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Lithium batteries whitepaper

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Introduction

Despite significant fire incidents, it is apparent that the broad maritime community and logistics supply chain remain predominantly unaware of the hazards and potential consequences when a lithium-ion battery fails and goes into thermal runaway.

When a lithium-ion battery fails, the speed of failure (seconds), production of significant quantities of toxic, corrosive and flammable gases (000's of litres) as well as the rapid development of intense heat and explosive situations (+450°C) continue to be underestimated.

This paper has been produced to provide some insight into this phenomenon as we move towards a "greener" power source. While there may only be a small perceived risk, the following text profiles some of the numerous challenges and raises awareness of the potentially catastrophic situations caused by a battery failure.

Recognising the various challenges presented by Li-ion batteries, the topics covered in this paper include background science on Li-ion batteries, the dangers associated with transporting them and why they arise, battery testing and correct declaration. The paper also provides a review of current dangerous goods (DG) regulatory provisions, focusing on the International Maritime Dangerous Goods (IMDG) Code, with recommendations for change or further work. The final section of the paper discusses the current state of the firefighting provision and changes that could be implemented.

Today, lithium-ion (or "Li-ion") batteries are an everyday essential item found throughout the world and in almost every household or workplace in one form or another. They are found in portable devices such as mobile phones, mobility devices, recreation, manufacturing and power storage, through to larger products, such as electric vehicles (scooters, bicycles, cars, buses and trucks) and even superyachts and ships. Their size to power ratio, storage and output makes them ideal units in the 21st century where technology is essential in our lives. Given their ubiquitous uses and rapidly increasing demand, it is no surprise that global shipping volumes are also increasing rapidly.

However, this technology comes at a cost and in the event of failure, it can have catastrophic consequences. There are clear dangers and safety concerns to take into account when transporting Li-ion batteries. It is important to recognise that the supply chain also handles these batteries and related products throughout their lifespan: used, second-hand and end-of-life.

Li-ion batteries are generally very safe in terms of the risk to individual consumers. Notwithstanding the small individual risk, with increasing numbers being shipped, and increasingly larger consignments in each shipment, transport casualties have been significant and are expected to become even more common in the future.

Awareness of risks is increasing in all modes of transport, as well as nationally in domestic and other settings. Recently, serious and sometimes catastrophic incidents involving lithium batteries have become more commonplace, with fires related to batteries reported in nearly all modes of transport (ship/air/land) as well as in warehouses/storage and during use.

1. The science of lithium-ion batteries

1.1 Li-Ion Batteries - components & how they work

Li-ion batteries come in many forms. They can consist of a single battery cell like AA and AAA batteries, which are single-cell cylindrical Li-ion batteries. However, usually a Li-ion battery is constructed of connected cells, which can be connected in parallel to increase the current, in series to increase the voltage, or a combination of the two. These connected cells are known as a module, which are incorporated with other components to form a battery pack, this is illustrated in figure 1. Figure 2 shows a diagram for a typical battery cell, the key terminology is provided below this figure.

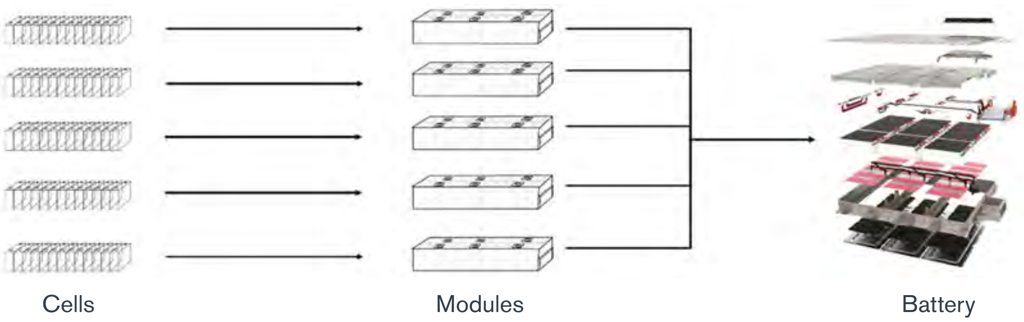

Figure 1 *- Schematic showing how cells are arranged into modules as a component of a complete battery. [Journal of Energy Chemistry, 2021, 59, 83]*

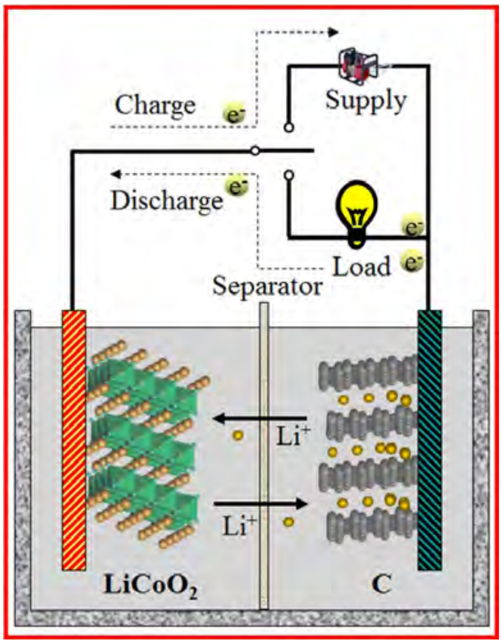

Figure 2 *- Schematic diagram of the fundamental structure of Li-ion batteries. The anode is carbon, and the cathode is $LiCoO_2$ in this image. [Energy Science and Engineering, 2015, 3, 385]*

Terminology:

- **Ion** - an atom or molecule that has a positive or negative electric charge due to loss or gain of electron(s). In the case of Li-ion batteries, the ion involved is Li^+.
- **Electron** - an electron is a stable particle that has a negative charge, they are found in all atoms and act as the carrier of electricity in solids. Electrons are denoted as e^- for short.
- **Primary battery** - those that cannot be recharged, i.e. single use.
- **Secondary battery** - these are rechargeable, such as Li-ion batteries.
- **Dendrites** - metallic branch-like structures that grow on the negative electrode during charging. These are detrimental to the battery life and can result in a short circuit.
- **Lithium-ion batteries** - A lithium-ion battery or Li-ion battery is a type of rechargeable battery composed of cells in which lithium ions move from the negative electrode through an electrolyte to the positive electrode during discharge and back when charging.
- **Lithium-metal batteries** - This is a different type of battery design from lithium-ion, using electrodes made from metallic lithium. Although both types are sometimes generically referred to as "lithium battery", lithium-metal batteries are usually small single-cell primary (non-rechargeable) batteries, used to power devices such as watches, calculators, car key fobs or flashlights. Due to their smaller size and method of construction, they are generally less of a safety concern than Li-ion batteries. Unless specifically stated otherwise, this paper is concerned with rechargeable Li-ion batteries, not lithium-metal batteries.

