve the electrolyte performance is to move to a solid-state electrolyte [120].

16.5 Lithium nickel manganese cobalt (NMC)

NMC is the most popular type of cathode for automotive applications and is being used in a lot of marine applications as well. It is a type of layered oxide, a class that also includes LCO. NMC contains both manganese and cobalt. The manganese has poor structural stability but good chemical stability, and the cobalt has the opposite. When combined in a cathode, they complement each other. Nickel has intermediate properties. Because manganese and nickel are also more environmentally benign and abundant, the trend is to include as little cobalt as possible in modern NMC batteries. However, going above a certain level of nickel causes the SEI layer to grow thicker [121]. NMC offers a specific capacity of 170 mAh g^{-1} [122]. It should be noted that manganese and cobalt are largely present to stabilise the electrode structure and prevent various problems with nickel instability, which presents dangers and difficulties all the way from manufacturing to cycling of the battery in practice. Therefore, the lower the percentages of these components that can be included, the better the capacity will be, but the greater the technology required to make the batteries safe [123].

Today the most common composition of NMC has been NMC622, which describes a cathode that is 60% nickel, 20% manganese and 20% cobalt. While NMC622 is outperformed on specific energy by NCA, it is safer than NCA. There is currently a lot of research being done into 80% nickel, 10% manganese and 10% cobalt electrodes (NMC811). NMC811 falls into the wider research area described as ‘nickel-rich layered oxide cathodes’ and this area is widely considered to be the future of nickel-based electrodes for lithium and lithium ion batteries, offering up to 300 Wh kg^{-1} compared to today’s 250 Wh kg^{-1}, with a 215-220 mAh g^{-1} specific capacity of the NMC811 electrode and a higher discharge potential [124, 125]. However to date, increasing nickel content, while increasing initial discharge capacity, is associated with unavoidable capacity loss in the first few cycles of the battery and a severely increased risk of thermal runaway due to the tendency to release oxygen from the electrode material, as well as phase change of the electrode to a spinel structure [50, 126, 127]. Many of these problems can be mitigated, similar to NCA, by encapsulating nanoparticles of NMC811 in a safer material such as lower-nickel NMC. Forecasts for bringing NMC811 to market are within the 5-year timeframe (by 2025) [123]. However, for marine use, a safer, lower-nickel variant of NMC will probably still be used because of the safety risk, unless combined with a solid-state electrolyte to improve the battery safety.

Vision of the Fjords Tour Boats (Grimes, CC BY-SA 2.0)

16.6 Lithium nickel cobalt aluminium oxide (NCA)

Lithium nickel cobalt aluminium oxide (NCA) has found widespread use in automotive and is the battery chemistry manufactured by Panasonic for Tesla (which stands alone in not using NMC for battery-electric vehicles) [128]. It has the benefit of having lower cobalt content than NMC (15% vs. 20% for NMC622) [124]. Aluminium does not itself store lithium, but it stabilises the cathode, resulting in improvements in electrochemical performance and stability [122, 129]. NCA has similar safety characteristics to NMC [130]. However, while NCA offers outstanding capacity at 200 mAh g^{-1} in commercial cells [122], it does not in its pure form have good reversibility or cycling life, due to side reactions forming a thick SEI layer on the surface of the cathode. A thin layer of carbon or phosphate coating such as LFP applied to nanoparticles of NCA significantly mitigates this issue, and while commercial makeups remain proprietary, it may be a solution such as this that allows Tesla to use NCA in their electric vehicles [131]. To date there is no record of NCA being applied in marine applications. Given that the exact formula of its only successful commercial application is proprietary to Panasonic, a marine application would for now require a contract with Panasonic/Tesla to provide the battery. However, the fact that the increased performance of NCA comes at a trade of reduced safety is unattractive for marine applications, and the increased safety features required onboard would likely offset the increased performance.

16.7 Lithium iron phosphate (LFP)

LFP (chemical formula $LiFePO_4$) has a long cycle life due to small volume change in the cathode [98]. LFP uses abundant elements and very good safety, because the oxygen is tightly bound to the phosphorous, and has good power when properly designed [121]. It forms an olivine structure in the cathode which naturally creates ideally sized channels for lithium ions to pass through with minimal disruption to the structure of the cathode. LFP has lower energy density (163 Wh kg^{-1}) than NMC or NCA [98], but considerably lower material cost. However, the cost of cells is currently higher than NMC because of the difference in production volumes. LFP is also a good candidate cathode for sodium ion batteries [121].

A bottom-up pricing estimation found that LFP would have costs of $148.9 kWh^{-1}, when manufactured in a 35 GWh production capacity factory, relative to $138.3 kWh^{-1} for NMC622, or $132.4 kWh^{-1} for NCA [132]. However, other sources rank the prices differently, with LFP cells having lower material cost than NCA by approximately 25% [98].

