

Applications of Microcapsule Technology in Lithium-Ion Batteries: A Review

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ABSTRACT

With the rise in popularity of electric vehicles and portable electronic devices, having a reliable, lightweight and long-lasting battery is crucial. This has led to the mass commercialisation of lithium-ion batteries (LIBs) because they offer several advantages over other battery technologies. Over the years, one of the concerns was with the ease the batteries can burn or explode when subjected to certain extreme conditions. In order to build trust in these products and to expand the technology into more diverse applications, safety aspects of the batteries has become a key area of research. One aspect of improving the safety by reducing the flammability of the battery is the addition of certain chemicals that stop or suppress the thermal runaway effect. However, this in-turn reduces the battery's capacity and life-cycle performance. Researchers have used the idea of encapsulating these chemicals thereby physically separating them within the (lithium-ion battery) LIB electrolyte system with a minimum effect on performance. This paper reviews some of the novelty that is currently being developed to encapsulate certain active chemicals to aid not only the LIB thermal safety but also to enhance their performance.

KEYWORDS

Lithium-ion battery, thermal runaway, microcapsules, capacity fading

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INTRODUCTION

The increasing concern about greenhouse emissions has prompted the adoption of various technologies to generate sustainable clean energy. These technologies encompass solar, wind, hydro, and tidal energy. However, a limitation of these energy sources is their inability to provide a consistent energy stream, which has led to the exploration of battery solutions for storing excess energy generated during peak production periods. As a result, there has been a significant surge in adopting not only pure electrical energy storage systems to supplement the grid infrastructure but also to transform the transportation sector to low carbon emission alternatives primarily through the adoption of battery electric vehicles (BEV). A LIB is a rechargeable battery type widely used in various applications, including consumer electronics, electric vehicles, and energy storage systems. LIBs typically consist of positive and negative electrodes made of materials capable of intercalating lithium ions during charge and discharge cycles, an electrolyte that facilitates the movement of lithium ions between the electrodes, and a separator that prevents electrical short circuits. During charging, lithium ions are extracted from the positive electrode and inserted into the negative electrode, and during discharging, the reverse process occurs. LIBs are favoured for their high energy density, long cycle life, and relatively low self-discharge rate compared to other rechargeable battery types. With the emergence of LIBs as one of the primary energy storage systems for the portable electronic and BEVs there has been an increase in research focus on developing safer and long-lasting batteries that do not suffer from excessive capacity decay and thermal safety events. This can be seen graphically in figure 1 where the focused research that pertains specifically to safety aspects of LIBs has significantly started to increase from 2015 onwards as the uptake of larger battery packs in various applications has globally also increased. Of the approximately 13 000 journal articles published in 2022 in the field of LIBs, about 2 000 (15%) related to the specific topic of safety within the battery usage. Figure 1 has data extracted from SCOPUS and WEB OF SCIENCE using search strings *Lithium-ion batteries OR LIB's OR LIB*.

By the addition of preventative additives such as flame retardants directly into the LIB chemistry was shown to subsequently hinder its electrochemical performance. Some recent studies showed that by adopting the encapsulation of such active compounds and including them into the electrolyte matrix, its effectiveness in suppressing the thermal event was shown and to some degree still maintain the electrochemical performance of the battery in application.¹⁻³

The concept of encapsulation is found throughout nature and used extensively in the chemical and pharmaceutical industry. Typically, an egg can be considered as a macroscale version of a capsule, where a calcium-based shell would protect the yolk and germinal disk. Microencapsulation is often described as the process of enclosing a substance in a fabricated shell or integrated chemical structure.^{1,4} The encapsulated material is referred to as the core material and can be in the form of gas, liquid or solid. The capsule type depends on the phase that is being encapsulated and the method needed for encapsulation. It is also important to consider the reactivity of the shell material towards the material being encapsulated during the encapsulation process. Generally, the microcapsules are inert and will not interfere with the normal chemical processes of its surrounding until it reaches the targeted area or condition. Microcapsules usually respond to an

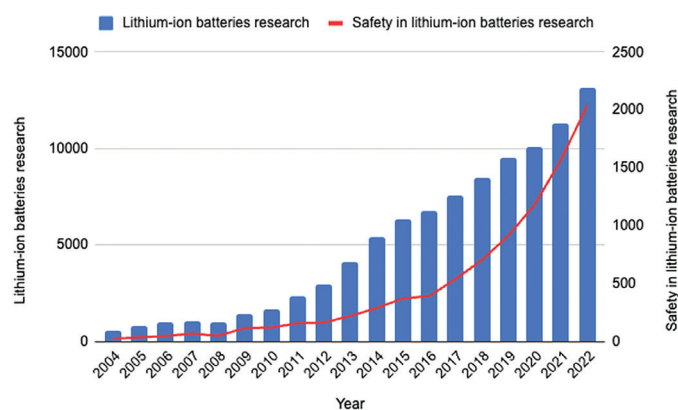


Figure 1: The number of articles published per year on the research focused of LIBs and related safety aspects over the past 23 years.