Components of Li-ion batteries:

- **Electrode** - the electrical conductors in the battery through which electrons flow to create a current.
- **Cathode**[1] - the positively charged electrode where the Li ions are moved to during discharge. Examples of cathodes include $LiCoO_2$, LFP ($LiFePO_4$) or NMC ($LiNiMnCoO_2$).
- **Anode** - the negatively charged electrode where the Li ions move from during discharge. Carbon (i.e. graphite) is the most commonly used anode material.
- **Separator** - used to isolate the two electrodes from one another and is usually made up of a microporous polymer membrane. Critically, the membrane prevents the two electrodes from contacting but allows the Li ions to pass through its pores.
- **Collector** - bridging components (usually metals such as aluminium or copper) that collect the current generated at the electrodes and connect with the external circuits. The collector is found at the end of the electrode.
- **Electrolyte** - the organic solution that the Li ions pass through. The Li ions move through the electrolyte, from the anode to the cathode. This organic solution is usually flammable, as such, electrolyte compositions all have similar risks due to their flammable nature.
- **Outer casing** - the first layer of protection from thermal and mechanical damage. The casing needs to be able to withstand mechanical force, such as puncture, without breaking and it must also protect the internal components from being damaged.

Figure 2 demonstrates the fundamental structure of a Li-ion battery. In this example the cathode is $LiCoO_2$ but the same principles apply to other cathodes. Electrons flow through an external circuit; during discharge the electrons flow from the anode to the cathode, whilst the Li ions flow through the electrolyte from the anode to the cathode. During charging, the battery is connected to an external electrical supply and the reverse occurs.

Various configurations of Li-ion cells are available (see table 1). In addition to these configurations, button cells also exist, however these are not usually Li-ion batteries.

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[1] NMC cathodes are used in high energy density batteries, which are often used in electric vehicles (EVs). They are less stable than LFP cathodes, with shorter lifespans and greater sensitivity to thermal degradation.

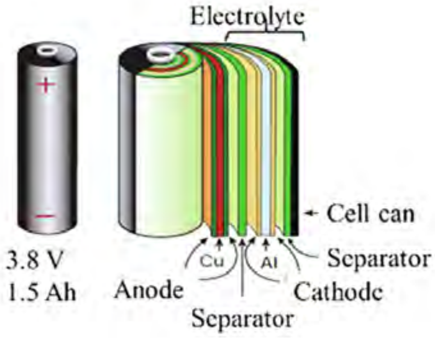
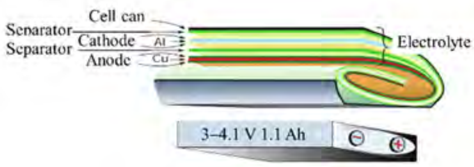
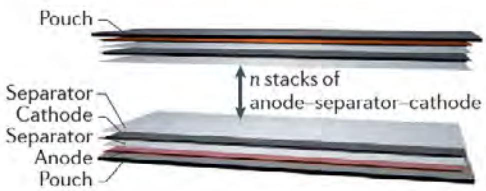
Battery type	Physical characteristics	Picture	Typical uses
Cylindrical 	The separator and electrodes are wound into a tight cylinder and placed in the casing; the electrolyte is poured in and the battery is sealed. Battery packs of cylindrical cells are less space efficient, due to their shape, but are easier to cool.	 *[Journal of Energy Chemistry, 2021, 59, 83]*	E-bikes, medical devices, power tools, Electric vehicles.
Prismatic 	Made up of large sheets of electrodes that are sandwiched between separators and rolled up before flattening so that they fit into a cubic housing. They can also be assembled by stacking the electrodes in layers rather than rolling. Prismatic cells are thinner and more space efficient but have poor heat dissipation.	 *[Journal of Energy Chemistry, 2021, 59, 83]*	Mobile phones, tablets, and other lightweight electronic devices. They are also used in electric vehicles and scooters.
Pouch 	The electrodes and separators are stacked in the cell container, which is a sealed flexible foil, usually an aluminium plastic film. Pouch cells offer greater flexibility over cylindrical and prismatic cells for fitting the cell to a particular device shape but they can withstand less pressure than a metallic shell casing.	 *[Nature Reviews Materials, 2016, 1, 16013]*	Used in laptops, tablets and electric vehicles.

Table 1 *- Types of battery cells.*

Examples of EV battery packs are shown in Figure 3.

Figure 3 *- Examples of the positioning of the battery packs in EVs, which is found in the chassis..*

1.2 Hazards associated with Li-ion batteries

Whilst Li-ion batteries are a great technology that allow for storage of large amounts of energy in small spaces and with high energy densities, they presently have numerous safety concerns. It is well documented that the batteries can fail in dangerous ways, causing fires, explosions, toxic gas emissions and associated hazards. Some have failed dramatically with no prior warning, or with such speed that there is no time to react to any warning signs.

The risks presented by batteries can be categorised into three types: mechanical, electrical and thermal abuse.

a) Mechanical abuse

External local damage to the Li-ion batteries such as impact, indentation, or punctures etc.

Upon damage to the casing, air can enter the battery and react with the active components and electrolyte. These reactions will generate heat.

Mechanical damage which deforms the casing could lead to severe internal component damage or breakage. Breakages in the current collector and separator can allow the electrodes to come into contact, resulting in a short circuit.

Accidents will always be a part of everyday life. Damage (contact, crushing, water submersion etc.) of any battery will potentially cause it to fail or become unstable. In the case of vehicle collisions, given that in pure EV's the batteries are likely built into the chassis, impacts may result in them being compromised.

It is difficult for a layperson to know if a battery has been damaged internally following an accident (unless it starts to heat and vent vapours). It may only become apparent after the event during charging. This is also relevant in relation to transporting second hand EV's on a ship, how would the crew or stevedores know if a vehicle had been involved in an accident, particularly if the shell had been repaired. The battery is not a visible, external component, so assessing the condition of the battery would be extremely difficult.

b) Electrical abuse

Overcharging or over-discharging the battery.

