

Energy Storage Publishing

The International quarterly for manufacturers and users of electrochemical power www.bestmag.co.uk

bestmag

Batteries & Energy Storage Technology **No. 65**
Summer 2019

Standing the test of time!



Are lithium batteries on safe foundations?



Inside

ESS feels the heat

The Big Easy energises BCI 2019

Bi-directional chargers for EVs



Plus all our regulars

BATTERIES & ENERGY STORAGE TECHNOLOGY

Batteries and Energy Storage Technology magazine (ISSN: 1741-8666) is published four times a year (January, April, July and October), by Energy Storage Publishing Ltd., 70 Goring Road, Worthing BN12 4AB ENGLAND and distributed in the USA by Mail Right International, 1637 Stelton Road B4, Piscataway, NJ 08854. Periodicals Postage Paid at New Brunswick, NJ.

POSTMASTER

Send U.S. address changes to BEST c/o 1637 Stelton Road, B-4, Piscataway NJ 08854

EDITORIAL OFFICE

Energy Storage Publishing Ltd
70 Goring Road
Worthing BN12 4AB
ENGLAND
TEL +44 (0) 845 194 7338
FAX +44 (0) 845 194 7339

MANAGING DIRECTOR

Vic Giles
vic@bestmag.co.uk

ADVERTISING/SALES

Gary Pavey
advertising@bestmag.co.uk

EDITOR-IN-CHIEF

John Shepherd
john@energystoragepublishing.com

TECHNICAL EDITOR

Dr Michael McDonagh
mike@energystoragepublishing.com

SOUTH ASIA ASSOCIATE

Dipak Sen Chaudhuri
dipaksc@yahoo.co.in
+91 98314 37792

OFFICE ADMINISTRATION

Gill Keys
accounts@energystoragepublishing.com
subscriptions@bestmag.co.uk

NON-EXECUTIVE CHAIRMAN

Gerry Woolf
gerry@bestmag.co.uk

PRINTED IN ENGLAND

Tilting points in history

Fifty years ago this summer, those of us of a certain age will recall being glued to the television screens watching Neil Armstrong become the first human to step onto the surface of the Moon, followed minutes later by Buzz Aldrin.

Armstrong's words, beamed back to Earth for all to hear, summed up the momentous achievement: "That's one small step for man, one giant leap for mankind."

Another 50th anniversary of a technological first is also being marked this year— the maiden flight of the supersonic airliner Concorde.

But how will the history of batteries reflect our efforts— when viewed in 50 years time? Lead-acid has of course been with us since the late 19th century, while the modern lithium battery was invented a mere 40 years ago. **Lead batteries have clearly stood the test of time but how will lithium fare in the near future?**

Lithium is very much the 'poster boy' of energy storage and EVs. However, it's also fending off questions of safety— in view of a series of ESS fires in Asia and North America— and having to defend its sustainability credentials. **Lithium is certainly coming under increasing scrutiny and, as our cover page asks, does it have the solid foundations to withstand the test of time?**

The famed leaning tower of Pisa has endured the ravages of time and with the cause of its tilt finally established, as late as 2003, still stands next to the Pisa Cathedral in the so-called Square of Miracles. Perhaps lithium battery tech is at a tipping point of its own. Whether miracles have had something to do with the tower's longevity or not, technology needs to rely on more than heavenly blessings.

Regulators, businesses and the general public will only put their faith in technologies that stand up to rigorous safety and performance checks. Which is why, in this issue, we take an in-depth look at some of the issues that have bedevilled lithium of late. Technical editor Dr Mike McDonagh evaluates the current state of play with the safety of lithium batteries— and finds answers for the future of this critical technology.

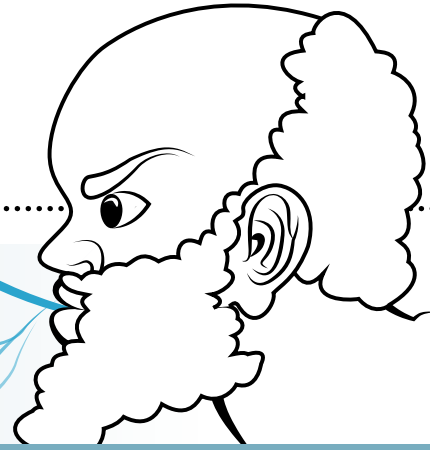
Meanwhile, the CEO of one ESS manufacturer criticises the lack of informed reporting on issues such as the BESS fires and says the reputation of the industry should not be tarnished as a result.

However the history of our industry gets tilted in the years ahead we hope you will enjoy reading about it in the pages of BEST magazine.



John Shepherd
Editor-in-Chief

Enjoy the issue.



Time to tackle a burning battery injustice

The benefits of batteries for energy storage are well-known to readers of this magazine. Here, Catherine Von Burg, CEO of ESS designer and manufacturer SimpliPhi Power, bemoans the lack of informed reporting on battery fires, and the chemistries involved, and says the reputation of the industry should not be tarnished as a result.

Batteries create energy security, in any application, on grid or off. But battery chemistries matter, and they are not all the same. Lithium batteries made with cobalt (NMC & NCA) are fundamentally toxic, get hot, catch fire, explode, and are dangerous. By contrast, lithium batteries made with iron phosphate (LFP) are non-toxic, do not generate excessive heat or erupt into flames and do not explode.

In April 2019, a serious explosion occurred at the McMicken energy storage facility in Surprise, Arizona. Owned and operated by the Arizona Public Service, the batteries in the McMicken facility stored energy generated from solar. Many details about the Arizona incident have not yet been reported to the public as the authorities, the utility, and the battery manufacturer are still investigating the explosion and endeavouring to determine its cause. After the explosion, the facility was immediately shut down. Grievously,



several firefighters who were called to respond to the explosion and ensuing fire were hospitalised with serious injuries.

Within days, *Bloomberg News*, which has steadily been covering the burgeoning energy storage market, appeared ready

to throw the whole battery industry under the bus. A report on the Arizona incident quoted Logan Goldie-Scot, a Bloomberg analyst, saying “if utilities and regulators deem energy storage unsafe, gigawatts of proposed storage deployments would be threatened”. This statement was made without any regard for battery chemistry and whether or not the lithium batteries used in the McMicken facility were cobalt-based—fundamentally toxic and hazardous— or that there is a choice amongst lithium-ion battery chemistries for a solution that is non-toxic and safe and that there is an alternative to cobalt based lithium-ion.

As the CEO of a fast-growing company designing and manufacturing

LFP energy storage systems that do not utilise cobalt, the likely cause of the fires, toxic hazards and explosions associated with “lithium-ion” batteries, it is clear that there is a real need for education to enable consumers to make informed purchasing decisions that have a real impact on public safety— *their* safety.

The crucial but largely unreported factor in many of the fires and explosions happening in the industry today— from a MWh utility installation in Brussels to LG Chem ESS systems to Tesla cars parked in garages— is battery chemistry. Most lithium-ion batteries (lithium manganese cobalt oxide NMC and lithium nickel cobalt aluminium - NCA) contain cobalt. Cobalt is toxic and hazardous. Lithium is not toxic or hazardous, but because reports on “lithium fires” do not distinguish the fundamental differences and hazards between available chemistries, *all* “lithium-ion” batteries are getting a bad reputation, whether they use cobalt or not.

This is a tremendous disservice to advancing the entire energy industry

Let's hear what you think

Got an opinion on the above or anything else? Then share it. We welcome views from all sectors of the battery industry— whatever the chemistry.

Contact: vic@bestmag.co.uk

that increasingly looks to batteries to create power reserves to optimise the grid, create access to power beyond the grid and to provide critical backup power in catastrophic failure of the grid. In addition, it is time for the industry as a whole, particularly in the face of the disastrous cobalt-based lithium battery fires, to realise that ‘energy security’ and ‘clean energy’ (renewable solar & wind generation), cannot be achieved with fundamentally toxic and hazardous batteries that put the end user, and all those along the entire supply chain, at serious risk.

The key factor in the thermal runaway fires reported in phones, laptops, hoverboards, cars, airliners, and even vape pens is not ‘lithium-ion’ *per se*. It’s the cobalt that’s in the vast majority of ‘lithium’ batteries. Cobalt dramatically increases the risk of uncontrolled or thermal runaway fires for three key reasons:

1. Lithium batteries that use cobalt generate significant heat. This necessitates expensive cooling, fire retardant systems and thermal monitoring systems. These often shut a storage system down if the cobalt-based lithium-ion batteries get too hot.
2. At the same time, cobalt lowers the temperature threshold, or thermal runaway point at which the chemical compound breaks down and burns. When a battery reaches that point, cobalt-based lithium (Li) compounds in thermal runaway release oxygen.
3. This fuels and “self-propagates” a highly toxic fire, making it dangerous for first responders and impossible to put it out until the oxygen in the compound burns out.