LFP batteries produced by Saft have already achieved Bureau Veritas safety approval for use on boats [8]. Valence Technology has produced a lithium iron magnesium phosphate, which presumably replaces some of the iron with magnesium. No academic research could be found to explain the operation of this battery, suggesting it is proprietary. It has achieved DNV-GL certification [133] and their batteries have already been used in several hybrid boats [134]. Manufacturer claims on cycle life range from 5000 cycles at 80% DOD with <3% self-discharge per month [135] to 10 000 cycles at 70% DOD before the battery reaches 70% of its initial capacity [136], with all manufacturers claiming LFP's extremely good intrinsic safety and long cycle life as key selling points.

The key challenges with LFP are the poor rate of diffusion of lithium ions through it, and its poor electrical conductivity, which for pure LFP are orders of magnitude worse than other current lithium ion battery chemistries. They are improved by incorporating carbon throughout the cathode, which provides conduction paths for both electricity and lithium ions. Future improvements may be achieved through increased nanostructuring of the cathode: decreasing the grain size reduces diffusion distances and improves surface area, raising the power [98]. The best method is to make nanoparticles of LFP that are coated in carbon [121].

LFP is near to application in Tesla electric vehicles aimed at the Chinese market. Here, the packing efficiency of LFP that is possible due to its increased safety and simplified battery management is being used to offset the reduction in specific energy of the cells. Termed 'cell-to-pack', this allows the LFP cells produced by CATL to reach 140 Wh kg^{-1} at the pack level, only 12.5% less energy dense than their NCA battery packs at 160 Wh kg^{-1}, despite the significantly bigger difference in cell specific energy. These battery packs are driven by a need to meet a certain price point to qualify for Chinese electric vehicle subsidies. To date, lithium iron phosphate produced by smaller manufacturers (such as those producing for marine applications) have been more expensive than NMC, but produced in bulk, lithium iron phosphate should be much cheaper than cobalt and nickel based alternatives, and CATL seem to be about to achieve this [137]. It is anticipated that for marine applications, the gap between LFP and NCA will be considerably smaller than 12.5% at battery pack/battery room level, due to the much greater safety of having high quantities of LFP in a tightly packed configuration compared to NMC or NCA.

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16.8 Lithium sulphur (LiS)

Sulphur (S) is an attractive material for a cathode for lithium ion batteries due to its 1675 mAh g^{-1} capacity and its relative abundance. However, it expands significantly on intercalation (around 80%), leading to cracking and electrode detachment. It also has problems with side reactions [50]. Due to these issues, Li-S batteries have short cycle lives, and it has been necessary to use sulphur in a composite cathode to achieve acceptable life of over 1000 cycles. The research on composite sulphur cathodes has included sulphur encapsulation in carbon nanotubes, blending sulphur with graphene, and thin films of sulphur bonded to carbon. Of these techniques, carbon nanotubes and graphene lead to 3D structures maximising the surface area and cycling stability of the electrode, but only the thin film, a 2D structure, is currently practical at large scale using established roll-to-roll manufacturing techniques [138].

This restriction to thin film electrodes in practically achievable cells is particularly limiting because the central challenge to lithium sulphur batteries is the amount of sulphur that can be stored per unit surface area on the cathode, which remains half that which is needed to achieve a suitable energy density for transport use [138]. In terms of overall cell performance, this surface area limitation leads to predictions that future commercialised Li-S cells will have 400-600 Wh kg^{-1} specific energy – around twice that of current lithium ion cells – but be limited to the same energy density. Furthermore, it should be noted that any high quoted cycle numbers for Li-S in the literature are due to an excess of lithium and electrolyte, due to consumption of these components by side reactions. In conclusion, given the requirement for high cycle stability in marine applications to power very high numbers of duty cycles, sulphur does not appear attractive; it is better suited to applications where the increased specific energy is worth the drop in cycle life, such as niche aerial applications

[139]. It is not clear that Li-S will ever be able to compete in high-cycle life applications (≫1000 cycles), due to the side reactions.

16.9 Conducting polymers

Conducting polymers are polymers with a conjugated carbon backbone that conducts electricity. Their conductivity is dependent on 'doping' – a term used outside of its traditional meaning in semiconductors, referring to the introduction of ions adsorbed at various sites on the polymer chain. The presence of increasing numbers of these ions increases the conductivity, and it is the insertion and removal of these ions from the polymer bulk that stores charge. In the case of lithium ion batteries, the stored ion is lithium itself [140].