Usually, batteries are charged to a voltage which corresponds to a specified state of charge. Undesirable electrochemical reactions can take place due to overcharging or over-discharging the battery.

Overcharging or over-discharging can occur due to manufacturing faults or damage to battery cells and ineffective monitoring of the voltage by the battery management system (BMS) in the device.

The consequences of overcharging and over-discharging are similar. Overcharging batteries results in electrolyte decomposition on the cathode surface, which increases the battery temperature. During overcharging, excessive Li-ion migration from the cathode causes the cathode to become unstable. In oxygen-containing cathodes, this can result in the release of oxygen. The oxygen reacts in heat generating side reactions; the increase in gases and side reactions can lead to battery rupture. The excess Li ions deposit on the anode forming lithium dendrites (see terminology). Dendrite growth can reach the stage where they pierce the separator, resulting in short circuit, which can have catastrophic repercussions.

In over-discharge, the Li ions move in the reverse direction where Li ions are continuously released from the anode. This process can reach the stage where the copper current collector is oxidised and releases copper ions. These copper ions can deposit on the cathode surface, eventually leading to short circuit.

Using an incorrect charger for a lithium-ion battery pack can cause a range of problems. Most chargers for Li-ion batteries are designed to prevent overcharging. However, using the wrong or a defective charger can cause overcharging or over voltage of the battery pack leading to breakdown of the battery structure with overheating and swelling of the casing.

While new products will typically be manufactured to hold a safe state of charge for transportation, this could be problematic through the supply chain if one considers second hand, used or end of life equipment, phones, computers, cameras where the state of charge and condition of potentially hundreds of individual items is unknown.

Users of lithium battery packs must be careful of over-discharge as much as overcharging of the battery. A Li-ion battery should never be allowed to discharge completely such that the voltage falls below 2V. This issue can happen when the battery has not been in use for some considerable time, or it's been placed into storage for long period of time allowing it to discharge. With the voltage below 2V, both the cathode and the anode begin to break down.

The anode current collector will start to dissolve as the copper dissolves into the electrolyte. The copper ions begin to precipitate into metallic copper that can cause short circuit when the battery is charged above 2V.

While there are various contexts where this risk may materialise, it is particularly relevant in relation to handling of recalls, recycling or end of life equipment that may have been left for a considerable period of time.

A lithium-Ion battery pack should never be charged in cold temperatures (below 32°F/0°C). Charging at this temperature can cause lithium plating (this is when the lithium ions collect along the anode's surface as metallic lithium becomes deposited there). This plating cannot be removed; it becomes permanent. Once this occurs, the battery becomes more susceptible to damage such as high-rate charging that can lead to short circuits. It can also become more easily damaged from crushing or impact.

c) Thermal abuse

Subjecting batteries to extreme temperatures.

Extreme temperature can refer to external temperature or where the local temperature (inside the battery itself) is too high. There may also be localised high temperatures within the battery itself due to poor design or manufacture. Theoretically, battery cycling should not cause safety accidents as the heat generated during normal use should not be enough to cause sharp increase in temperature. However, the electrode heat release rate is often higher than the cooling rate. There is some heat dissipation by radiation, however some heat is likely to remain within the battery. If heat continues to accumulate rather than dissipate, this can lead to heat generating side reactions taking place. The temperature at which these reactions occur depends on the Li-ion battery composition. Thermal stress or shock can result in a build-up of pressure, which may eventually lead to an explosion.

There has been a suggestion that 60°C is the critical temperature, above which Li-ion batteries are prone to fail. Whilst the temperature for battery failure is battery chemistry dependent, this temperature can act as a helpful reference.

When shipping Li ion batteries, one should consider the route and likely climatic conditions. Temperatures inside a dry van shipping container can reach a factor of 2 over the ambient temperature. In the summer months through the Middle East, this could see temperatures inside a shipping container reach 80°C.

As charging can lead to the production of heat, it is very important to allow the heat to dissipate from the battery. For example, charging a mobile phone on a soft surface, such as a bed, pillow or in a pocket, can insulate the battery and prevent the heat from dissipating away, leading to possible failure.

1.3 Consequences of abuse

Whatever the failure, it can be a small or large event and happen over time or in milliseconds with dramatic, explosive and devastating consequences. Once failure starts, it can lead to thermal runaway, which is very difficult to stop. This is illustrated below in figure 4.

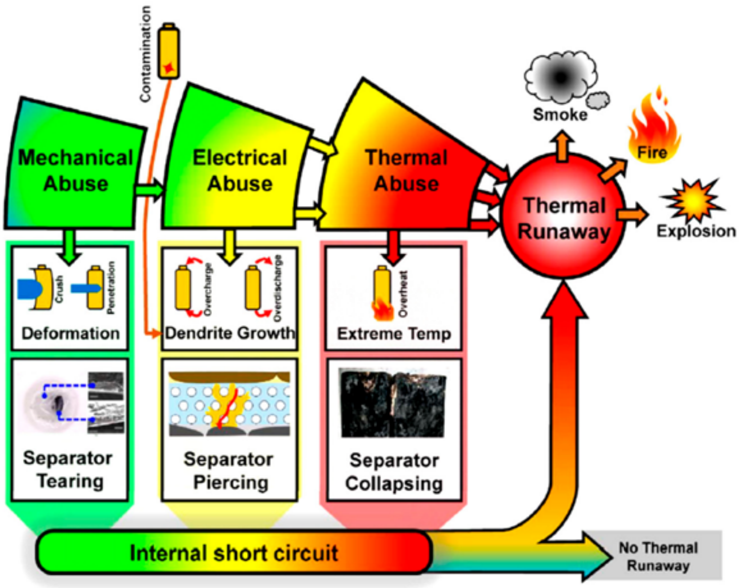


Figure 4 *- The possible consequences of the various types of abuse. [Ghiji M, Edmonds S & Moinuddin K (2021) A Review of Experimental and Numerical Studies of Lithium Ion Battery Fires, Applied Science, 2021, 11, 1247]*

a) Thermal runaway - when the heat generated by the Li-ion battery reaches a stage where it becomes self-sustaining. Thermal runaway results in battery temperatures rising exponentially. This can be caused by heat, impact, crushing, penetration, overcharge, defects, manufacturing and design flaws or contamination. Thermal runaway is difficult to stop once started, and can result in explosion, fire, or release of smoke/gases.