This has prompted local, federal and international agencies to crack down on and recall thousands of lithium batteries. New York City has initiated strict (although currently stalled) 9540a lithium battery safety tests, required whether a lithium battery has cobalt in it or not.

“**The crucial but largely unreported factor in many of the fires and explosions... is battery chemistry.”** Von Burg

Reports that declare ‘lithium-ion batteries have exploded’, can catch fire and are dangerous, without identifying the specific chemistry—or raw materials—that make these batteries likely to burn (such as cobalt), inaccurately and egregiously tar an entire industry.

SimpliPhi Power has always chosen to only use the most environmentally benign and safe chemistry—LFP that does not contain cobalt. *It’s true that I have a vested interest in clarifying this issue, but so should anyone concerned with both safety and sustainability.*

So why have other companies chosen and continue to choose cobalt-based lithium chemistry, even in the face of increasing fires? *Cobalt is cheaper.*

The Federal Aviation Administration has given SimpliPhi “special permission” for air transport clearance globally for four years running.

Now we are working with UL and DNV-GL (New York Battery & Energy Storage Technology Consortium) to subject our LFP cells and batteries to the most rigorous tests established to validate that our chemistry and batteries are safe. This independent,

rigorous third-party test data will enable customers to make informed purchasing decisions when it comes to batteries at the residential, commercial and utility point of installation.

Recently, the US Energy Storage Association has been presented with an opportunity to prioritise safety as an early commitment. I am hopeful that discernment between “lithium-ion” battery chemistries will become an important part of the discussion concerning public safety and reliable storage solutions. Batteries provide access to power for those who live beyond the limits of the grid, critical backup

power for those who are tied to the grid, the ability to strengthen our aging grid infrastructure, as well as the means to store the ever-increasing amount of energy generated from renewable sources. We need these systems to be safe and reliable. +

BESTmag technical editor Dr Mike McDonagh writes: It is true that LiFePO₄ cathodes in a lithium-ion cell are the safest of all lithium-ion chemistries. They present an extremely low, even negligible risk in normal use. However, it would be very concerning if readers believed it is not possible for LiFePO₄ batteries to catch fire or explode—they can. I know this because I have done abuse tests on LiFePO₄ cells. They contain highly volatile organic solvents in their electrolytes that have a very low flashpoint, which can ignite. No electrochemical energy storage chemistries are devoid of risk, even established chemistries like lead-acid. The mechanisms and reasons for lithium-ion fires are covered in detail in the safety article in this edition of *BESTmag*.

Li-ion EV and BESS batteries— a solid foundation for the future?

Technical editor, Mike McDonagh evaluates the current state of play with the safety of lithium batteries and finds answers for the future of this critical technology.

According to climate scientists the planet is experiencing an unprecedented rate of increase in both atmospheric and marine levels of CO₂. According to NASA, land and sea temperatures, along with sea levels, are rising far faster than in any post ice age recovery period that we have ever measured. According to the European Commission, transport, of which the road sector is 70%, accounts for almost one quarter of the total of Europe's greenhouse gas (GHG) emissions. This compares with national electricity generation for domestic and industrial sectors that combined, produce almost one half of the European GHG emissions. For this reason, there is extreme pressure on governments worldwide to take effective, and if possible,

immediate measures to reduce CO₂ levels. Measures that include transport electrification, grid and domestic level energy storage are currently on the hot topic list of government led initiatives.

The EU Parliament's environment committee has agreed a proposal to enforce a 20% target for sales of EVs by 2025. Their ultimate aim is to phase out ICE engines entirely by 2040. As all of *BESTmag* readers are aware, this transition is not an easy one. The main reasons for lack of take-up of electric vehicles are: the range (energy density), the recharge time, the cost and the safety of current EV battery technology. There are also issues around the charging infrastructure and the logistics of home charging,

particularly for full EV vehicles where owners may live in apartments or terraced houses on busy streets. For this reason, there is renewed interest (and government funding) in many developed countries in battery R&D to find chemistries and technologies more suitable for the EV application.

At present, the reality is that there is no real technological alternative to lithium-ion batteries for EV use. And with the aforementioned pressures on governments it seems highly likely that we will be putting growing numbers of lithium-ion batteries into both electric vehicles and battery energy storage systems for many years to come. That is despite the current concerns over safety and sustainability (see *BESTmag* summer and autumn 2018).



Fig 1: APS installation in Surprise, Arizona, which caught fire then exploded in April 2019 seriously injuring firefighters

With that in mind, this article will examine the state of play for technologies that are aimed at reducing or removing the current safety risks associated with lithium-ion batteries and will comment on their effectiveness and probability of implementation.

The environmental and safety concerns of using lithium-ion batteries have some parallels with the UK nuclear industry, in particular Sellafield, which is now a closely guarded and sealed-off area of land where spent toxic nuclear fuel is both treated and stored with very little hope of finding a solution to its processing or safe disposal. Whilst the lithium-ion battery is nothing like as dangerous as nuclear fuel, the same issues of longer-term consequences vs. short term solutions are an apt analogy. Ploughing ahead to meet the single objective of GHG emissions may be storing up yet another future problem with environmental, safety and cost repercussions. Along with EV batteries, the burgeoning number of BESS installations of 5MW and greater looks set to continue rising using

lithium-ion chemistries. The risk posed by fires from both of these industries is becoming a concern. According to South Korea's government, more than 20 ESS units have been completely destroyed by fires in the last year. Companies like Samsung SDI have suspended any further installations with a corresponding loss in sales revenue. In a similar incident a 2MW/2MWh lithium-ion grid scale battery storage facility in Arizona USA suffered from initially a fire then an explosion injuring firefighters, one critically and two seriously, is now under



Fig 2: Colleague's Volvo hybrid EV caught fire overnight whilst on charge

investigation **Fig 1**.

Whilst the hybrid EV may have a much smaller battery (20-25kWh) the consequences of a spontaneous fire are potentially deadly. **Fig 2** shows a fire incident at a colleague's home in the UK. This was a Volvo hybrid car that caught fire whilst on charge.

In addition to the fires, as many are aware, the recycling of lithium-ion batteries is yet to become a commercial reality. However, there is a growing trend for using 'second life' automotive lithium-ion batteries in ESS applications where the lower energy density from degraded cells is acceptable. Whilst this measure extends the period before the batteries reach their end of life, it can also increase the risks associated with this technology.

One of the dangers in this strategy is the possible growth of internal cell dendrites resulting from the continued charge/discharge cycles until the capacity has degraded to 80% of nominal. Cells that are subject to this problem are more likely to suffer from internal short circuits, which can trigger a sequence of chemical events leading to fires

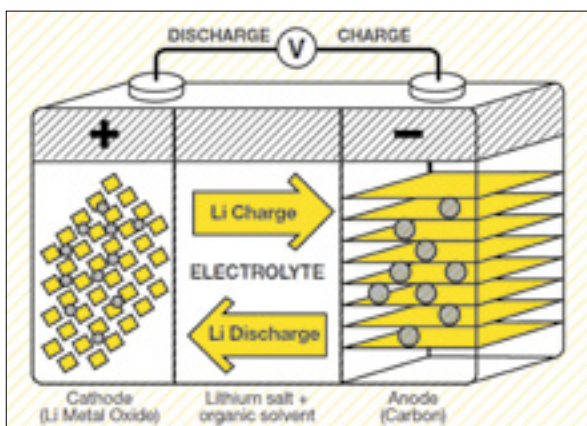


Fig 3: Simplified schematic showing the operating principle of a lithium-ion cell

or even explosions, particularly in large BESS installations or recycling storage facilities.

BEST Battery Briefing reported earlier this year, manufacturers and users of battery storage systems have backed an industry-led initiative in the US to “prioritise safety” in the production and operation of equipment.

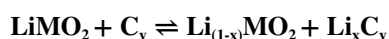
So, what are we going to do?