The data shown in the graph was extracted from SCOPUS and WEB OF SCIENCE using search strings *Lithium ion batteries OR LIB's OR LIB*

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external stimulus to release the core material. Microencapsulation is used in a wide field of applications such as in active drug delivery in pharmaceuticals, petrochemistry, food, cosmetics, civil engineering and the battery industry.⁴

In the pharmaceutical industry, microencapsulation is used to increase the stability, bioavailability and the controlled release of actives in a large variety of medical applications. This allows the shelf life, efficacy, and safety of active pharmaceutical ingredients (APIs) to be improved by encapsulating them in microcapsules.^{4,5} Additionally, targeted applications of the API can be achieved to certain body tissues or organs using microencapsulation that rely on targeted drug delivery systems for the slow release of certain formulations by either oral or injectable medications. Most of the capsules fabricated for pharmaceuticals, petrochemistry, food, cosmetics, civil engineering and the battery industry are meant to either increase performance⁶, act as self-repair mechanisms^{7,8} or to aid in the controlled release of encapsulant at a specific target or environment.^{9–13} Figure 2 gives a typical representation of microcapsules, illustrating both single-core and multi-core configurations. These microcapsules are applicable in the scenarios mentioned earlier.

MICROCAPSULES AND TYPES OF ENCAPSULATION

Coacervate encapsulation

This is a type of encapsulation that involves separation of two phases, namely the coacervate phase (dense phase that forms capsules) and a continuous phase that forms the surrounding boundary. Coacervate microcapsules can either be simple or complex coacervates.¹⁴ Complex coacervation is a type of microencapsulation that involves neutralization of two oppositely charged polyelectrolytes.¹⁴ This type of encapsulation is normally used in the food and drug industry in order to prevent oxidation of bioactive molecules where different types of cores can be formed using this type of encapsulation. Glomm et al. (2023)¹⁵ reported on the encapsulation of salmon oil to prevent oxidation. This was achieved using bovine serum albumin and acacia gums to form a coacervate.

Simple coacervation allows for the formation of hydrophobic shells on top of hydrophilic substances with a low interfacial energy and has been reported by Wang et al. (2023).¹⁵ They showed the formation of a zein coacervate, a type of simple coacervate to adhere to cherry tomatoes in order to lengthen their shelf life. During the process of encapsulation, the hydrophilic regions interact with the water while the hydrophobic regions form coacervates on the surface of the tomatoes.¹⁵

Interfacial polymerization

This is a type of encapsulation which involves polymerization of monomers around the core material and requires an interface of two immiscible phases. There are 4 main types of polymeric shells used for interfacial polymerization. These include polyurea, polyurethane, polyester and polyamide where the polymer selected depends on the function of the microcapsule needed in application and the type of material being encapsulated. Yan et al. (2023)¹⁶ demonstrated the

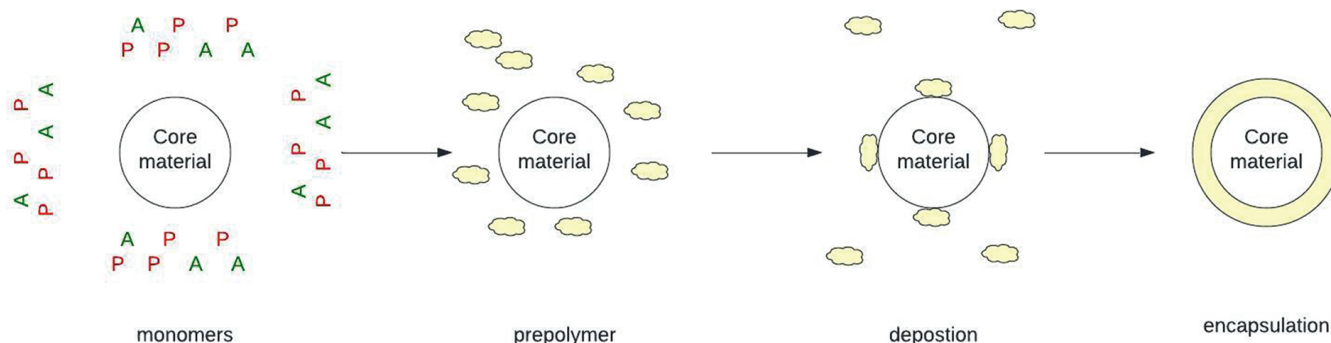


Figure 3: Interfacial polymerization process

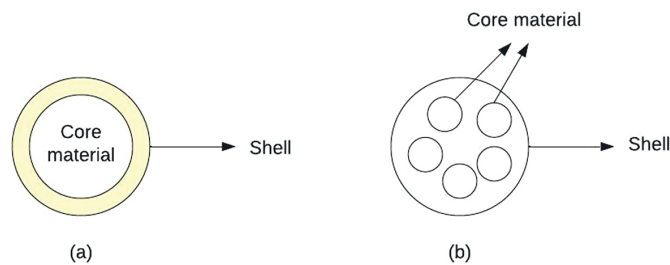


Figure 2: Common morphology of microcapsules: (a) single core microcapsule (b) multi core microcapsule.¹⁴

formation of a polyurea shell by interfacial polymerization in order to encapsulate n-eicosane which was used for high thermal energy storage applications. The polyurea shell showed good stability during electrochemical cycling with no reported morphological changes. Zhao et al. (2023)¹⁷ discussed the use of both interfacial polymerization and free radical copolymerization to form double shell lignin microcapsules which are a type of polyurethane shell microcapsules. The outer layer lignin-polyurethane shell was formed by biomass lignin as a chain extender and the inner layer was formed by polymerization of styrene and N-isopropylacrylamide. Figure 3 depicts the use of two reactive monomers to form a polymer shell around the core material at an interface between two immiscible liquids.