The first sign of thermal runaway will be increases in temperature, with increasing rates of temperature increase. This heat generation will be detectable before the battery reaches thermal runaway. Thermal runaway leads to the breakdown of various components within the cells resulting in release of gases, explosion, fire etc.

Figure 5 *- Example of the different gases emitting from a battery during a thermal runaway event.*

b) **Explosion risk** - toxic, flammable, and potentially explosive gases are produced during thermal runaway, which can ignite to cause an explosion.

c) **Vapour cloud** - if the secreted gases do not ignite straight away, they create a vapour cloud. Upon ignition, any explosion can be destructive and damaging to people or property, especially in a confined space. Li-ion batteries release a vapour cloud which is sometimes confused with smoke, but consists of a range of toxic/explosive gases, as listed below.

Hydrogen (c. 30% - 50%)	Explosive
Carbon monoxide	Toxic
Hydrogen fluoride	Toxic
Hydrogen chloride	Toxic
Hydrogen cyanide	Toxic
Organic solvent droplets	Explosive
Ethane, methane and other hydrocarbons	Explosive

It is important to note that the densities of these gases vary and, as some are denser than air (e.g. hydrogen chloride), they may roll along the floor. This is especially pertinent with regards to EV battery failures.

We understand from industry sources that a total of up to 6,000 L/kWh of vapours can be released during battery failure. A significant portion of the released vapours is comprised of hydrogen fluoride and related fluoride gases. These gases have been identified as a major toxic and corrosive hazard (hydrogen fluoride becomes hydrofluoric acid in water). Experiments[2] have shown that battery fires have the potential to release significant amounts of hydrogen fluoride, up to 200 g per kWh capacity. Extrapolating this experimental figure, the hydrogen fluoride vapour release may be as high as 20 kg for a 100 kWh battery system, such as those used in long-range EVs. Such a large quantity of gas is likely to result in short-term exposure toxic or corrosive injury either by inhalation or from unprotected exposure to associated acid. Hydrogen fluoride inhalation can be particularly dangerous, even fatal. It can be additionally problematic because after exposure, the dose has several hours' delay before any effect is evident.

The latest large long range EV's have around a 200 kWh capacity – this potentially equates to a total vapour release of around 1.2 million litres from one vehicle during failure. Extrapolate this to 10 such EV's onboard any vehicle ferry/pure car, truck carrier (PCTC)/container ship and authorities will not want that ship anywhere near a port during a battery related incident! In these circumstances, the ship should perhaps warn all other ships in vicinity to implement positive pressure in accommodation and engine room to keep the fumes out.

Lithium battery fires burn for long periods and can reignite hours, days, or even weeks later; this can occur multiple times. Firefighting usually requires putting the battery in large volumes of water. They are much harder to put out than a fire from, say, an internal combustion engine (ICE) or indeed many chemicals. Foam, CO_2 and other suppressants are wholly ineffective in fighting a li-ion battery fire, water appears at present to be the only effective suppressant.

The impact of these hazards and consequences on safety measures and firefighting in case of accidents are discussed in greater detail in section 3 of this paper.

[2] *Larsson et al [Scientific Reports, 2017, 7, 10018] DOI:10.1038/s41598-017-09784-z*

1.4 Safety systems in battery design

Various systems are in place to ensure the battery safety.

Battery management system (BMS) - electronic system within devices that oversees the battery pack to ensure it operates within its safe operating area. It monitors the battery's state, optimises battery performance, estimates the battery's operational state through calculations and reports this status to external devices.

Physical safety systems - examples include safety vents, temperature cut-off (TCO) circuitry, positive temperature coefficient (PTC) thermistors, and shut down separators. Safety vents allow for the release of gases that may build up inside the battery, reducing the effects of thermal runaway. TCO devices activate outside the normal operating temperatures of the battery, whilst the PTC thermistors increase the resistance as temperatures rise.

Chemical additives - added to the electrodes or the electrolyte during manufacturing to prevent dendrites forming on the electrodes or promote the formation of the interface between electrolyte and electrode during operation. Electrolyte additives reduce the flammability of the electrolyte used.

External safety systems - safety systems such as thermal barriers, cooling liquids etc. designed to help prevent the battery from reaching thermal runaway. However, due to the short amount of time it takes to reach thermal runway from the onset of increasing temperatures, it is often too late by the time these are deployed.

2. Transport regulations

Li-ion batteries are transported in a number of different contexts, each requiring different logistics and presenting different transport risks. These include:

a) New and unused batteries shipped on their own in dedicated packaging.
b) New batteries shipped as part of packaged electronic equipment (e.g. laptops, mobile phones or cameras).
c) Used or reconditioned batteries in working order, either on their own or built into equipment or vehicles.
d) Batteries shipped as part of EVs, either in new or in used EVs (Note: even in new EVs, the batteries have undergone at least some charging and discharging and are therefore technically used batteries).
e) Defective batteries shipped for reconditioning, recycling or disposal.

Transport regulations are complex and depend on the type of battery, the mode of transport and whether they are shipped on their own or built into equipment.

The relevant regulations are the IMDG Code for transport by sea, IATA by air and ADR by road. All three of these sets of regulations are based on the UN Model Regulations on the Transport of Dangerous Goods, adapted where appropriate for specific circumstances for each mode. Unless specifically stated otherwise, references in the following are to the UN Model Regulations, copied identically into the IMDG, IATA and ADR regulations.

The regulations cover requirements for the construction and testing of batteries, classification and declaration of shipments, packaging and stowage. The below summary is not intended to replace the full regulations but to provide a guide to the overall scope.

2.1 Requirements for construction and testing of batteries

Section 2.9.4 of the UN Model Regulations sets out the construction and testing requirements for batteries for transportation. This section appears identically in the IMDG, IATA and ADR regulations.

The cell or battery must be tested according to the Manual of Tests and Criteria, Part III, Section 38.3. The manual lays out the tests to be followed for classification of Li-ion cells and batteries, please refer to the manual for further details. These tests should be conducted prior to the transport.

> The testing requirements under Section 2.9.4 need to be satisfied only once for each type of battery, but do not require separate testing for each manufactured battery or production batch. This testing is more a type approval for the design of the battery, but cannot detect risks arising from manufacturing inconsistencies or defects, low-quality raw materials or components, or risks arising only when batteries are built into equipment or during use.