In this article we will look at the current lithium-ion battery designs and the causes of the fires that have been reported. We will also look at what the industry is doing to improve safety and prevent the causes of these fires with new electrolytes, separators, internal and external fire prevention measures. The first issue to understand is: **what is there in the construction and materials used in the present lithium-ion designs that lend themselves to this combustion susceptibility?**

For those few who are not familiar with the technology, **Fig 3** shows a simplified diagram of the operation of a lithium-ion cell and its material construction. As can be seen the source of voltage and current comes from the Li^+ ions that are contained in the

electrodes and the electrolyte. The reactions on charge and discharge can be generally described as:

discharged **charged**



M = metal such as Co, Mn, Ni etc.
C = carbon electrode

Unlike most other electrochemical storage systems, the function of the electrolyte is to act as carrier of the ionic species that are transferred back and forth between the two electrodes rather than relying on a chemical reaction to transfer valence electrons. The faster the transfer, the greater the power delivery and the possible charging rate. For this reason, the electrolyte and separator must present minimum resistance. In

the case of the separator, the thinner the better and in the case of the electrolyte, the less surface tension and the higher the conductance the better. To achieve this, the most suitable and commercially available electrolytes are organic solvents. Unfortunately, the low surface tension also means a higher vapour pressure that can lead to increased internal cell pressure, even at low temperatures. **Table 1** gives a list of the current most common electrolyte materials and **Table 2** contains the most prominent of the lithium salts used in current LIB designs.

The electrodes are the stores for the lithium ions and have the property of providing the interstitial spaces for the ions to accumulate and be reduced or oxidised depending on whether the cell is being charged or discharged.

Table 1: Properties of the most important organic solvents used in LIB electrolytes

Electrolyte Components	CAS Registry No.	Structure	Melting/ Boiling Point (°C)	Dielectric constant ϵ (25°C)	Viscosity η (cP, 25°C)	Vapor Pressure (torr)	Flash Point (°C)	Auto-Ignition Temperature (°C)
Dimethyl carbonate (DMC)	616-38-6		2 / 91	3.1	0.59	18 at 21°C	18	458
Ethyl methyl carbonate (EMC)	623-53-0		14 / 107	3.0	0.65	27 at 25°C	25	440
Diethyl carbonate (DEC)	105-58-8		-43 / 126	2.8	0.75	10 at 24°C	25	445
Propylene carbonate (PC)	108-32-7		-49 / 242	65	2.53	0.13 at 20°C	135	455
Ethylene carbonate (EC)	96-49-1		36 / 248	90 (at 40°C)	1.9 (at 40°C)	0.02 at 36°C	145	465
Ethyl acetate (EA)	141-78-6		-83 / 77	6.0	0.45	93 at 25°C	-4	4
Methyl propionate (MP)	554-12-1		-84 / 102	5.6	0.60	64 at 20°C	11	469
Ethleneglycol dimethylether (DME)	110-71-4		-58 / 84	7.2	0.46	48 at 20°C	0	202
Tetrahydrofuran (THF)	109-99-9		-108 / 65...66	7.4	0.46	143 at 20°C	-17	321

Salt	T _{Decomp.} in solvent [°C]	Al-corrosion	Conductivity (1.0 M, EC/DMC, 25°C)	Electrochemical stability until	Characteristics
LiClO ₄	>100	No	8.4 mS/cm	4.5 V vs. Li ⁺ /Li	Not sensitive to hydrolysis; no formation of HF; explosive
LiAsF ₆	>100	No. Passivates Al current collector.	11.1 mS/cm	4.5 V (cathodic) / 6.3 V anodic vs. Li ⁺ /Li	Good SEI formation. Toxic degradation products.
LiBF ₄	>100	No	4.9 mS/cm		Strong Lewis base; decomposes and forms HF
LiPF ₆	>70	Effectively suppresses Al corrosion	10.7 mS/cm	4.8 V vs. Li ⁺ /Li	Very sensitive to hydrolysis
LiCF ₃ SO ₃	>100	Yes	>10 mS/cm		
LiN(SO ₂ F) ₂	>100	Yes: Insufficient passivation of Al electrode	>10 mS/cm	4.8 V vs. Li ⁺ /Li	Not sensitive to hydrolysis, no formation of HF; expensive production

Table 2: Properties of the most important salts used in lithium-ion batteries

The anodes are generally carbon-based materials, the most common being graphite due to its layered structure. The cathodes are generally based on metal compounds that provide the lattice structure that can contain the lithium ions. The process of intercalation of the ions into the electrode structures is one of intense scrutiny. This provides the key to accommodation of ion capacity (energy density) and the voltage of the intercalation reaction (power density). Both of these properties are vital in determining vehicle performance and range as well as cost/kWh of the EV battery.

If we want to determine the causes of the flammability of lithium-ion batteries, the first and foremost culprit to examine is the electrolyte, which is a highly volatile organic solvent with a high vapour pressure and low temperature flashpoint (**Table 1**). This is the source of the fires reported in the media. The fire producing mechanisms are believed to be: decomposition of the electrolyte and cathode to

produce flammable gases and oxygen as a highly combustible mix, and/or venting of the flammable electrolyte vapour at higher temperatures. The other contributing factors are centred round the high power available to create heat with rapid discharge and charge of cells, the parallel/series connections needed in high capacity applications like electric vehicles, the control of individual cells by the BMS and the parameters built into the CPU of the BMS.

Looking at the two prime causes of lithium-ion battery failure we can put down a sequence of events that lead to the point of combustion. This will give a clue as to how these fires can be prevented, handled, or avoided completely. The onset of a fire is often called thermal runaway. There are several reasons why a lithium-ion battery or cell can start its progression down this path. However, the two principal reasons are: physical damage or manufacturing fault that creates a short circuit, or overcharge conditions that start a

sequence of irreversible chemical events within the cell. There are three definable stages that occur from the initial conditions or event through to the combustion of flammable components:

1. Initiation of a high energy event such as a short circuit or overcharge condition.
2. Breakdown of internal components and increase of internal cell pressure to release flammable gas.
3. Thermal runaway caused by exothermic chemical reactions and combustion or explosion of flammable materials.

To understand what is going on at each of these stages we need to look at the construction and chemistry of current lithium-ion batteries. The main components are the metal oxide cathodes, carbon-based anodes, organic solvent electrolyte, polymer separator and metal or plastic case material. The electrolytes are a mixture of organic solvents and an electrolyte salt compound such as LiPF₆ or LiBF₄, usually in a mixture of a cyclic (ethylene/propylene carbonate.) and a linear (di-methyl/di-ethyl carbonate) ester.

The major downside of these organic solvents are their flammability and potential environmental impact. They are the main source of fires associated with lithium-ion battery installations. The separator is a thin polypropylene or polyethylene film that is prone to liquid softening above 120°C. When softened they are less able to prevent internal short-circuits from dendrite growth or manufacturing defects. The cathodes are not intrinsically



flammable but can break down with the production of oxygen when internal cell temperatures rise above 130°C. This oxygen can accelerate the reaction rate and possibly contribute to an explosion. The carbon anode will burn under the right conditions of heat and oxygen availability. The case material is generally steel, particularly for road vehicles, which are more prone to high impact damage than hand devices such as power tools or laptop computers.

Although not directly combustible, the cathode material is an important factor in the early stages of a combustion sequence. It is this component that determines the voltage or power that is released when a short circuit, for example, creates a power surge. The higher the voltage the greater the power ($P=VA$). The use of cobalt, which provides cathodes with the highest voltage cells, does increase the chances of initiating a combustion sequence by raising internal cell temperatures by either overcharging or from a short

circuit. Another reason, is typified by the NMC electrode where nickel oxide will release oxygen at higher temperatures thereby creating ideal combustion conditions. Another problem is that of plating lithium metal onto the cathode from deep discharge (less than 2V/cell) and low temperature conditions.

Looking at the first stage where a high-power event would create heat and raise internal cell temperature, it is overcharge and short circuits that are the most likely to initiate this. Tesla for example have fitted strengthened underbody shields to prevent fire causing incidents like that of 2013 when a battery pack caught fire after it was damaged by road debris.

Dendrites can form during the life of a lithium-ion battery due to a combination of factors including its charging and discharging profile during use. This is one of the factors that makes second use of automotive batteries a higher risk than using new cells. In this case the separator can be penetrated if the degree of

dendritic growth is severe or the separator is faulty **Fig 4**.

Again, it is a high-power energy release from the short, which creates heat, that starts the thermal runaway sequence. This heat input and temperature rise initiates the next event, which is the breakdown of the cell's materials. There are several reactions involving the electrolyte, cathode and separator material: the breakdown of the metastable compounds in the SEI layer, synthesis of flammable gas, predominantly methane, from the electrolyte and the physical softening and breakage of the separator, which allows short circuits. In the final stage the lithium metal oxide cathode can decompose, which releases oxygen into the cell creating flammable, sometimes explosive conditions. Because the inside of the cell is a closed system and almost adiabatic, temperature rise can be extremely rapid. Whilst there is no real order to the reactions described here, there are temperature-related events that can be proposed, which are illustrated in **Fig 5**.