Sol-Gel microencapsulation

This is a type of encapsulation that involves the formation of an emulsion of immiscible phases. In sol-gel encapsulation, a sol (colloidal dispersion of solid particles in a liquid) is transformed into a gel network which creates a solid shell. Park and Jo (2023)¹⁸ demonstrated the encapsulation of molten salt using a TiO₂ shell in a surfactant free environment. The surfactant free microcapsules that formed were used in an energy storage application that showed better thermal reliability because the surfactants usually have a lower decomposition temperature than the shell and core material which will lead to early failure in the structural integrity of the capsule.¹⁸ Silica based sol-gel microencapsulation have become a popular choice to make sol-gel microcapsules. Zheng et al. (2023)¹⁹ fabricated phase change materials using paraffin as the core and SiO₂ as the shell. Sodium silicate was used as a precursor and their results showed that the sol-silica system stability was dependent on pH and slight shifts in pH by about 0.5 can affect the final shell formation.¹⁹

Spray-drying

Spray drying is a type of microencapsulation process that involves the use of a liquid solution that is atomized into droplets and then dried either by hot air or freeze drying containing the substance of interest. This type of technique allows the formation of soft- or hard-shell microcapsules depending on the type of shell material used. Two primary forms of atomization are employed in these processes and are referred to as monoaxial spray-drying, which takes place when a single

liquid is present in a two-fluid nozzle, or coaxial spray-drying, where two concentric liquid solutions are utilized within a three-fluid nozzle. This type of encapsulation process is commonly used for biochemical active materials. Berraquero-Garcia et al (2023)²⁰ reported on the encapsulation of polysaccharides, proteins and peptides using monoaxial spray-drying.

Electro-spraying

This type of encapsulation requires the application of an electric field to dry the formed nano or microcapsules. During formation, the feed solution passes an electrostatically charged nozzle which then causes the meniscus of the droplet to be polarized to form a Taylor cone. When the feed solution passes through the nozzle, the voltage increases thereby prompting an increase in surface tension of the solution which in-turn breaks the droplet that is then deposited onto a collector where it can evaporate. Bakola et al. (2019)²¹ reported on the encapsulation of dipyridamole, an antithrombotic drug, by means of electrospray encapsulation using a poly (L-lactic acid) capsule. The study reported on the successful encapsulation of dipyridamole, but the capsules that formed would be double in size relative to the average size of poly (L-lactic acid) blanks²². Shlyaphikov et al. (2016)²² explored the option of electro spraying DNA fragments. Their study showed that DNA fragments shorter than 5 kilo-base pairs were not damaged during the electro-spraying process. However, those longer than 5 kilo-base pairs were damaged upon formation of the Taylor cone.²²

Flow focused encapsulation

Flow encapsulation has become a more popular synthesis technique due to its ability to control the capsule sizes with a relatively narrow size distribution. The size of the capsules can be controlled using flow rates and related weight percentages of the mobile and dispersed phases.^{10,23–27} The most traditional method used for encapsulation is the emulsion process and depends predominately on the agitation speeds for size control. Xu et al. (2020)²⁸ showed that higher rotation speeds yielded a narrower size distribution. With a lower effective amount of the core material in each capsule. This in-turn would affect the amount required in the final release process in application. Size uniformity is also important to ensure higher rupture efficiency with an even distribution of the core materials during the rupture process.⁹

Multiple emulsions flow chemistry refers to the use of microfluidic systems to generate multiple emulsions, where two immiscible liquids are dispersed within another immiscible liquid to form droplets of one liquid within the droplets of another. When fabricating a single-phase emulsion, the mobile and dispersed phase must be immiscible. For double emulsions, the inner and outer drops must remain immiscible, whereas for multiphase emulsions the compartments next to each other must remain immiscible. This is summarized in Figure 4 where emulsions are produced using a water phase (W) and an oil phase (O). The multiphase liquid micro-emulsions process is used in the pharmaceutical and food industry as delivery shuttles of the active ingredients for a variety of applications.^{11,12,29}

Watanabe et al. (2021)¹³ showed the use of a biopolymer composed of hexadecane and cellulose acetate to fabricate a microencapsulated paraffin-based material. Their studies revealed that when the weight % of the core material was increased, the shell thickness would decrease, and the corresponding shell diameter would then increase because of an increased volume. The work also revealed the negative effects of using a nucleating agent on the shell porosity, instead of using crosslinking agents to decrease the shell's porosity.¹³ Souza et al. (2018)⁸ showed that by using a double emulsion technique, it would improve the shell properties such as the effective payload, the permeability and its rigidity in efforts to encapsulate an aqueous core. This was done by making use of a flow focused device for a monodisperse w/o/w emulsion.⁸ When fabricating microcapsules with microfluidic devices, the correct surfactants should be used to