Batteries that have passed all applicable tests are connected to form a battery assembly with a rating of ≤6,200Wh This battery assembly does not need to be tested if it is equipped with a BMS that monitors the battery assembly and prevents short circuits, over-discharge between the batteries and any overheating or overcharging of the assembly.

The cell and battery must incorporate a safety venting device and be equipped with a means of preventing short circuits. The battery is also required to have an effective means to prevent reverse current flow for batteries containing cells or series of cells connected in parallel.

The cells and batteries must be manufactured under a quality management programme that meets the criteria in Section 2.9.4.

> The requirements of Section 2.9.4 can be met by in-house quality management and do not require a third-party certification.

The key relevant product quality management parameters are set out in the following numbered items listed in Section 2.9.4.5 as follows:

.2 the relevant inspection and test, quality control, quality assurance, and process operation instructions that will be used;

.3 process controls that should include relevant activities to prevent and detect internal short circuit failure during manufacture of cells;

.4 quality records, such as inspection reports, tests data, calibration data and certificates. Test data shall be kept and made available to the competent authority upon request;

.9 procedures to ensure that there is no damage to the final product.

Manufacturers and subsequent distributors of cells or batteries must make available the test summary specified in the Manual of Tests and Criteria, Part III, subsection 38.3, paragraph 38.3.5.

The wording suggests that the test summary is not a required document for submission to the carrier as part of the standard shipping documents but needs to be specifically requested on a case-by-case basis. Given the dangers associated with Li-ion batteries when issues arise, it is recommended for this document to be provided and checked prior to loading as standard.

2.2 Classification and declaration of Li-ion batteries

Batteries and devices that contain batteries are classed as DG and must conform with specific packaging and shipping regulations.

The UN Model Regulations and the IMDG Code contain multiple entries for batteries (see table 2). Each entry is assigned a specific UN number as well as a hazard class, which for all relevant battery entries is "Class 9 – Miscellaneous". Discussing all the different types of batteries, including lithium-metal batteries, is outside the scope of this paper. .

Entry	Class	UN No.
LITHIUM BATTERIES INSTALLED IN CARGO TRANSPORT UNIT (lithium-ion batteries or lithium metal-batteries[3])	9	3536
LITHIUM-ION BATTERIES (including lithium-ion polymer batteries)	9	3480
LITHIUM-ION BATTERIES CONTAINED IN EQUIPMENT (including lithium-ion polymer batteries)	9	3481
LITHIUM-ION BATTERIES PACKED WITH EQUIPMENT (including lithium-ion polymer batteries)	9	3481
LITHIUM-METAL BATTERIES (including lithium-alloy batteries)	9	3090
LITHIUM-METAL BATTERIES CONTAINED IN EQUIPMENT (including lithium-alloy batteries)	9	3091
LITHIUM-METAL BATTERIES PACKED WITH EQUIPMENT (including lithium-alloy batteries)	9	3091
BATTERY-POWERED VEHICLE	9	3171

Table 2 *- The different types of battery categories according to the UN Model Regulations and IMDG Code.*

[3] *UN3536 applies only to batteries installed in containers for the purpose of providing power external to the container, as a mobile power unit, but not to batteries designed to power equipment inside a container, e.g. data recorders or tracking devices.*

Currently, UN 3171 covers all battery-powered vehicles, irrespective of battery type, whereas for the other UN numbers, they are divided depending on whether they contain Li-ion batteries or not. In addition, UN 3171 covers battery-powered equipment, but only if the batteries are not of the Li-ion type. In view of the distinct risks associated with Li-ion batteries, and the rapidly increasing number of EVs powered by them, a distinct UN number for Li-ion battery powered EVs would be preferable (see further in section 2.4).

2.3 Special Provisions

Much of the detailed requirements for the transportation of batteries can be found in Special Provisions (SP), which complement the classification into individual UN numbers.

The Special Provisions found in the UN Model Regulations (and hence the IMDG/IATA/ADR Codes) for Li-ion and Li-metal batteries are similar, as are the Special Provisions for Li-metal and Li-ion batteries contained or packed in equipment. Between the Li-ion and Li-metal batteries, the key difference is the addition of SP 348 for Li-ion batteries. For batteries (Li-ion and Li-metal) packed in equipment, there is the addition of SP 360 and 390. The Special Provisions for each type of battery are listed in the table below.

Battery type	Lithium-metal batteries	Lithium-metal batteries contained in equipment	Lithium-ion batteries	Lithium-ion batteries contained in equipment	Lithium batteries installed in cargo transport unit	Battery-powered vehicle
UN number	UN 3090	UN 3091	UN3480	UN 3481	UN3536	UN3171
Special provisions	188	188	188	188		
	230	230	230	230		
	310	310	310	310		
			348	348		
				360		
	376	376	376	376		
	377	377	377	377		
	384	384	384	384		
	387	387	387	387		
					389	
		390		390		
						961
						962

Some of the key Special Provisions are discussed in the subheadings below.

SP 188

Li-ion or Li-metal batteries are not considered DG if they meet all of the eight requirements listed in SP 188. Such batteries do not have a UN number and do not need to be specially declared. This applies to relatively small batteries where each cell contains not more than 1g lithium and for a battery in aggregate of not more than 2g (for lithium-metal or lithium-alloy cells). For lithium-ion cells, this applies for a watt-hour rating of no more than 20Wh per cell and no more than 100Wh on aggregate per battery. Exempt batteries must be tested in accordance with Section 38.3 of the UN Manual of Tests and Criteria, marked appropriately and packaged in compliant packaging that can withstand a 1.2m drop without damage to the batteries therein. Packaging must not exceed 30kg gross mass.

SP 360

Vehicles only powered by Li-metal batteries or Li-ion batteries must be assigned to UN 3171 BATTERY POWERED VEHICLE.

SP 376

This provision covers Li-ion and Li-metal cells or batteries that are identified as damaged or defective, such that they no longer conform to the type tested according to 38.3 of the Manual of Tests and Criteria. This may include cells or batteries that are defective for safety reasons, that have leaked or vented, that have sustained physical or mechanical damage and others. Cells and batteries that have been identified as defective are liable to rapidly disassemble, dangerously react, produce a flame or a dangerous evolution of heat and more.