Whilst this is not a chronological order of events, it does show how hot the internals of the cell need to be in order to initiate a true thermal runaway condition.

In the last stage, i.e. combustion, the internal pressure of the cell is raised due to the increasing vapour pressure of the electrolyte caused by the higher temperature. The internal pressure exceeds the limit of the pressure relief valve on the cell and hot vapour along with the products of the electrolyte

200°C	$\text{Li}_x\text{CoO}_2 = \text{LiCoO}_2 + (1-x)\text{Co}_3\text{O}_4 + (1-x)\text{O}_2$ $\text{Co}_3\text{O}_4 = 3\text{Co} + \frac{1}{2}\text{O}_2$ $\text{CoO} = \text{Co} + \frac{1}{2}\text{O}_2$	Breakdown of cathode SEI layer to produce oxygen that fuels the fire
150°C	$2\text{Li} + \text{C}_3\text{H}_4\text{O}_3 (\text{EC}) = \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4$ $2\text{Li} + \text{C}_4\text{H}_6\text{O}_3 (\text{PC}) = \text{Li}_2\text{CO}_3 + \text{C}_3\text{H}_6$ $2\text{Li} + \text{C}_3\text{H}_6\text{O}_3 (\text{DMC}) = \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_6$	Electrolyte deteriorates and reacts with lithium ions to produce potentially flammable gases
100°C	<p>Polypropylene separator begins to liquify</p> $(\text{CH}_2\text{OCO}_2\text{Li})_2 = \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + \frac{1}{2}\text{O}_2$	<p>Polypropylene separator fails to prevent dendrite penetration or other internal short circuit mechanisms</p>

and SEI layer are explosively released. Most organic electrolytes, typically EC and DMC have a room temperature flash-point and a high vapour pressure (>4 kPa) at 25°C. On average the electrolyte has an energy content 1.5 to 3 times the electrical

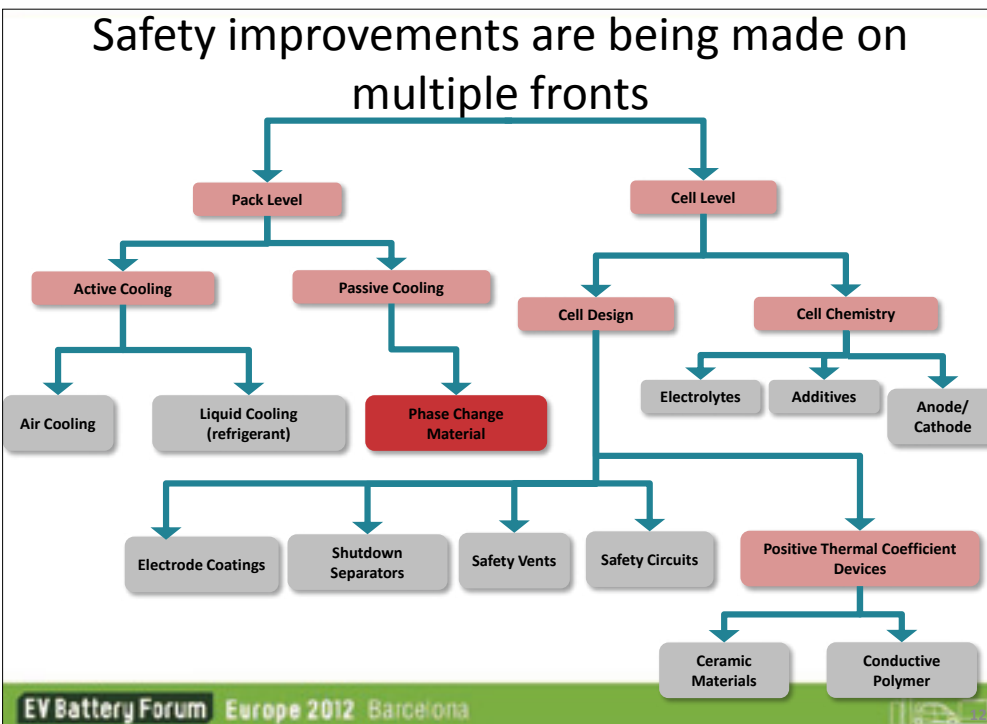
energy stored in the cell. This mix of fuel from the electrolyte, oxygen provided by the cathode breakdown and the heat resulting from the high battery power combine to give the near perfect 'fire triangle' warned of by fire-fighting organisations.

Fig 5: Temperature related reactions inside a lithium-ion cell

Fig 6: Current activity schematic for lithium-ion battery safety improvement

So far, we have seen how lithium-ion batteries with their existing materials and current designs can present a fire risk. The questions to ask are: **can these risks be mitigated or even completely removed and what development work is being carried out to address this problem?** The single answer is quite a lot. Fig 6 shows a line diagram of current measures being investigated by various companies to mitigate or remove the fire risk from lithium-ion batteries. Bearing in mind that there are several elements that contribute to the initiation and progression of a potential fire, we can see that there are a lot of solutions being developed to combat each of those elements. In this article, however, we deal with the currently adopted or most promising of the remedies. These fall into 4 main categories:

- **Physical**— Container materials and cushioning electrolytes, better manufacture to stop faults/dendrites to prevent stage 1.
- **Electronic/BMS**— monitor charging/discharging, temperature, battery shutdown to prevent stage 1.
- **External methods**— Fire extinguishing to prevent stage 3 damage. Heat absorbing phase changing materials between cells to regulate temperature and prevent stage 1.
- **Chemical**— New electrolytes: non-flammable liquids, solid polymer to prevent stage 1. Electrolyte additives to prevent stage 1. New separator materials to prevent stages 2 and 3.



Looking at each category in turn:

Physical

The simplest method to prevent damage to the cell that can create a short circuit is to increase the strength of the outer casing. Typically, plastic cases could be replaced by nickel steel or stainless steel to provide extra rigidity and help to prevent both deformation and penetration of the case material from creating an internal short circuit. There are also internal constructional methods that use a foam metal current collector or silica in the electrolyte to form an impact absorbing GEL. In all current designs there is a pressure relief valve that releases internal gases and vapour from the cell if its temperature exceeds a set value (approximately 130°C). This has the benefit of preventing internal combustion of the released gases and electrolyte but raises the risk of increasing or initiating an external fire.

Electronic

It is the BMS that controls the battery response to input and output currents. It's well established that the higher the current density applied to a cell, the more likely it is to form lithium metal dendrites that can pierce the separator to create a short circuit. High current and overcharging conditions can generate heat within a lithium-ion cell that may initiate the first stage of cell degradation, i.e. the breakdown of the SEI at around 90°C, described above. The BMS should be designed to prevent this as well as detect the onset of temperature rise. The difficulty is

that in large complex cell arrays such as an EV battery, there are 1,000s of cells, each needing to be temperature monitored and individually controlled. Not impossible but expensive.

One method proposed is to charge with high current density pulses. This method advocates the periodic charging of lithium-ion batteries with short pulses of up to 15mA/cm². The researchers found that at the higher currents dendrites that were forming began to merge, smoothing out the surface. At 15 mA/cm² the temperature increased to 40-60°C, which facilitated the diffusion of li ions back from the dendrite tips to the electrode surface **Fig 7**. This temperature was not high enough be detrimental to other cell components. For this method to be effective, the BMS must allow these higher current impulses.

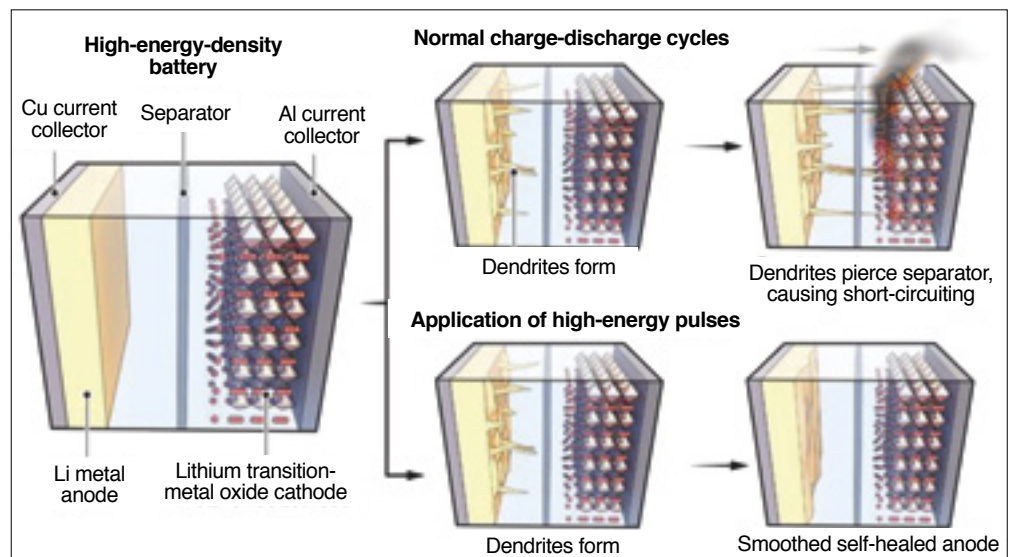
The BMS can control and prevent cyclic pattern related damage. What it cannot do is prevent current induced thermal runaway resulting from internal defects, active material degradation or external

cell damage that can cause an internal short circuit. At least one of the 21 reported fires in South Korean lithium-ion BESS installations the last 2 years was related to a BMS failure.