Polyaniline has actually been used in a commercial battery in the 1980s *vs.* a lithium metal anode and has shown specific capacity up to around 150 mAh g^{-1} – similar to $LiCoO_2$. PEDOT has shown specific capacity to 70 mAh g^{-1}, polypyrrole to 82 mAh g^{-1}, and polythiophene to 82 mAh g^{-1}. These are the only conducting polymers receiving detailed attention as cathodes due to the fact that they are the most researched conducting polymers generally, are made of accessible constituent chemicals, and are easy to make [140].

However, the biggest benefit of conducting polymers is gained by their incorporation into composite electrodes, where the flexibility of the polymer provides resilience, the conductivity is improved, and electrolyte permeation into the electrode is also improved. They can play this role in either the cathode or anode. This has included LFP or LMO nanoparticles blended with polypyrrole to increase capacity and stabilize charge/discharge characteristics, with increased electrical conductivity, decreased diffusion distances and therefore higher ionic conductivity [140]. It is not known what role conducting polymers play in commercial lithium ion batteries, but their role can be thought of as an alternative composite material to carbon, providing similar benefits in electrical conductivity and nanostructuring, rather than as a material to make an anode or cathode exclusively from.

16.10 Lithium-rich including lithium nickel manganese oxide (LMNO)

Lithium-rich is a class of cathodes based on a greater storage of lithium in a manganese-based material, possibly also containing nickel or cobalt. They offer improved theoretical capacity (>250 mAh g^{-1}) and high potential (>4.6 V), good thermal stability and lower cost (in the absence of cobalt). At the moment, they suffer from irreversible capacity loss on the first cycle and voltage decay beyond that [50, 125].

Lithium nickel manganese oxide (LMNO) is a nickel-based cathode that does not contain cobalt. It is currently being developed by several small private battery companies such as SVOLT [141, 142]. It has a stable spinel structure that has regular, connected sites for lithium ions to be stored. Its chief advantage, apart from lacking cobalt, is the very high voltage it offers (4.7 V *vs.* Li/Li^+). However, this is not compatible with today's electrolytes and even with higher discharge voltage it does not offer the specific energy of NMC or NCA [125, 142]. It also suffers from unfavourable capacity fade [143].

Overall, lithium-rich attracts a lot of research attention. It will be an interesting cost-effective option if it can be commercialised. It is thought to be one of the technologies that should arrive within 10 years but is currently at TRL 1-2. The most promising aspect, apart from increased specific energy, is the potential elimination of cobalt.

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17 Sodium

Sodium-ion batteries are the most researched battery type after lithium-ion. There are many good reasons to be excited about sodium ion batteries. They operate in a similar way to lithium ion batteries and can therefore use similar electrolytes and electrode materials. This means that sodium ion batteries could be manufactured in the same factories using the same equipment as lithium ion batteries. The best property of sodium is that it is abundant and can be extracted cheaply from saltwater. However, compared to lithium ion, sodium has many of the same problems (flammability of sodium itself and organic electrolytes, dendrite formation) but is also a larger ion with less electrochemical potential. The larger ions degrade the electrode materials faster than lithium. Overall then, sodium ion batteries will never compete with lithium ion on specific energy or energy density, and it will be hard to them to compete on cycle life. However, if at least the cycle life aspect can be resolved satisfactorily, then sodium ion batteries are appealing for use on the grid. A prototype 18650 sodium ion cell has been reported with specific energy of 90 Wh kg^{-1} [49, 144]. Based on several reports of specific energy values based on electrode materials only, it is reasonable to expect that mature sodium ion cells will reach 100-150 Wh kg^{-1}. At best then, it will still be outperformed by LFP [144].

It should be possible to avoid cobalt and nickel by focussing on cathodes made from transition metals such as iron, manganese, titanium and vanadium. Once fully commercialised, the cost of a sodium ion cell is likely to be only 10-20% lower than lithium ion, since the lithium in the batteries is only a portion of the cost and the rest of the cell is very similar [144]. Overall, it is likely that all transport applications will focus on lithium-based batteries within the next 20 years.

However, as with lithium, solid-state technology may bring substantial improvements in specific energy, safety, and cycle life. It is possible that if solid state sodium batteries can be successfully developed, they may reach specific energies competitive with today's lithium ion batteries [145]. This may prompt their use in some marine applications, particularly those with short distances to travel. Reasons for adopting this technology might include a trend towards protectionism over lithium supplies, if the world's supply remains concentrated in just a few nations, or if the public becomes conscious of the impact of lithium mining, operators may choose sodium for environmental reasons. Therefore, solid-state sodium (noting that the solid-state electrolyte will likely be different to that for lithium) may see applications in the 15-20 year timeframe.

The following graph shows a sodium ion battery using an electrolyte that is analogous to contemporary lithium ion batteries ($NaPF_6^-$ *vs.* $LiPF_6^-$), with a layered transition cobalt dioxide cathode ($NaCoO_2$). This cathode offers a 150 mAh g^{-1} capacity and average discharge voltage of 3 V [144].