Defective cells and batteries should be packed and transported in accordance with packing instruction P911 or LP906 (see later). They should be marked as "DAMAGED/DEFECTIVE" in addition to the proper shipping name and the transport document should include the statement *"Transport in accordance with special provision 376"*.

SP 377

This provision concerns Li-ion batteries and Li-metal batteries to be transported for disposal or recycling. These can be packed with or without non-lithium batteries. These batteries may be packed in accordance with packing instruction P909 of 4.1.4.1 (see later).

These batteries are not subject to the requirements of Section 2.9.4.

The packages should be marked as "LITHIUM BATTERIES FOR DISPOSAL" or "LITHIUM BATTERIES FOR RECYCLING". The transport document should include the statement, *"Transport in accordance with special provision 377"*.

Damaged or defective Li-ion batteries, as well as batteries transported for disposal or recycling must be specially packed and identified in the documentation. They are likely to be high-risk consignments as they no longer conform to the tested type. However, there is no individual test requirement to identify the risks posed by such shipments.

SP 387

This provision states that for lithium batteries that contain both primary Li-metal and rechargeable Li-ion cells should be assigned to UN 3090 or UN 3091, as appropriate. This means that whilst the Li-ion batteries are also present, the UN number corresponding to the Li-metal battery is used.

Batteries declared as UN 3090 or UN 3091 may contain rechargeable Li-ion batteries in addition to primary Li-metal batteries. Such shipments may therefore present greater transport risks than is apparent solely from the UN number.

SP 390

When the package contains a combination of lithium batteries both in equipment and with equipment, then the package and transport document should include both 'UN 3091 LITHIUM-METAL BATTERIES PACKED WITH EQUIPMENT' for Li-metal batteries and 'UN 3481 LITHIUM BATTERIES PACKED WITH EQUIPMENT' for Li-ion batteries. For packages that contain both Li-metal and Li-ion batteries both contained in and with equipment, then the transport documents should indicate both 'UN 3091 LITHIUM-METAL BATTERIES PACKED WITH EQUIPMENT' and 'UN 3481 LITHIUM BATTERIES PACKED WITH EQUIPMENT'.

When shipping Li-ion batteries by air, IATA regulations specify a maximum state of charge (SOC) of 30% of their rated capacity. No such SOC criteria are currently in place for transportation by sea, or other surface modes.

2.4 Classification of EVs[3]

EVs are currently regulated under UN 3171 BATTERY-POWERED VEHICLE only if transported by sea (IMDG) or air (IATA). For classification purposes, battery-powered vehicles are defined in SP 388 as including cars, motorcycles, scooters, electric bicycles, wheelchairs, lawn tractors, boats and aircraft. Vehicles are covered by UN 3171 regardless of the type of battery, including lithium batteries. Lithium battery-powered equipment (e.g. lawnmowers, cleaning machines or model boats/aircraft) is instead assigned to entries UN 3091 or UN 3481, as appropriate.

The IMDG Code contains two additional special provisions applying to battery-powered vehicles within UN 3171. These are not part of the UN Model Regulations, but have major implications for the transportation of EVs on car carriers, ro-ro ships or car ferries..

SP 961 (IMDG only)

EVs that are stowed in spaces designed and approved for the carriage of vehicles are exempt from the Code if there are no signs of leakage from the battery, engine, fuel cell, compressed gas cylinder or accumulator, or fuel tank when applicable. When packed in a cargo transport unit, this exemption does not apply to container cargo spaces of a ro-ro ship. In addition, vehicles powered solely by lithium batteries and hybrid EVs must in most cases meet the provisions of section 2.9.4. If the lithium battery installed in a vehicle is damaged or defective, the battery should be removed.

> EVs do not need to be declared as DG or identified to the carrier when loaded into the vehicle decks of car carriers, ro-ro ships or car ferries. As a result, the carrier will not generally know how many EVs are on board, or where they are located on the ship.
>
> Vehicles with defective or leaking batteries, or where the batteries do not meet the type approval testing requirements, need to be declared as DG in all circumstances. However, identification of such defective batteries is not generally practical or even possible at the point of loading and there are no provisions for individual safety inspections.
>
> This is a significant safety concern, especially in case of used vehicles and batteries as would be expected on car ferries. However, as previously mentioned the batteries will have undergone at least some use even in new vehicles.

SP 962 (IMDG only)

Vehicles that do not meet the requirements for exemption in SP 961 are classified as Class 9. The installed batteries must be protected from damage, short circuit, and accidental activation during transport. Again, the batteries must in most cases meet the provisions of section 2.9.4.

2.5 Packaging

Using the correct packaging for shipping Li-ion batteries is an important factor to consider, with use of non-compliant packaging having the potential to lead to dangerous situations. Choosing the correct packaging and means of transportation is critical.

The IMDG Code provides details on packing instructions, including packaging material, which is provided for Li-ion and Li-metal batteries (including those packed with or contained in equipment). The applicable packing provisions for UN 3090, 3091, 3480, and 3481 are:

- P903: applies to cells or batteries and the equipment they will power.
- P908: applies to damaged or defective Li-ion or Li-metal cells and batteries, including those contained in equipment.
- P909: applies to batteries or cells transported for disposal or recycling - these can be packed together with non-lithium batteries.
- P910: this applies to production runs consisting of not more than 100 cells or batteries and the pre-production prototypes of cells or batteries when transported for testing.

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[3] *There is a submission to the UN Sub-Committee of Experts on the Transport of Dangerous Goods in December 2022 recommending the assignment of a new, specific UN number for lithium battery powered vehicles.*

https://unece.org/sites/default/files/2022-09/ST-SG-AC.10-C.3-2022-70e.pdf

- P911: applies to damaged or defective cells and batteries liable to rapidly disassemble, dangerously react and produce a flame, dangerous evolution of heat or dangerous emission of toxic, corrosive or flammable gases or vapours under normal conditions of transport.
- LP903: applies to large packagings for UN 3090, 3091, 3480, and 3481.
- LP904: applies to large packagings for single damaged or defective batteries and single items of equipment containing damaged or defected cells or batteries of UN 3090, 3091, 3480, and 3481.
- LP905: applies to large packagings for production runs consisting of not more than 100 cells or batteries and to pre-production prototypes of cells or batteries when transported for testing.
- LP906: applies to large packagings for damaged or defective cells and batteries liable to rapidly disassemble, dangerously react and produce a flame, dangerous evolution of heat or dangerous emission of toxic, corrosive or flammable gases or vapours under normal conditions of transport.