External

There are two main methods of preventing fire by external means. One is to stop the cell, or block, temperature from rising above the critical level, the other is to extinguish a fire as it starts. The first method generally utilises cooling fins between cells for either liquid or air circulation. Another is to sandwich the cells between layers of heat conducting material that absorb and provide heat to lithium-ion cells. Phase change material (PCM) is an example of a passive system that absorbs heat in a solid to liquid transition and releases it when the reverse occurs. PCMs have a proven track record in other industries and many are commercially available that operate in the temperature range required for current lithium-ion

Fig 7



chemistries. The other option is to put a fire out once it starts. Many BESS installations are provided with an inert gas fire extinguishing method that releases a gas such as argon to swamp a container and prevent oxygen access. Thamesgate, on behalf of S&C Electric Europe, supplied an IG55 argon/nitrogen inert gas fire suppression system for a 6MW/10MWh lithium-ion battery substation in Leighton Buzzard, UK in 2014. In this design, controllers connected to smoke and hydrogen detectors were fitted inside the battery containers.

The problem with all external systems is that they do not treat the cause of the lithium-ion fire but the symptoms. In the heat management equipment, severe damage causing a short circuit would not be mitigated by extracting heat from around a cell. With fire extinguishing equipment it is too late to save equipment or the battery.

Chemical

This section is the area of most R&D activity and needs to be separated by the cell component

that is modified. These components are: separator materials, electrodes and electrolyte.

Separators

There is a plethora of solutions being explored in which the separator plays a key role in either preventing dendritic short circuits or preventing combustion. To prevent dendrite shorting there are two strategies: one is to make the separator stronger, particularly at high temperatures, and the other is to use the separator as an early warning system. The latter uses a partially conducting layer that, when penetrated, will reduce the cell voltage sufficiently to alert the BMS. The battery will still remain functional. Another strategy is to ‘electrochemically consume’ the lithium dendrite in a sandwiched layer of silica nanoparticles when it touches the separator.

The separator can also be designed to carry a flame-retardant chemical (triphenyl phosphate) inside a co-polymer shell (PVDF – HFP). When the outer shell melts at higher temperatures, it releases the

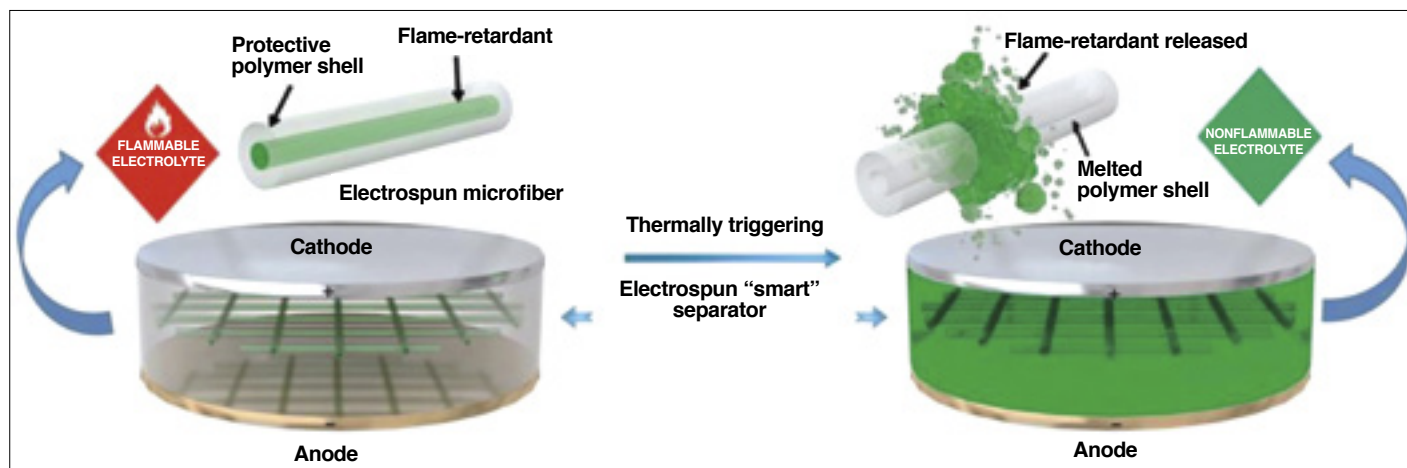
flame retardant to prevent a fire from developing **Fig 8**. This technique has the advantage of not reducing battery performance when compared with methods that have the additive in the electrolyte.

Electrode materials

The aim is to prevent dendrite growth due to incorrect or high charge/discharge currents. Under these conditions Li deposits on the anode when the metal deposition rate exceeds that of the diffusion rate. The root cause, however, is the uneven SEI distribution on the surface, which can nucleate dendrite growth (action of points). The SEI layer can be improved by additives either directly applied to the electrodes or as an additive to the electrolyte. In the former case the formation process is critical to ensure a uniform deposition to prevent irregularities that may seed dendrite formation.

Other methods include coating of the cathode with a thin protective layer to prevent direct contact of the cathode with the electrolyte. This reduces

Fig 8: Method of using separator fibres to release fire retardant additives into lithium-ion electrolytes



the tendency to create side reactions that generate heat. The coatings would be inorganic Li^+ conducting films or stable organic compounds. Another avenue of research is to have a coating of thermally sensitive material deposited onto the current collector. This acts as a switch to cut off or greatly reduce the current flow when the temperature goes above the critical 80°C . The active ingredient is basically a high expansion polymer doped with conducting species that expands when heated. The expansion reduces the density of the conducting particles thereby increasing the resistance. It is designed to cut off the current flow completely at a set temperature.

SEI boosting additives such as vinylene carbonate (VC), which react on the surface of the anode generating a more stable SEI, can be included in this category. Another class of additives would be N,N-dimethylacetamide (DMAc) that reduces the reactivity of LiPF_6 inhibiting the reactions between the electrode materials and electrolyte. In both cases the breakdown of the electrolyte and electrodes resulting in the formation of combustible gases is inhibited.

Electrolyte

There has been intense activity to reduce the flammability of the organic solvents used in the electrolyte formulations for lithium-ion cells. These range from flame retardant additives to replacement of the current electrolyte with solid state conducting polymers or non-

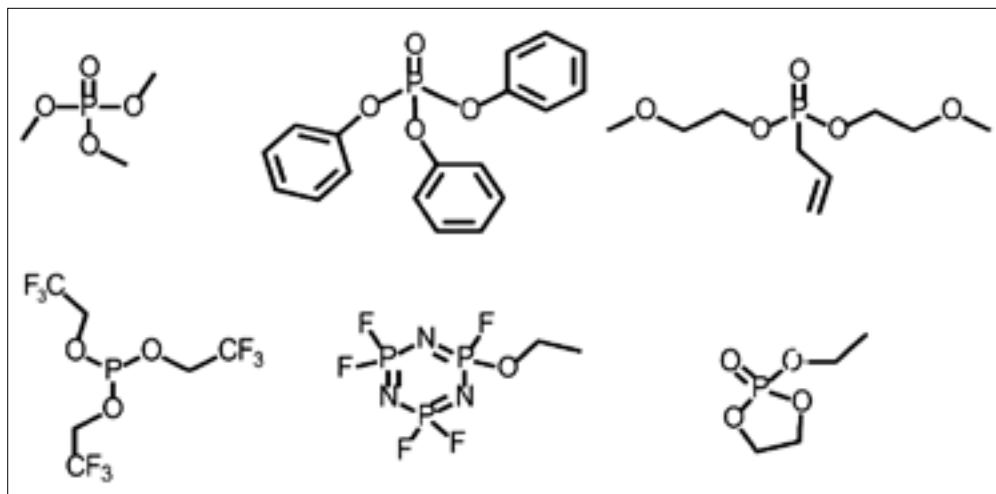
volatile liquids. The additives fall into two main categories: protection against overcharging and prevention of fires from any source.