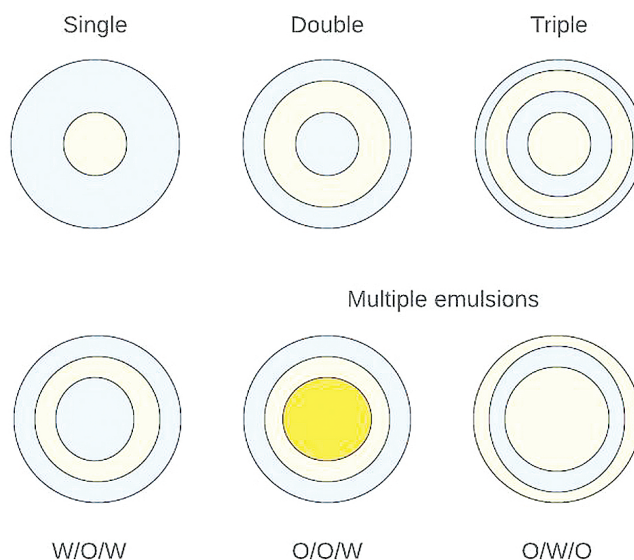


Figure 4: Types of emulsions and emulsions phases.^{11,13}

prevent channel blockages. Surfactants can also affect the permeability of the shells due to hydrophile-lipophile in-balances that are present in the selected surfactant.^{30,31}

LIB'S AND MICROCAPSULES

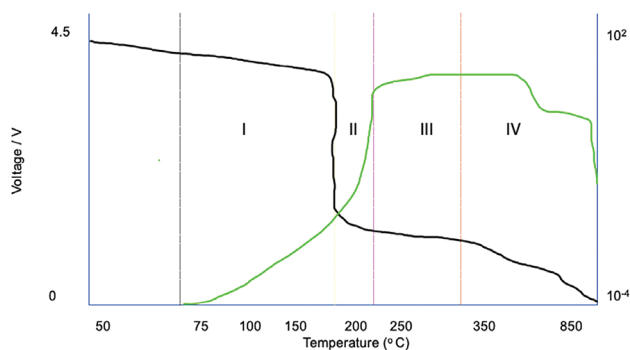
Safety in LIB's and microcapsules

Thermal runaway

Thermal runaway in LIB's refers to a condition where the internal temperature of the battery rapidly increases due to a failure in its thermal management system, leading to further temperature increases and eventually resulting in a thermal explosion or fire.³² This phenomenon can happen in different ways that are either triggered by an internal (within the cell) event or externally due to a mechanical, thermal, or an electrical trigger^{33–35} that causes the battery to reach the self-propagating thermal runaway scenario. Feng et al. (2018)³⁵ described the penetration of the cell by a solid object as a mechanical issue where the separator is damaged that results in the anode and cathode material to touch thereby causing an internal short circuit. This can lead to a rapid increase in temperature to a point where the thermal event becomes self-propagating. During thermal events like external overheating (when the environment or operational temperatures are exceeded) there is a greater chance of the separator to shrink that leads to an exothermic reaction between cathode and anode material within a volatile electrolyte that will result in a thermal event. An internal short circuit that occurs near the electrode edges of a cell can release small amounts of energy that is sufficient to achieve temperatures between 130–160°C. These reactions would then lead to further increases in cell temperature and the degradation of the active material and combustion of the electrolyte.^{35–37} According to Ren et al (2021)^{38,39} the primary source of heat generation in LIB's thermal events occurs between the anode and cathode reactions, rather than between the anode or cathode with the electrolyte.^{38,39} External electrical triggers that can lead to a thermal runaway event can include overcharging, over-discharging or an external short circuit. Externally, the control of the charging and discharging of the battery module or pack are usually done by the battery management system (BMS) that also monitors the temperature status of the battery. Advanced systems allow for the thermal monitoring at the cell level, even within a large battery pack.³⁶ Other internal triggers could come from contamination such as water in the electrolyte or foreign solid particles. Water would contribute to the decomposition of the electrolyte and the unwanted particles, depending on their composition, can lead to the damaging of the separator that results in an internal short-circuit.³⁶ Table 1

Table 1: Events that can lead to a thermal runaway event in a LIB's.

| Event | Description | Temperature range (°C) | Reference |
|-------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|-----------|
| Increased rate of reaction | Refers to how quickly the lithium ions can move between the anode and the cathode during charge and discharge cycles. | >80 | 35 |
| SEI decomposition | SEI refers to a thin layer that spontaneously form on the electrode surface during initial stages of charging and discharging which acts as a barrier between the electrode and electrolyte thereby providing battery stability. The decomposition of a thin film that forms on the surface of the anode when the battery is first charged. | 60-85 | 35 |
| Anode/cathode-electrolyte reactions | At high temperatures, the electrolyte may decompose, leading to the formation of reactive species such as free radicals, which can react with anode or cathode material | 130-160 | 35 |
| Separator shrinkage | When the temperature within the cell rises rapidly, the separator material breaks down and can cause it to shrink | 110-150 | 35 |
| Cathode decomposition | At high temperatures, the cathode material can decompose and release oxygen, which can react with the flammable electrolyte and cause an exothermic reaction. | >130 | 40 |
| Heat release | Occurs when the heat generated from exothermic reactions cannot be effectively dissipated, leading to a further increase in temperature. This can result in a self-accelerating reaction, causing the battery to reach temperatures well above its normal operating range. | 120-230 | 40 |