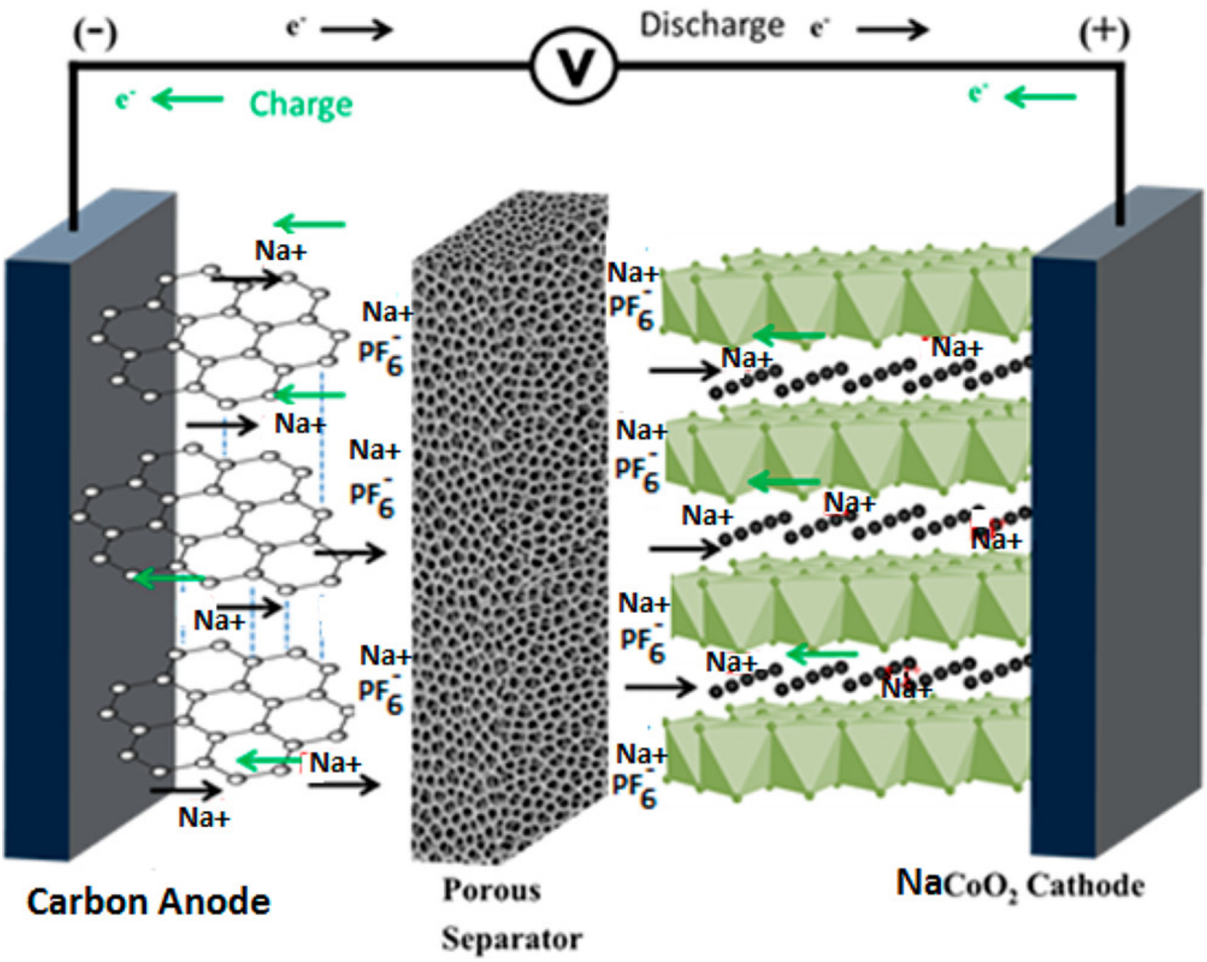

Figure 6 – Operation of a sodium ion battery with carbon anode and $NaCoO_2$ cathode. Reproduced with permission from the American Chemical Society, copyright 2020 [144]

18 POTASSIUM

Potassium (K) is another alternative to lithium. Unlike sodium, it can intercalate in graphite to nearly its full theoretical capacity (279 mAh g^{-1}). A potassium battery has even been brought to market in a portable media player although specifications were never released. Potassium batteries, like many alternative battery research chemistries, are receiving more and more research interest. However, the current research is all at TRL 1-2, with problems including electrode expansion many times greater than lithium ion batteries, lower specific energy and energy density (160 Wh kg^{-1} for the actives, so approximately 80 Wh kg^{-1} for a cell), and poor cycle life [146].