The details of these packing requirements are outside the scope of this paper, and close reference should be made to the provisions referenced above when packing and consigning shipments of batteries. Special attention is drawn to the provisions of **P908/LP904** (damaged or defective batteries), **P909** (batteries for disposal or recycling) and **P911/LP906** (damaged or defective batteries liable to rapidly disassemble, dangerously react and produce a flame or dangerous evolution of heat or vapours under normal conditions of transport).

Packing provisions P911 and LP 906 apply to damaged or defective batteries liable to react dangerously, ignite and/or produce vapours in normal conditions of transport and require the packaging performance to be verified by a test specified by the Competent Authority, and the verification report to be made available. However, there are no guidelines on how to identify such dangerous shipments and distinguish them from other damaged or defective batteries carried under the less stringent packing provisions P908 and LP904.

2.6 Call to action

With technology rapidly advancing and batteries increasing in trade volume and individual capacity, regulations have been slow to catch up. The above review has identified a number of specific concerns:

1. **Test certificates**

   Although there is a requirement for manufacturers to test batteries, and for manufacturers and subsequent distributors to make the test summary available, there is at present no explicit requirement on shippers to submit either the test summary or any document issued by an independent laboratory when consigning lithium-ion batteries for transport. This is despite the fact that such testing is a requirement for exemption of certain types of batteries under SP 188. Without this documentation, the carrier cannot verify whether the requirements have been satisfied, increasing risk during transport..

2. **Classification of lithium-ion powered electric vehicles**

   At present, UN 3171 covers battery-powered vehicles and equipment. This includes all electric vehicles, including Li-ion powered EVs, whereas SP388 specifically excludes equipment (other than vehicles) powered by lithium-ion batteries (those are assigned the respective UN numbers for the batteries they contain). This appears an anomaly. In view of the distinct hazards associated with lithium-ion batteries and the rapid increase in volume of manufacture and transport of lithium-ion powered EVs, a separate UN number for such EVs would provide greater clarity, with specific requirements for declaration and documentation (e.g. state of charge, battery chemistry, type of battery, capacity and/or details on safety system in place). This proposition will be discussed by the UN Sub-Committee of Experts on the Transport of Dangerous Goods in December 2022.

3. **Exemption for EVs carried on ro-ros and car carriers**

   At present, SP 961 excludes EVs carried on ro-ros and car carriers from the requirements under UN 3171. Because of this, carriers do not generally have a list of all EVs on board, or their respective locations. Revoking this exemption would allow carriers to plan stowage locations and the monitoring of EVs during the voyage in greater detail, with a view to developing early detection, evacuation and/or firefighting procedures..

4. **Mandatory markings for EVs**

   At present, there is no requirement for EVs to be identified either during consignment procedures or by external markings on the vehicle. Mandatory marking would assist stowage and emergency response.

5. **Preventing short circuits**

   Batteries are required to be packaged in such a way as to prevent short circuit, but there is no explicit requirement as to how this may be achieved, e.g. by covering the terminals.

6. **State of Charge (SOC)**

   When shipping Li-ion batteries by air, IATA regulations specify a maximum SOC of 30% of their rated capacity. No such SOC criteria are currently in place for transportation by sea, or other surface modes of transport.

7. **Battery condition on loading**

   Current regulations do not take into consideration that a significant proportion of batteries are transported immediately after having been used or charged, as is the case for EVs having been driven onto a ro-ro or car carrier. Enhanced risk detection procedures may include checks before loading on SOC and battery condition/temperature.

8. **Damaged or defective batteries**

   These no longer conform to their design safety testing and therefore may present unforeseeable levels of risk. Current regulations contain stringent packing requirements for shipments that are considered high risk, but do not specify how such high-risk shipments are identified and differentiated from “low-risk” damaged or defective batteries.

3. Fire risks and emergency response

3.1 Challenges following ignition and propagation

The very first thing to remember when considering any response to a lithium-ion battery fire – of any type - is that in the first instance what you will likely be seeing is not smoke, but potentially highly toxic vapours and fumes. The old rule of going low when a fire occurs because smoke rises does not apply to battery fires due to the different properties and densities of the vapours being produced.

Lithium-ion battery fires are very difficult to extinguish. Associated problems with firefighting include the following:

- They are generally within sealed units and their location in a piece of equipment or vehicle can prove very difficult to access and penetrate with a fire-extinguishing medium.
- Larger quantities of water are required to extinguish lithium battery fires. For example, for an electric car you can expect to need around 136,000L of water over four hours instead of 10,000-17,000L over 30 minutes for a combustion engine car.
- Li-ion battery fires have a sustained flame and are difficult to supress because the batteries are self–supporting.
- Re-ignition can occur a considerable time after the fire has been extinguished.
- More resources will likely be required to bring an incident under control and to a conclusion.
- Toxic vapours are flammable, with some lighter and some heavier than air in different proportions. The vapours will therefore not all rise and act like smoke.

Another risk that is sometimes forgotten or even ignored, is the potential for electrocution from the batteries if they are part of a bigger unit. As highlighted above, significant quantities of flowing water will likely to be required to extinguish a major vehicle fire. One major manufacturer actively advises against submerging the vehicle in water (particularly in a steel container) due to concerns over the electric shock hazards associated with the size of the batteries contained.

The concern of electrocution should not be underestimated when trying to tackle these incidents either onboard a ship or in road traffic accidents as there is the potential risk of serious injury and/or even death.

Firefighting tactics and equipment provided (particularly on ships) will likely need to be revised and updated to cope with the different properties of these fire types.

Some professional land-based fire services are adopting a defensive tactic when it comes to tackling these fires by simply allowing the vehicles to burn out naturally while they protect the surrounding area. If the battery is small enough, professional firefighters typically opt to submerge it in water for at least 24hrs. In some areas they have adopted this policy with electric cars, by purchasing a Hiab flatbed truck with crane, to allow them to lift and place the burning vehicle into a vat of water.

The decision to leave a fire until it reaches the decay stage and eventually burns out is not an option for seafarers. Seafarers have to consider a number of factors not least of which includes adjacent vehicles and potentially hazardous materials stowed in the same area, passengers, and the location of lifesaving appliances should the fire spread.