In the first category overcharge is prevented in two ways: ionic redox shuttle and polymerisation. With the redox shuttle method additives are oxidised on the cathode at higher voltages then diffuse to the anode where they gain electrons and then diffuse back to the cathode. This mechanism lies dormant until the activation voltage for oxidation of the additive is reached. These are generally organometallics that are blended to provide an oxidation trigger at prescribed over-voltages. Generally, this is 0.3 to 0.5 volts above the normal cathode charging voltage. The second shutdown category operate by either a polymerisation process that is voltage specific or by releasing a gas that triggers a current cut-off mechanism. The polymerisation approach is permanent and will make the battery or cell inoperable.

In the second category,

where a temperature rise is initiated by any process, including overcharge, thermal runaway has to be avoided by preventing the creation of those compounds that contribute to combustion. Amongst a wide variety of compounds, the most researched are organic phosphorous and organic halogenated compounds. For environmental reasons it is the phosphorous compounds that are preferred over the halogen containing species. The principle of operation is that the combustible gases resulting from the electrolyte and cathode breakdown at higher temperatures are prevented from forming. Because the organophosphates have free radicals **Fig 9**, they can combine with OH^\cdot and H^+ ions, which are produced as intermediate products to the combustible gases that result from heating of the electrolyte. The use of flame-retardant organophosphates is the subject of a high volume of research effort and an in-depth analysis of this is outside the scope of this article. However,

Fig 9: Typical structures for organophosphates used as flame arrestors in lithium-ion electrolytes



there is a caution that this group of chemicals is also the basis of some nerve gases and their use has to be strictly controlled. A further negative consideration is that addition of these compounds, due to their higher viscosity and lower dielectric constant, also reduces the effectiveness of the electrolyte in transporting Li^+ ions.

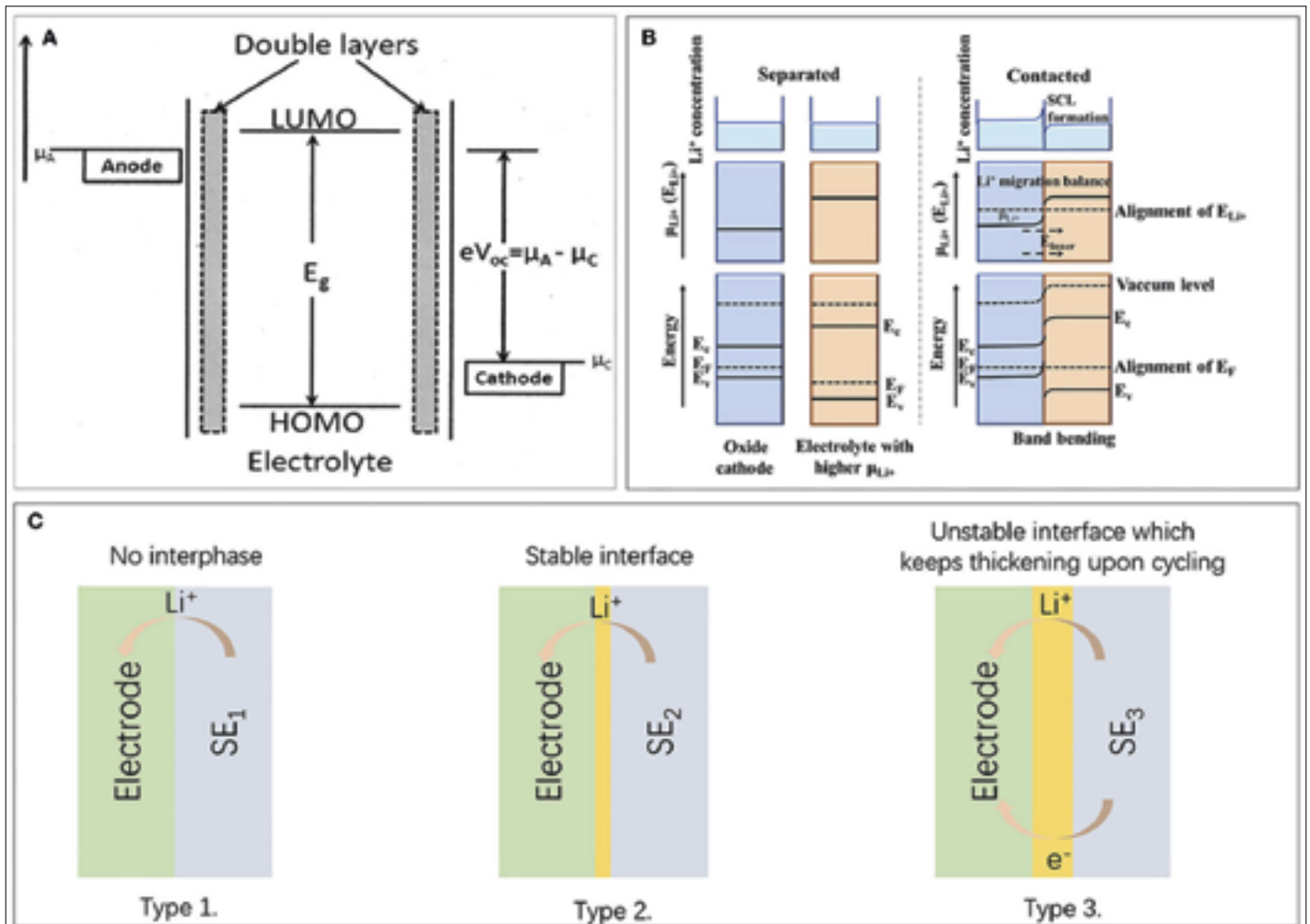
The methods described so far have the common objective of stopping a potential fire. Logically speaking, the better solution is to remove the source of the fire. The fuel in the combustion triangle is the highly

volatile electrolyte in the current LIB design. This is the common factor in all of the cathode chemistries currently on the market. The two key properties that make this material successful as an ion carrier are also responsible for its combustion characteristics. In an ideal world the electrolyte would have the ion transfer ability but with low viscosity and high electrical charge carrying ability. Two possible routes to achieve this would be an inorganic highly conductive solvent or a solid-state ion conducting polymer. Both of these routes have their

challenges but because of the potential rewards, both are being pursued.

Looking first at the solid-state electrolyte, this is still in a highly experimental stage although breakthroughs such as that made by Cornell University are making the news. The basic problem with a solid electrolyte is the electrode/electrolyte interface. Two solids butting together inherently are prone to a high resistance interface. Add to that the expansion and contraction of both electrodes during the lithiation and delithiation processes associated

Fig 10: Voltage operating window and interphase stability for solid lithium-ion electrolytes



with charge and discharge cycling, then the nature of the problem becomes evident. Key to good performance and long cycle life is the SEI formed between the electrode surfaces and the electrolyte. The chemical bond has to exist that allows ion and charge transfer at the interface. In addition, the electrolyte has to have a voltage window that allows transfer for the Li^+ ion between cathode and anode. This window is shown to be defined by its boundaries **Fig 10A**, which are the LUMO (lowest unoccupied molecular orbital and the HOMO (highest occupied molecular orbital). **Fig 10B** shows the electronic structures of the electrodes, electrolyte and Li ions represented by Fermi levels before and after contact of the electrodes and electrolyte.

In **Fig 10C**, three scenarios for formation of an interface layer are described. Type 1 is a stable interface with no chemical reactions that, whilst ideal, is almost impossible to achieve. Type 2, which undergoes controllable chemical side reactions including bonding, is electronically insulating whilst still allowing Li^+ migration. Type 3 shows the most commonly occurring interface where reactions are not controllable and continuous growth of the layer occurs with battery use. The practical aim of most current research is to achieve a type 2 layer with controllable properties. The commercialisation of a process that can achieve a viable type 2 layer is still some way off.

From the preceding

descriptions of remedies, it would appear that the prospect of a non-flammable liquid electrolyte does seem to be the most attractive, provided that the problems of viscosity and ionic conductance can be resolved. **One solution would be to have an inorganic solvent that could provide a high di-electric constant and low viscosity.** Research into this area is progressing and there is a company, Innolith, that seems to have gained ground in this area. At present they have a 2 MW/1MWh frequency regulation BESS installed at Snook Substation in Hagerstown Maryland USA. This has been in grid connected service since October 2017 and has a 98.52% performance rating.