19 MULTIVALENT METAL BATTERIES

Multivalent metals are those whose ions carry more than one charge. Magnesium, calcium and zinc form ions with 2 charges (Mg^{2+}, Ca^{2+} and Zn^{2+}) and aluminium forms ions with 3 charges (Al^{3+}). The benefit is that although the electrochemical potential of these metals cannot compete with lithium, their specific capacities are made competitive by the fact that each ion transfers multiple electrons. For example, aluminium has a specific capacity of 3.0 Ah g^{-1} *vs.* lithium at 3.9 Ah g^{-1}, and its capacity is 8.0 Ah cm^{-3}, much higher than lithium at 2.06 Ah cm^{-3}. It is cheap, easily recyclable, and the most abundant metal in the Earth's crust [49].

However, these batteries, which are all at TRL 1-2, are plagued by the issue that with two or more electrons absent, the ions interact very strongly with the cathode and cannot easily be cycled in and out of it. So far, no good reversible behaviour has been shown for any of the multivalent metal batteries when intercalation of the ions themselves into the cathode has been attempted. The research is still at a very early stage, and many researchers believe reversible intercalation of multivalent ions will never be achieved [49].

However, when a room temperature ionic liquid ($AlCl_3$-[EMIm]Cl) is used as the electrolyte with an aluminium anode and a graphite or conducting polymer cathode, it is possible to store $AlCl_4^-$ ions instead of Al^{3+} ions in the cathode. The unusual operation of this battery is shown in Figure 10. Because $AlCl_4^-$ only has a single charge, very good reversible behaviour is found, and the Al-graphite battery has been demonstrated to be stable over thousands of cycles with excellent power up to 490 Wh kg^{-1}. However, the room temperature ionic liquids are very expensive, assembly in a controlled environment is required, and in the end only lead-acid performance levels are obtained (62 Wh kg^{-1} for the actives, so approximately 30-40 Wh kg^{-1} for a battery cell) [147]. Therefore, there is very little economic driver towards commercialising this type of battery [49], though progress is being made on alternatives to the ionic liquid electrolyte [148].

It is also possible to construct an aluminium battery with an aqueous electrolyte. However, the use of water restricts the voltage of the battery and forces the use of an intercalation anode rather than using aluminium metal. The aqueous aluminium battery has been shown to have good specific power of 300 W kg^{-1} but poor specific energy of 15 Wh kg^{-1} (for the active materials only). Therefore, it is similar to a supercapacitor in its performance [149], is at TRL 1-2, and will not see use in marine applications.