Other equipment that is being more widely purchased and utilised are thermal imaging cameras (handheld and drone equipped), fire blankets (large and small) for use on anything up to a car in size, as well as items to help prevent electrocution such as rubber gloves, intrinsically safe hooks and safety harnesses.

The challenges that this type of incident can cause are further exacerbated depending on where it happens and what's involved. A thermal runaway that occurs on board a ship at sea, for example, is much more severe than a thermal runaway that occurs in an isolated roadside vehicle.

Whether it be a ro-ro, ro-pax or PCTC, an EV fire is likely to be potentially difficult to locate in the event of a thermal runaway incident. This is because the deck or compartment is enclosed (like an oven) and this space is likely to fill very rapidly with the toxic vapours initially. Thereafter, there will be the generation of smoke from the combustibles as the fire develops rapidly between vehicles if containment measures have not, or cannot be, deployed in short order remotely.

Any delays in locating a fire within a vehicle deck will undoubtedly lead to the fire spreading to other combustibles and the propagation of the fire to a point where it will be very difficult to extinguish with the limited resources provided on board a ship. Evidence suggests that fires can develop in a matter of minutes between adjacent vehicles. Vehicle decks have ventilation systems to ensure compliance with air exchanges per hour but these can both help and hinder locating a fire.

There is no doubt that there will continue to be a significant challenge when it comes to dealing with the hazards and speed of fire development with these batteries. It may well need to be a combination of methods that are required when attempting to bring an incident under control. Such methods and potentially updated and improved monitoring systems and equipment need to be urgently considered. Examples of these are listed below:

- Improved automatic fire detection alarm systems (AFA) such as including CCTV with thermal imagery to increase the likelihood of early detection. Perhaps associated with designated zones for the cargoes carried.
- Improved and more expanded gas detection systems built into the cargo holds or car decks.
- Sprinkler, HI-FOG or improved and perhaps expanded capacity drencher systems.
- Fire blankets.
- Positive pressure ventilation (PPV) firefighting carried out by experienced personnel.
- Appropriate and upgraded personal protective equipment (PPE) including more appropriate fire suits, longer duration and lighter self-contained breathing apparatus (SCBA) etc.
- Provision of hand-held thermal imagery equipment for use by shore as well as shipboard personnel.
- Compartmentation for larger areas to slow the spread of fire.
- Review of statutory regulations (HSE, SOLAS & STCW) and standards with a push for urgent changes to ensure all parties in the supply chain are trained in the potential hazards and consequences and prepared to respond appropriately.
- Additional specific, shore-based, practical training for ship and shore-based staff.

IMDG Code general guidelines for fire and spillage are sensible and comprehensive for the personnel expected to deal with any incident, such as wearing SCBA and hazardous material suits. However, the general fire schedules do not specifically take into account the evolution of toxic gases. Given the potential for intoxication from gases with much lower toxicity than hydrogen fluoride (phosphine and carbon monoxide), strategies should be adopted from the spillage schedule, i.e. measures to prevent gases penetrating into other parts of the ship.

Figure 6 *- Example of Thermal Runaway in roof mounted batteries involving a hybrid Paris Bus on 19.04.2022*

3.2 Risk prevention

Risk prevention and proper risk assessments should be developed immediately to try and mitigate the issues highlighted in this paper. These should be combined with the installation of better fire identification and fighting equipment and the improvement of understanding by all parties in the supply and handling chain.

Prevention, risk assessment, knowledge and understanding while not sufficient, is a valuable target in areas of the globe where equipment is limited or non-existent.

Basic prevention should include:

- Monitoring when and where such devices and batteries are charged, ensuring that they are on hard surfaces and ideally not charged overnight and left unattended.
- Preferably charging items associated with hobbies or mobility outside of accommodation or workplace, for example mobility scooters, bicycles and scooters. Priority is to consider and ensure an incident doesn't affect the ability to exit and escape any spaces should an battery failure incident occur.
- Avoiding storing or charging at very low or very high temperatures. Always allow for ventilation in hot environments and do not leave in direct sunlight.
- Avoiding leaving on a continuous charge when a device is not in use.
- Never covering batteries, chargers or charging devices whilst they are plugged in and charging.
- Protecting batteries from being mechanically damaged as far as possible.
- Preferably sourcing branded, genuine battery replacement from reputable suppliers, if required. Copies or generic chargers, charging cables and batteries may look the part but may not have the appropriate safety mechanisms built in.

The biggest challenge to any industry will be the transport of these batteries. While there will always be an inherent risk, that risk will certainly increase for end-of-life batteries and batteries for disposal.

Currently, the regulatory testing requirements are largely focussed on type approval for the construction of new batteries. There is no specific regulatory requirement for individual testing of each batch at the time of production although manufacturers may do so as part of their internal quality control procedures. In addition, batteries are often not new when shipped, and are not tested at the current point of their life cycle. Even nominally "new" batteries installed into EVs will have undergone at least some use prior to transportation as they will have been charged and driven at least once when boarding the ship.

Whilst IMDG Code provisions are available for scrap and batteries for recycling, these provisions are not, in our opinion, adequate as they do not include used or reconditioned batteries. More testing should also be implemented for scrap and batteries for recycling to check their condition before they are loaded into containers.

As the shift towards EVs continues, we will likely see an increase in the number of cars being modified from combustion to EV engines- some of which may be undertaken as a DIY- conversion. No regulations have been put in place regarding second-hand EVs or modified/converted vehicles.

Looking to the future, the hope is that technology will be developed to enable remote evaluation of EVs and their batteries. This technology would detect a fault using telematics and/or an app to generate an alert that a problem may be developing. The earlier the detection, the quicker that containment measures can be implemented to protect the area and any persons in the vicinity.

Further reading

Lithium battery guide for shippers September 2021
U.S. Department of Transportation
Read more...

Manufacturing scalability implications March 2021
Joule
Read more...

Lithium-ion battery risk bulletin August 2022
Allianz
Read more...

Best practices for the transport of electric vehicles onboard vessels June 2022
ABS
Read more...

Electric vehicles onboard passenger roll-on/roll-off (ro-ro) ferries July 2021
UK MCA - MGN 653 (M)
Read more...

Lithium battery recycling safety advisory note May 2017
U.S. Department of Transportation
Read more...

Guidance on the carriage of Alternative Fuel Vehicles in ro-ro spaces May 2022
European Maritime Safety Agency
Read more...

brookesbell.com
ttclub.com
ukpandi.com