**Figure 5:** Stages of thermal runaway in batteries adapted from Ren et al (2021).³⁸

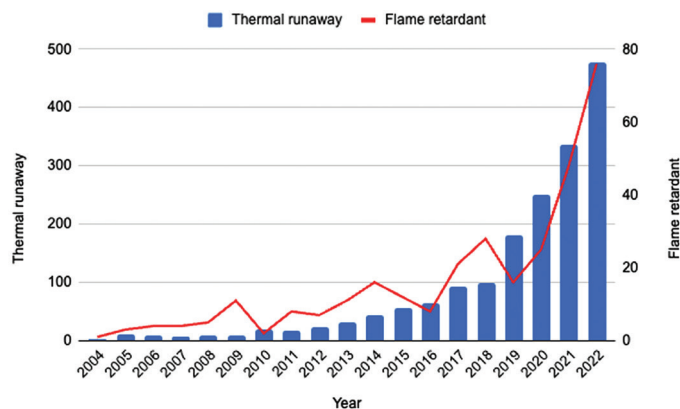
summarises the thermal events that can occur as a cell or battery heats up and approaches the thermal runaway event where it becomes self-propagating.

Ren et al (2021)³⁸ showed how the voltage of the cell would be influenced by the increase in temperature of the cell above 150°C (Figure 5). The cell voltage drops drastically as events like cathode decay, separator shrinkage and short circuiting starts to occur.

Self-heating usually starts at temperatures around 80°C and is due to the cathode and the SEI layer that starts to decompose (first part of stage I in Figure 5). At this point there is no inherent effect on the voltage of the cell. From 80°C to 170°C (second part of stage I in Figure 5) there is a gradual decrease in the cell voltage due to the increased occurrence of cathode/anode-electrolyte reactions and the melting of the separator material. Above 170°C (Stage II in Figure 5), the thermal event becomes self-propagating with a significant increase in the temperature rate. Any preventative heat or flame retardancy be it internally or externally should become effective below this temperature. Stage III and IV would be considered as being completely self-propagating that often leads to enough internal pressure that can result in an explosion.

Over the last 18 years, research papers that were published specifically on the topic of thermal runaway in LIB's is summarized in Figure 6. The data extracted from SCOPUS and WEB OF SCIENCE using search strings *Lithium ion batteries OR LIB's OR LIB AND thermal runaway/ flame retardants* shows that over the last 5 years, there was a significant increase in publications that considered the use of flame retardants. In 2022 about 16% of the journal articles published were specific on the addition of flame retardants to reduce the effect of thermal runaway in LIB's.

Flame retardants are used to mitigate thermal runaway risks and have emerged as important additives in lithium-ion batteries. They act by suppressing combustion using nitrogen or halogen reaction

**Figure 6:** Research done on thermal runaway and the use of flame retardants to mitigate its effect.

The data shown in the graph was extracted from SCOPUS and WEB OF SCIENCE using search strings *Lithium ion batteries OR LIB's OR LIB AND thermal runaway/ flame retardants*

pathways, formation of physical barriers that prevent heat spreading, char protective layer formation.

Different types of flame retardants have been examined in terms of their compatibility with the cell's electrode and electrolyte. These can be classified based on their main chemical constituents, that include phosphorous-based compounds, fluorine-doped compounds, amines, and diols.

Phosphorous-based flame retardants

Most known phosphorous based flame retardants are added directly to the electrolyte or mixed with the cathode material. Wang et al (2019)⁴¹ showed that the electrochemical performance of such cells is negatively influenced when higher weight percentages of up to 20% of retardant are added. The higher amounts of retardants improve the self-extinguishing times (SET) that are typically measured in seconds per gram (sg^{-1}) of flame retardant added or just in seconds (s) only. The main reason for the reduction in the electrochemical performance is their high affinity towards lithium-ions which are produced at the anode during the SEI layer formation. This then obstructs the progression of the SEI layer formation and reduces the amount of lithium ions that can pass through the layer during the charge and discharge process.⁴¹

Wang et al (2019)⁴¹ explored the option of using triethyl phosphate and triethyl phosphite as flame retardants. The results showed when higher weight percentages of triethyl phosphate up to 20wt% do not have any significant effect on the cell's performance when compared

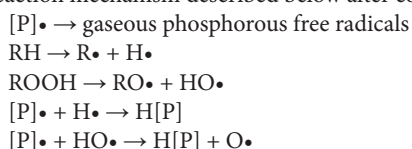
to similar amounts of triethyl phosphite. It was shown that triethyl phosphate tends to stabilize the electrolyte and retains about 99% of the capacity after 100 cycles. However, the use of triethyl phosphite decreases the cell performance with time, this is because of the oxidation decomposition of trivalent phosphorus contained in triethyl phosphite during cycling.⁴¹