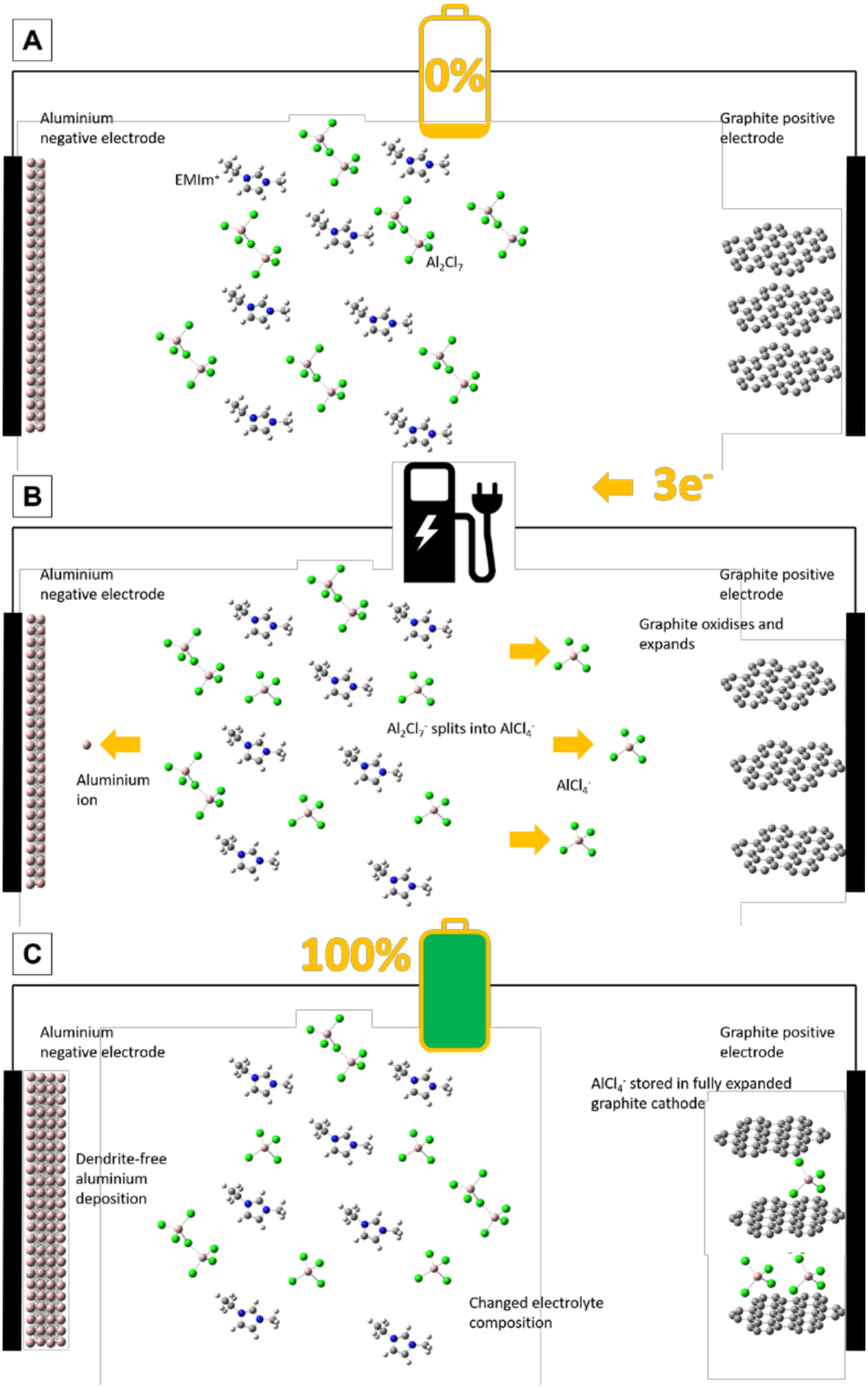

Figure 7 – Charging of a battery with aluminium anode, graphite cathode and AlCl3-[EMIm]Cl electrolyte showing A) fully discharged, B) charging, C) fully charged (Reproduced under CC-BY-4.0 from [49])

Other metals have shown even less progress so far. Magnesium is held back by its very high internal resistance and no good electrolytes have been found [150]. Calcium suffers from undesirable formation of a SEI layer, with very slow ion diffusion [151], while zinc suffers from severe dendrite formation when used as an anode in a rechargeable battery (this problem is avoided for flow batteries) [152-156].

20 METAL-AIR BATTERIES

The theoretical maximum performance that can be obtained from any battery is the metal-air batteries, which react oxygen at the cathode with a metal such as lithium or aluminium at the anode to produce electricity. These batteries are an intermediate between fuel cells and normal secondary cells, because they involve a flow of air (or oxygen) through the positive side of the battery to provide the reactant. Overall, rechargeable metal-air batteries remain firmly at TRL 1-2, and are expected to reach the market at the earliest in the 15-20 year timeframe. Even if/when they reach commercialisation, they will probably still have low power performance, due to the inherent sluggishness of the oxygen reaction [157], and are predicted to reach at most 950 Wh kg^{-1} and 1 100 Wh l^{-1} in practice [99], despite the theoretical max specific energy of 3 500 Wh kg^{-1} [50].

Metal-air batteries can use as anode any of Li, Na, K, Mg, Fe, Zn and Al, amongst others. Electrolytes may be aqueous or non-aqueous. The cathode will often be porous to allow direct supply of air. Overall the batteries have features of both batteries and fuel cells. Research on metal-air batteries outdates that on lithium ion batteries and single-use zinc-air batteries were commercialized as early as 1932. The aqueous and non-aqueous systems have significant differences. In aqueous batteries, a passivating oxide or hydroxide layer on the metal surface is required due to the reactivity of these metals with water [157].

Zinc-air, for example, has a theoretical specific energy of 1353 Wh kg^{-1} and a theoretical working voltage of 1.65 V, though in practice it achieves 350 to 500 Wh kg^{-1} (for a non-rechargeable battery). The power capability is poor due to the rate limitations of the air catalyst. Rechargeable zinc-air batteries have less than 60% round-trip efficiency due to significant overpotentials at the air electrode. There is a great challenge in finding catalysts that are good for both discharging and recharging the battery, though good progress has been made in the last decade. Nevertheless, round trip efficiency is still less than 65% compared to lithium ion at 90%. Furthermore, zinc in particular (worse than lithium) is prone to forming dendrites. While a range of additives can somewhat mitigate this behaviour, it is not a solution. Two options that do solve this problem are mechanically recharged batteries and zinc-air flow batteries. Mechanically recharged batteries use the battery as a one-way flow battery, and then recover the reacted metal anode material for recharging outside of the battery. They received a lot of research attention for EV applications in the 1990s. Zinc-air flow batteries are currently being pursued towards commercialization by ZincNyx Energy Solutions [157].