The basic operating principle of the battery is similar to that of a conventional lithium-ion design with a metal oxide cathode and a carbon anode. The electrolyte is made from dissolving lithium tetrachloroaluminate in sulfur dioxide to form the low viscosity

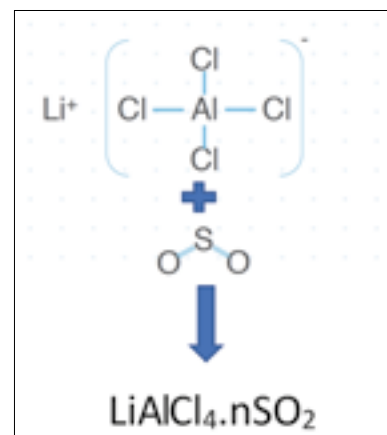


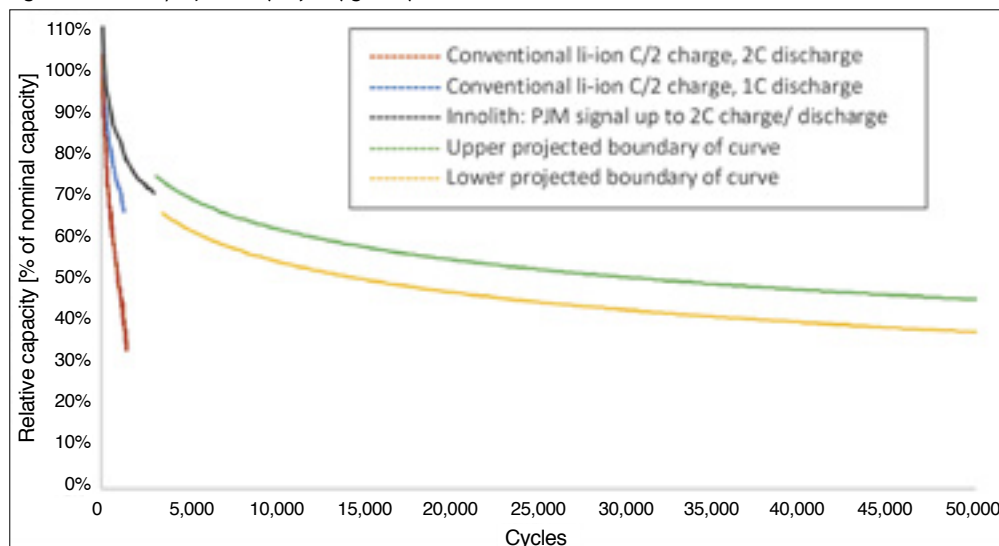
Fig 11: Innolith inorganic electrolyte

solvate $\text{LiAlCl}_4 \cdot n\text{SO}_2$ (**Fig 11**).

Unlike conventional LIB chemistry there is no SEI layer on the cathode. The anode SEI layer is an inorganic compound $\text{Li}_x\text{S}_y\text{O}_z$, which does not deteriorate or thicken over time. This is the main reason for its longevity and negligible IR increase with cycling.

Although reticent to disclose their cathode materials, Innolith have published information that show that in terms of cycle life, their technology outlasts conventional lithium-ion batteries by at least a factor of 10. In **Figs 12A and B** their

Fig 12a: real and projected life cycle figures for Innolith and conventional lithium-ion cells



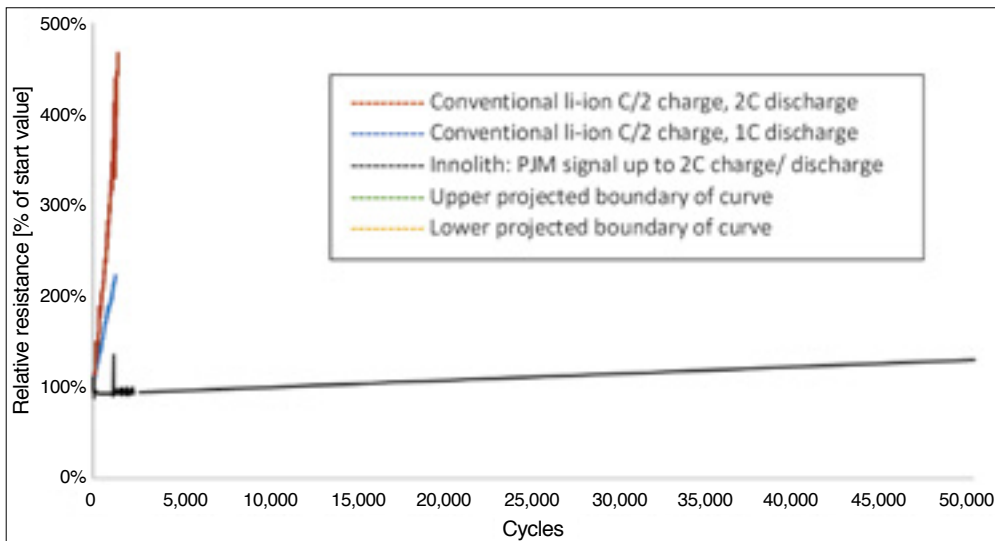


Fig 12b: Internal resistance changes for Innolith and conventional lithium-ion cells

new electrolyte battery is cycled in a 2C charge discharge regime projected over 5 years where it is still achieving more than 40% of capacity. According to these results the batteries do not stop working. They simply degrade slowly over time. So far there is no identified failure mechanism.

They also claim that with the right cathode they can tap energy from electrochemical reactions as well as the ion transfer energy of conventional LIBs. According to Innolith they can with their chemistry, support conversion reactions to provide a 1kWh/kg cell energy density. Although this sounds too good to be true, the prime objective here is to prevent lithium-ion fires in order to make the technology safe to use. No costs are yet available but according to the company, with the higher cycle life and consequent energy throughput, the value for money of their technology is an order of magnitude better than conventional chemistries.

With an existing 2 MW battery installation still fully functional after 2 years in service, there appears to be a basis for this claim.

Outlook for safer lithium-ion batteries

Despite the dangers and new concerns for lithium-ion technology, it remains the only feasible and commercial option for EV and hybrid vehicle applications. Increasing environmental pressure to reduce CO₂ emissions continues to be a driving force for road traffic electrification. Likewise, efficient use of grid scale electricity supply and growing use of renewable energy generation requires larger scale BESS installations with potential for catastrophic failures. With this pressure the need to have a safer battery technology that can meet the performance requirements is paramount. Looking at the currently available solutions of electrolyte additives and mechanical plus chemical

shutdown methods there are questions concerning their effectiveness. The flame-retardant additive route invariably has a negative impact on performance, whilst the shutdown mechanisms prevent the battery from operating. The electronic route using a BMS to control individual cells based on temperature or current/voltage imbalances is only effective if the cells are undamaged.

Clearly the best option is to remove the fuel that creates the fire. To this end the solid electrolyte and the inorganic solvent electrolyte are the preferred options. At this stage, the performance and manufacturing issues with the solid electrolyte approach mean that large scale working batteries are some way off. This leaves the inorganic electrolyte as perhaps the best option to pursue. Given the work done so far by Innolith and the field trials in progress, the smart money would be on this approach being the most likely to be commercially available in the next couple of years. Another benefit is that if the life projections are valid it should give the industry some breathing space to come up with the much-needed commercial recycling process. That is for another article, but for now, with an inorganic solvent electrolyte, we could be looking at a safer and better lithium-ion battery for our future EV and energy storage requirements. Welcome news for the industry and even more welcome news for our beleaguered ecosystem. +

ESS feels the heat

Investigators are scrambling for answers after a series of fires at energy storage systems in South Korea and a more recent incident in the US.

John Shepherd reports on the efforts to retain public confidence in ESS in testing times and expand its use.

More than 20 energy storage systems across South Korea went up in flames over the past year or so, prompting the government to ask business and domestic users not to use their devices as a temporary safety measure.

As *BESTmag* went to press, an explanation of sorts had emerged following an expert review. But scrutiny of ESS technologies is continuing after a grid-scale facility exploded in a separate incident in the US.

There is no immediate threat to the increasing adoption of ESS facilities in homes, businesses and on an industrial scale worldwide. Indeed, the backing of major global institutions such as the World Bank, for mass deployment of energy storage is a positive signal.

In May, the bank announced the launch of an international “technology-neutral” partnership to expand the use of ESS in developing countries.

But despite such support, regulators will need to be convinced that the industry has a grip on the situation— and regulators, ESS manufacturers and operators alike will need

Top right: Fire engulfs an energy storage system at a cement plant in South Korea. Courtesy: North Chungcheong Province Fire Service Headquarters
Bottom right: How local media reported the Arizona fire.