Dimethyl methyl phosphate (DMMP) is another phosphate-based retardant that has been studied under different parameters such as amount of DMMP used and its effect on conductivity and viscosity of electrolytes, it was found that an increase in the amount of DMMP used reduced ionic conductivity and increased viscosity of the electrolyte. Xiang et al (2007)⁴² used the material in a cell with LiCoO₂ as the cathode material and with LiPF₆/EC:DEC as the electrolyte. The results showed that there was an improvement of the SET from 140 sg⁻¹ (base electrolyte) to 0 sg⁻¹ (with 50% DMMP doped). This however severely affected electrochemical performance but addition of a small percentage 5% (v/v) of vinylene ethylene carbonate boosted the cell performance by improving the capacity and cycle life.⁴² When a flame retardant was used in a cell that used LiNi_{0.8}Co_{0.2}O₂ as the cathode, cells with 15 wt% and 20 wt% DMMP showed 1.8 s and 0.8 s SET times respectively. Their results showed that with the addition of 20wt% DMMP to the electrolyte had a comparatively similar cycling performance to cells with the base electrolyte after 16 cycles. According to Jiang et al that showed that by adding 10, 20 and 30 wt% of DMMP to the electrolyte had better capacity retention when compared to base electrolyte.

Triethoxyphosphazene-N-phosphoryldiethylester (PNP) was another phosphate-based compound that was investigated as a flame-retardant additive with LiMn₂O₄ as the cathode material in Li-ion cells. The research showed that up to 10 wt% of PNP would reduce the SET times relative to the base electrolyte while keeping the cycling performance close to the base electrolyte. Further increase of PNP inside the lithium cell affected the cell performance but improved SET times.

Jiang et al (2022)¹ reported the use of cresyl diphenyl phosphate (CDP) and triphenyl phosphate (TPP) as flame retardants in cells that significantly reduced the cell performance in terms of its capacity. The addition of up to 20 wt% of each to the cell electrolyte would reduce the capacity retention up to 46% and 54% respectively and would not be ideal for use in commercial products. The authors showed that the TPP addition would cause poor cell performance because of the continuous destruction of the cathode / electrolyte interface. The advantage of wanting to use TPP or CDP is because they are low cost effective flame-retardants. Different approaches for the use of TPP were investigated by Ye et al (2020)² that fabricated a polyimide (PI)-TPP-Cu current collector with flame retardancy capabilities. Their results showed that the flame retardancy was dependent on the current collector's thickness, with the 9µm thick collector outperforming the thinner counterparts. 20 wt% of TPP embedded on a polyimide separator had a SET of between 25 - 30 sg⁻¹ when compared to the SET time of 90 sg⁻¹ that was reported by Jiang et al (2022)¹ when TPP was not embedded in anything.

At high temperatures, the electrolyte can generate a flammable vapor, such as a gaseous carbonate solvent (RH), which can decompose in a flame and produce H• radicals. These radicals react with the oxygen from the cathode to create HO• radicals. The HO• radicals can be regenerated and accumulate by reacting with hydrogen (likely from the decomposition of the electrolyte and trace water), resulting in a sequence of free radical reactions that support combustion. In general, phosphorous based flame retardants can be described to follow the reaction mechanism described below after combustion of alkyl esters:



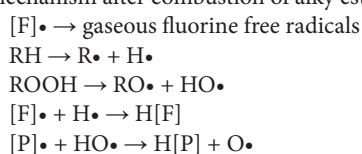
Fluorine-based retardants

Fluorinated electrolytes function with antioxidants properties which are essential for reducing the shuttle system. A shuttle reaction refers to a process in which an intermediate molecule or ion are shuttled between two distinct locations or environments, usually within a larger chemical system. This intermediate can often act as a carrier of energy or charge, allowing it to transfer from one location to another which can contribute to thermal runaways.⁴³ Tris(2,2,2-trifluoroethyl) phosphate (TFP), is a fluorine and phosphate -based flame retardant and its use in LIB was reported by Gu et al (2021), their work also pointed out that mixing it with γ -butyrolactone (GBL) formed a non-flammable electrolyte. Its performance was studied in a graphite/LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cell that made use of a LB 301 electrolyte (LiPF₆ DMC:EC (1:1)) and showed a 90.8% capacity retention at room temperature and pressure (IC).⁴³

Ethoxy-(pentafluoro)-cyclotriphosphazene (PFN) was used as a performance enhancer and to improve the safety in lithium-ion batteries. Li et al (2018)⁴⁴ tested its performance in LIBs made with LiNi_{0.5}Mn_{1.5}O₄ cathode material. The addition of more PFN promoted the electrolyte to degrade or oxidise to a denser material like Li₃PO₄ and to form a film on the cathode layer which aided in its cycling stability. The study showed that cells with 5 wt % of PFN in the electrolyte would result in the cell to have a higher specific capacity and a better coulombic efficiency. Their study also showed that the addition of 5 wt% PFN resulted in a SET time of 3s at the same time keeping the conductivity as high as 11.5 mS.cm⁻¹. The conductivity was similar to the cells with the baseline electrolyte which has a conductivity around 11.8 mS.cm⁻¹ that would report a SET time value 5s.⁴⁴

Oh, et al (2022)⁴⁵ investigated the use of 4,4'-(propane-2,2-diyl) bis(4,1-phenylene) disulfo-fluoridate (P2PFS) as a flame retardant in cells made with LiNi_{0.9}Co_{0.05}Mn_{0.05}O₂ cathode material. Their results showed that the SET times for a P2PFS with a 10wt% was 0.2s, this SET is comparatively low because the effect of the fluoro-sulfate groups in the additive would significantly suppress the flammability of the electrolyte material. The additive also improved the capacity cycling performance of the cell when compared to the cells made with the base electrolyte. They showed that the capacity retention was 94% after 70 cycles.