Lithium, sodium and potassium react too strongly with water to be used with an aqueous electrolyte without an expensive and difficult to manufacture protective ionic conducting membrane. Instead aprotic electrolytes are used that have a very different oxygen reduction reaction. The metals react to form oxides that are limited in solubility in the electrolyte and deposit on the air cathode. This reduces cathode surface area over time and shuts off the battery. This means the battery is limited in capacity by how much product can be built up on the air cathode, and the resulting capacity is far less than the theoretical capacity. A porous, maximal surface area electrode is required for optimal performance. Still, lower overpotential for Li_2O_2 decomposition is required, because the significant overpotential means the round-trip energy efficiency of Li-air is less than 75%. Sodium-air has lower overpotential, but even worse cycle life. There are also problems to be solved such as the issue with CO_2 binding with the catalyst and making it ineffective, the crossing of oxygen the ion conductor, and the stabilisation of the anode [157].

The solid oxide metal battery operates more like a rechargeable fuel cell and keeps the metal in an 'energy store' in some kind of transportable form like a slurry or a suspension. This avoids the issue of metal expansion, as the reacted metal is simply passed on through [158].

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20.1 Mechanically rechargeable batteries

Mechanically rechargeable batteries are really metal fuel cells and can also be considered a subset of metal-air batteries that use a metal-containing slurry in a non-rechargeable flow battery, where the discharged slurry is removed from the vehicle after use and replaced with fresh slurry. The used slurry is then removed to a centralised recycling facility where efficient recharging of the metal slurry is conducted. As a concept this peaked in the 1990s and clearly solves the problems associated with recharging of the battery in the cell itself. Additionally, the time to empty the slurry and refill it need be no longer than the time to refill a tank of fuel. In 1996, this system was proposed to have a specific energy of up to 200 Wh kg^{-1} and a power capability of more than 150 W kg^{-1} [159]. Clearly, this type of battery would require a major investment in infrastructure to 'recharge' the used slurry.

21 Metal-CO_2 batteries

The metal-CO_2 battery makes use of the fact that CO_2 is around 50 times more soluble than O_2 in organic electrolytes, with a theoretical specific energy of 1876 Wh kg^{-1} for Li-CO_2 and 1130 Wh kg^{-1} for Na-CO_2. Using lithium-CO_2 as an example, the battery operates by reacting lithium with carbon dioxide to form lithium carbonate and carbon [160]. The main issue is with recharging the battery, and reacting the carbon, which in the fully discharged state is plated onto the catalyst on the cathode, with the oxygen from the lithium carbonate to create CO_2 again. Recently, researchers claim to have achieved a fully reversible Li-CO_2 battery using a MoS_2 nanoflake cathode catalyst, achieving 500 cycles with no capacity loss. This is a significant claim but remains isolated at the moment [161], similarly to other research using ruthenium catalysts [125]. Other Li-CO_2 research has shown poor Coulombic efficiency and the need for significant overpotential to split lithium carbonate [50]. For the time being, the metal-CO_2 battery remains at TRL 1-2.

22 NICKEL/METAL HYDRIDE

Nickel metal hydride batteries use hydrogen as the active material. As they are charged, metal hydrides form on the anode, and during discharge, hydrogen is lost from the anode and the NiO·OH on the cathode is reduced to $Ni(OH)_2$. They contain large amounts of rare earth elements and transition metals, including La, Ce, Pr, Nd, Ni, Co, Zn, Mn and Al. Rare earths constitute greater than 10 wt% of the battery cell, making NiMH batteries a serious issue in terms of sustainability. However recycling processes do already exist partly due to the continuing use of NiMH batteries in hybrid cars [70].

NiMH batteries have lower specific energy, energy density and power density than lithium ion batteries – 50-110 Wh kg^{-1} and 1500 W kg^{-1}. They have much better safety than lithium at the cell level, a long cycle life of over 1000 cycles at 100% depth of discharge and require simpler electronic control circuitry. The batteries are easier to recycle than lithium in part due to their safety and are relatively environmentally safe. One of the key benefits is their performance at cold temperatures, making them suitable for use in hybrid vehicles in cold climates. They suffer from self-discharge and can completely discharge over six months. They have a cost below \$800 kWh^{-1} [162, 163]. However the most modern NiMH batteries were until very recently still being used by Toyota, which offered the non-plug in variant of the Prius hybrid car with either a lithium-ion battery or a NiMH battery [164]. Toyota will also use NiMH on the all-road version of the Prius for a long time to come due to its significantly improved cold weather performance. However Toyota is very much on its own in this regard, with other traction battery manufacturers, and indeed all pure electric vehicles in production exclusively using lithium ion [162, 165].