Main image: FM Global— one of the world’s largest commercial property insurers, has recently conducted large-scale fire tests on ESS for commercial applications and issued new installation guidance.



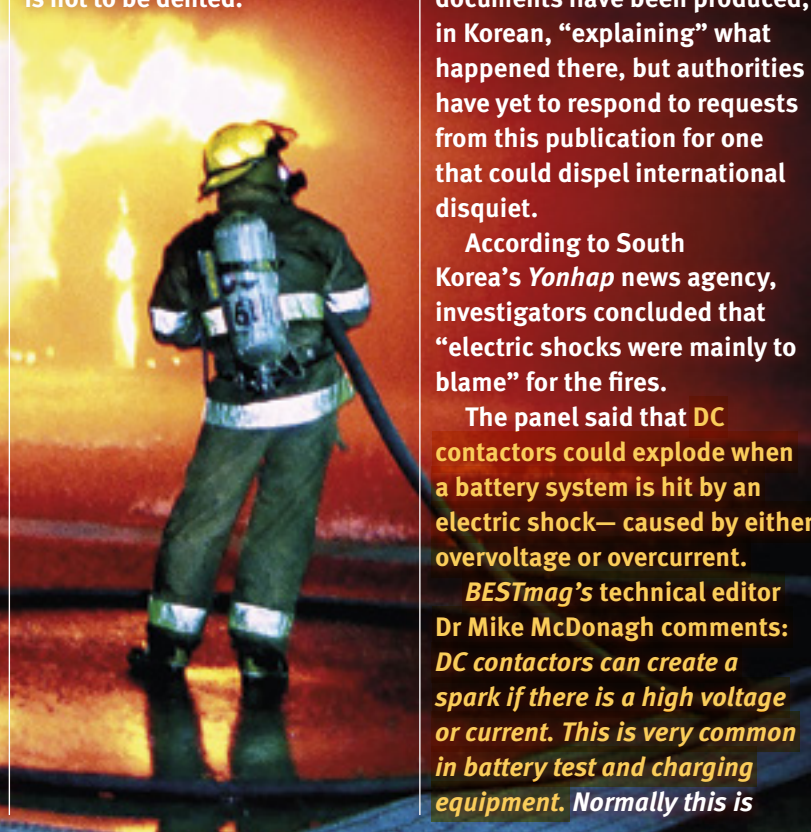
to ensure investigations into any incidents involving storage systems are open and transparent if public confidence is not to be dented.

To date, the South Korean government appears to have been less forthcoming about its domestic ESS difficulties. Yes, documents have been produced, in Korean, “explaining” what happened there, but authorities have yet to respond to requests from this publication for one that could dispel international disquiet.

According to South Korea’s *Yonhap* news agency, investigators concluded that “electric shocks were mainly to blame” for the fires.

The panel said that DC contactors could explode when a battery system is hit by an electric shock— caused by either overvoltage or overcurrent.

BESTmag’s technical editor Dr Mike McDonagh comments: **DC contactors can create a spark if there is a high voltage or current. This is very common in battery test and charging equipment. Normally this is**



58 **best**safety

prevented by opening and closing contactors when there is no current flowing and gradually increasing to the full value. IF this is the case then this is one very badly designed piece of kit.

As a result of the findings, the government said it would strengthen safety requirements of “major components” of ESS products, such as battery cells and power conditioning systems, although details have not been outlined to date.

ESS manufacturers have also been told they must install devices to combat the risk of electric shocks and to shut down operation of the ESS if overvoltage, overcurrent “or other abnormal symptoms are detected”, *Yonhap* said.

Perhaps more significantly, according to *Yonhap*, the panel did not apportion blame for the fires to domestic ESS producers. Two of the country’s leading ESS manufacturers, LG Chem and Samsung SDI, had yet to respond to *BESTmag*’s requests

for comment at the time of going to press.

According to the panel’s findings, 17 out of the 23 ESS products involved in the fires had been used to store electricity generated from solar and wind power facilities, while four others were used to store electricity at night for sale during peak demand during the day.

According to data from South Korea’s Ministry of Trade, Industry and Energy (MOTIE), a total of nearly 1,500 ESS systems are currently installed around the country representing a combined battery capacity of 4,773MWh. Of those units, a total of nearly 780 are reportedly used to store electricity generated from solar and wind power stations.

But concern over fires involving battery storage facilities is not confined to South Korea. In the US, an investigation was launched after an explosion at a lithium-ion grid-scale battery storage facility in the city of Surprise, Arizona, which is

operated by the Arizona Public Service (APS) utility.

APS said several firefighters and a police officer needed hospital treatment as a result of the “catastrophic failure” of the 2MW/2MWh system at its McMicken facility in April.

The McMicken facility was one of two such battery systems APS installed to test the technology’s performance in the desert temperatures of the area around Phoenix. The battery systems were supplied by AES—now part of the AES-Siemens Fluence group. The installations marked a return to grid-scale energy storage for APS after a 1.5MW ElectroVaya storage system at its Flagstaff facility caught fire in 2012.

As *BESTmag* went to press, the investigation was continuing and officials said it would take time to build a complete picture of the root cause of the accident.

However, investigators and APS have been keen to share as much information as they can.

The utility confirmed in June that investigators had begun safely discharging battery modules at McMicken, whose system comprises 27 racks of 14 modules each—with a total of 378 modules being removed.

In an interim update, APS said: “The team has developed precautions and contingencies should any modules behave erratically during the discharge process or cannot be discharged. The modules will be stored on site until the next phase of the work, which will include further inspection of any components that may help determine the root cause of the incident.”



Installation of the Surprise facility in 2016

APS said a “safe and secure area” had been established around the system in which to conduct inspections, disassembly and the investigative activities. “This included installing a climate-controlled tent around the immediate area of the battery and a temporary perimeter fence for safety and security reasons.”

The utility and the investigation team pledged to “share what they can of the ultimate findings, especially to the extent they are helpful to the industry and response agencies”.

Ironically, just days before the Arizona explosion manufacturers and users of battery storage systems backed an industry-led initiative in the US to “prioritise safety” in the production and operation of equipment.

The move came amidst ongoing concerns about the risk of fires from lithium cells and batteries.

The US Energy Storage Association (ESA) said 30 companies had already signed up to the new Energy Storage Industry Corporate Responsibility Initiative on launch at the ESA’s annual conference in Arizona.

Signatories include GE Energy Storage, Panasonic, LG Chem Power, EsVolta, Fluence, NEC, Highview Power Storage, Enel Green Power and Duke Energy.

The signatories and the ESA also launched a task force “to develop best practices for potential operational hazard prevention, end-of-life recycling and responsible supply-chain practices”.

ESA’s CEO Kelly Speakes-Backman said: “The US energy storage market nearly doubled in

Right: ACC commissioner Boyd Dunn raised home energy storage system concerns

2018 and is expected to double again in 2019, so this marks an ideal time for the industry to demonstrate their commitment to corporate responsibility.”

The energy storage community will need to focus all of its attention on the issue if it is to head off problems that could lie ahead as the result of greater regulatory scrutiny.

Regulators in the US have already warned that a major shake-up of safety standards might be needed for home battery storage systems in the wake of the Arizona accident.

Members of the Arizona Corporation Commission (ACC), which has oversight of APS, have asked that a member of its staff be involved in the McMicken investigation— in case lessons learned highlight a need to review energy storage system safety standards for homes, businesses, and for revised guidelines for firefighters and first responders called to tackle future incidents.

ACC commissioner Boyd Dunn said at a hearing with APS bosses: “Batteries are our future so your investigation is going to be critical.”

“I do have a concern that we take this opportunity to see if we need to address other issues,” Dunn said. ***“Do we need to look at building codes for batteries in homes and, are all building codes up to the level we feel are going to provide the safety we need?”***

Dunn said the “unique” nature of lithium-ion batteries and their risk of catching fire might mean “reaching out to the fire department to look at their procedures and see what can be done differently in future”.



APS president Jeff Guldner told commissioners: “Lithium-ion batteries are not new. They come in different scales for residential storage and (ours) are large installations, but we certainly share your concern that, as this technology becomes more important in the operation of the electric grid, we understand how to use it safely. That will be a major focus of the investigation.”

But Guldner made clear the importance of energy storage to the country and his utility’s commitment to battery technology. He told commissioners that some 800MW of batteries are connected to the US electric grid, “so it’s very important that we conduct this investigation... because this is where the industry is going”.

According to a recent report from the US Energy Storage Association and Wood Mackenzie Power & Renewables, the first quarter of 2019 was the largest ever single quarter for US energy storage deployments, “with an ever-growing pipeline of projects in development”. +