Fluorine based flame retardants follow the following reaction mechanism after combustion of alkyl esters:



Amine-based retardants.

Benzylamine (BA), dibenzyl amine (DBA), and trihexylamine (THA) have been studied in their use as flame retardants in lithium-ion batteries.⁴⁶ They were used in electrolytes that contained 1M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC), with a EC to EMC mass ratio of 1:1. Benzylamine and dibenzyl amine were found to be miscible with the electrolyte however, in turn reduced the ionic conductivity of the electrolyte and thereby increased the internal cell resistance. THA was found to be immiscible with the electrolyte mixture and blocked the ionic transport within the cell by blocking the movement of ions at the cathode due to the low solvation properties. The amines can react with ethyl carbonate to form derivatives of benzyl carbamate which then further reacts with ethyl carbonate in a LiPF₆ catalysed polymerization reaction that can be summarized in the following reaction mechanism (Figure 7).⁴⁶

Xia et al (2012)⁴⁷ looked at the potential of in-situ polymerization by studying the reaction of 1'1'-(methyle-di-4,1-phenylene) bismaleimide (BMI) in lithium-ion battery electrolyte composed of 1M LiPF₆ in EC/DMC/EMC at 1:1:1 by vol. Their work revealed that the chemical

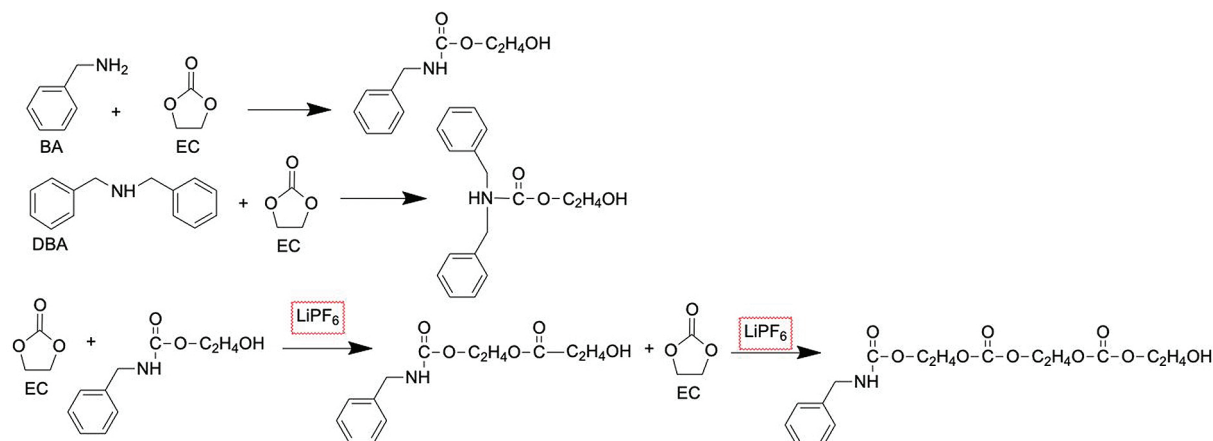


Figure 7: Reactions of BA and DBA with EC and LiPF₆ catalysed polymerization reaction.⁴⁶

reacts with the double bonds in the maleimide rings to form a homopolymer that was shown at temperatures above 116°C to solidify instantly with aid of a thermal initiator 2,2'-azobis(isobutyronitrile) as shown in Figure 8. The test cells studied showed little differences in their capacity cycling performance when compared to the cells made with the base electrolyte only.

1,2-ethanediamine and 1,3 propanediamine as additives to the electrolyte were also found to have the ability to react with the ethyl carbonate thereby decreasing its dielectric constant that results in a more compact and homogeneous electrode-electrolyte interface, which in turn can improve the distribution and effectiveness of flame retardant additives.⁴⁸ The reaction rate between either of the additives and ethyl carbonate increased with an increase in cell temperature that promoted the increase in the viscosity of the electrolyte until a final solid product was formed. This can be seen in the following reaction mechanism where the product formed would carbamide (Figure 9).

Diol-based retardants

1,2-ethanediol, 1,3-propanediol and 1,5-pentanediol can act in the same manner as 1,2-ethanediamine as an inhibitor within a cell. It was found that when added directly to the electrolyte mixture they instantly increased the viscosity of the electrolyte mixture thereby reducing the ionic conductivity. At higher temperatures the viscosity increases significantly thereby reducing the effect of a short circuit failure that effectively reduces the amount of heat emitted.⁴⁸ Selvas et al (2014)⁴⁹ that diols can react with both dimethyl carbonate and diethyl carbonate in the presence of phosphonium salts to form cyclic carbonates and linear bicarbonate products as shown in Figure 10. Unsymmetrical dialkyl carbonates are gels and these gels prevent ease of movement of ions involved in the shuttle reactions that lead to thermal runaway.