At the moment, the marine industry has shown no interest in NiMH batteries, largely preferring to follow the trends set by automotive. However, their long cycle life and ability to operate in colder environments is appealing, as is the existing recycling infrastructure. Their inherent safety would reduce the need for fire extinguishing equipment and might even avoid the need for a dedicated battery room, saving space and weight that would help to offset their reduced energy density compared to lithium ion batteries.

23 FLOW BATTERIES

Flow batteries pump two separate electrolyte solutions through a reactor cell, where the charge carrier is transported through a membrane. The reactants are then stored before reversing the system. They require at least two pumps and storage tanks, so the complexity is high and the energy density usually rather low. However one advantage is the decoupling of power and energy characteristics, because the power is determined by the size of the cell and the pumps (the rate at which the reaction can occur) while the energy is determined by the amount of electrolyte stored [166].

Vanadium redox flow batteries are the most researched and commercially successful type of redox flow batteries [167]. They offer the central advantage that they use the same active material on both sides of the battery, which means cross contamination is avoided and the electrolyte life extended almost indefinitely [166]. Compared to other flow batteries vanadium redox flow batteries also have fairly good efficiency and low levels of gas evolution [168]. 40% of vanadium is already recycled, so prospects for recycling vanadium redox flow batteries are good [67]. Price of vanadium redox flow batteries for grid use ranges between USD$200-750 kWh^{-1} [169].

The efficiency of flow batteries is lower than normal batteries due to the losses involved in pumping the electrolyte, and a narrow operating temperature range due to the need to keep the electrolytes at the ideal viscosity (between 10°C and 40°C for vanadium redox flow batteries, for example) [168].

Alongside vanadium, current technologies include iron-chromium, vanadium-bromine, vanadium-oxygen [167], iron-chromium, zinc-bromine, cerium zinc and bromine polysulfide [166]. Current redox flow batteries are not suitable for transport use due to their low energy density of <25 Wh kg^{-1} and high complexity [166-168]. Promising future batteries include the field of organic redox flow batteries, using lower cost active components [170], the soluble lead redox flow battery, offer some advantages such as the use of a single electrolyte without a separator [171], and the zinc-based hybrid flow battery, which offers higher voltage and lower cost than vanadium [169], but do not address the specific energy issue sufficiently to warrant further consideration for use in marine applications.

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Predictably, flow batteries containing lithium are the most likely to offer increased performance, potentially with electrolyte energy density five to ten times higher than vanadium, which could bring redox flow batteries into the energy density required for transportation. However, fundamental challenges remain that place this battery system at TRL 1-2 [172, 173]. Except for increased safety and the greater abundance of vanadium, it is hard to see what benefit these batteries offer over traditional lithium-ion batteries for most marine applications, which do not require tanks or pumps and will therefore have lower maintenance and better efficiency, as well as faster response time. For the foreseeable future, lithium ion batteries will also be cheaper for transport applications.

Port Liner propose that container shipping on inland waterways is suitable for vanadium redox flow batteries, and claim that four 6m container battery units could propel a 100 m container ship 230 km autonomously on a single charge, which they plan to start producing in 2021 [93]. However, no specifics are provided on the battery itself, and until data or a working concept appear, this should be considered an interesting but unproven idea on the basis of vanadium redox flow battery systems having specific energy of <25 Wh kg^{-1} *vs*. 86 Wh kg^{-1} (at pack level) for lithium NMC.

24 SUMMARY

In conclusion, the case has already been convincingly made for battery-electric and hybrid boats. Even with today's batteries, which have yet to achieve the affordability and performance to create mass appeal of electric cars, the business case is favourable for marine applications, providing the operator does not mind waiting a few years to pay off the increased capital expenditure. Batteries are getting cheaper and better faster than other technologies such as fuel cells, and consequently where the range of boats is short enough to allow battery-electric operation, fuel cells are not expected to compete. For longer journeys, hybrid systems allow 15-30% savings by allowing the battery to handle all types of fluctuating loads. This advantage will be maintained regardless of the choice of future fuel due to the inherent part load inefficiency of power converters.

The simplified picture of battery progress is this: today's lithium ion will be superseded by solid-state lithium in the next ten years, and by metal-air in some timeframe probably greater than 15 years from now. The more nuanced version takes account of various new cathodes, electrolytes, and anode technology that will provide incremental improvements along the way. Other battery technologies are not seriously expected to make a big impact in the marine sector, except in niche applications, or as proof of concept. Because boats are far more bespoke than cars, and because duty cycles are diverse, there might be any number of unusual solutions where circumstances allow and predicting them all is beyond the scope of this report. Decarbonisation of the marine sector is a difficult and important challenge, and it is also a fascinating one. This aim of this report is to provide useful information for those seeking to make a difference.

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