MICROCAPSULES IN LIB'S

Microcapsules have found their applications in LIB's primarily in their use to encapsulate agents to aid in the "self-healing" of either the anode or cathode during capacity cycling. This was done in order to reduce the effect of capacity decay over extended periods of cycling. In a simplistic way, the "self-healing" process can be seen as a potential solution to mitigate the degradation and failure of LIB's caused by mechanical and chemical stresses during charge/discharge cycles.⁵⁰ This would also reduce the possibility for a thermal event to occur due to cell material failure.⁵⁰ Other applications include the encapsulation of flame retardants which are released during the onset of the thermal runaway events and to act as performance additives and conditioning agents to improve or maintain capacity in a LIB.^{51–54} Studies in the use of various microcapsule shell types have shown to contribute to the capacity performance in LIB's, where their porosity would aid the cathode or anode to improve the mobility of the lithium ions of the overall electroactive material.^{50,55–57}

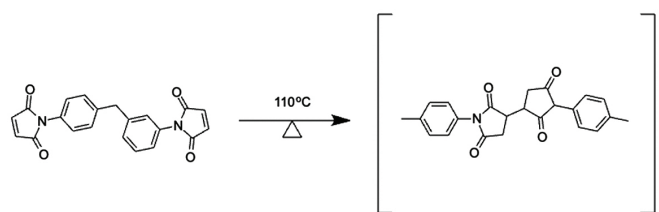


Figure 8: BMI polymerization reaction at 110°C to form polyBMI.⁴⁷

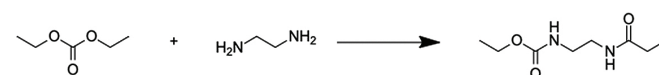


Figure 9: Reactions of diamines and diethyl carbonate.⁴⁸

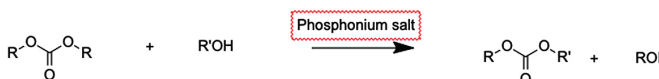


Figure 10: Synthesis of unsymmetrical dialkyl carbonates via transesterifications catalyzed by phosphonium salts

On the other hand, microcapsules that contain thermal shutdown chemistries should not be porous or allow for any diffusion of these chemistries in and out of the shell within the electrodes and electrolyte over the lifetime of the battery in application. This would decrease the cell's electrochemical performance as they tend to interact with the electrolyte thus hindering the lithium ionic transfer. To be effective in LIB's, microcapsules must be fabricated to maximise the encapsulation of the active core material and ensure an even distribution within the shells. This is crucial to prevent the increase of non-functional material such as the shell or capsule to the overall active components of the cell. This would in turn negatively impact the overall weight percentage of the microencapsulated additive and subsequently the mass of the cell. Baginska et al. (2018)⁵³ showed that there is a maximum number of capsules that can be added to the LIB before cell performance is negatively affected. Capsules that are added to LIB's should have little to no effect on the electrochemical performance of the LIB and only contribute to the overall mass to a small degree.

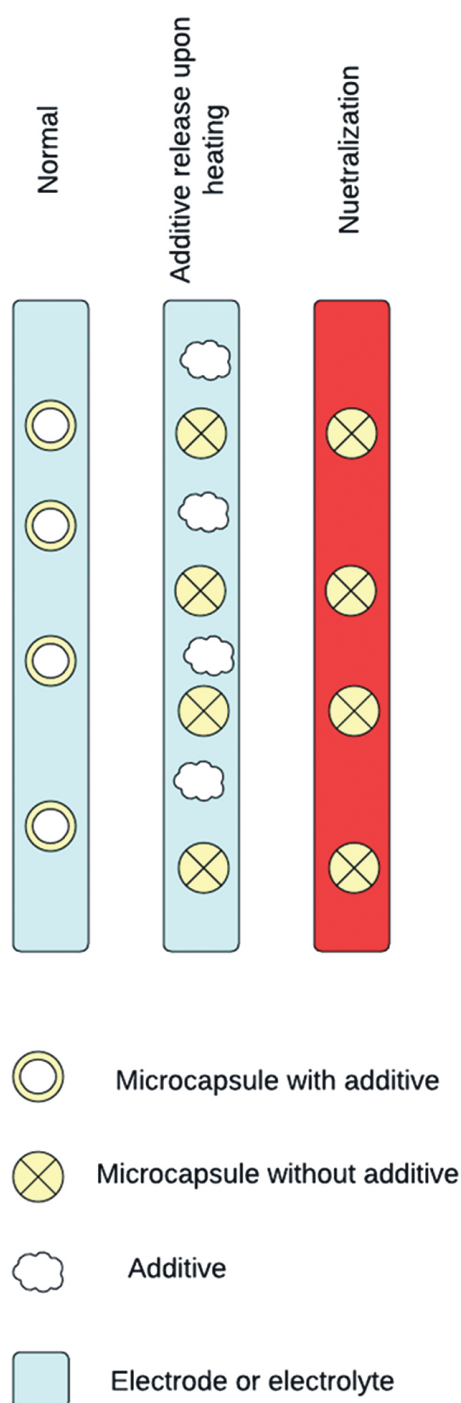
Microcapsules for thermal runaway

Table 2 summarizes the more common types of flame retardants used in LIB with a brief description of their main activity and reaction mechanism as mentioned in literature.

Microcapsules with additives within LIBs play a crucial role in enhancing safety, particularly during thermal runaway events. As depicted in Figure 11, these microcapsules function through several mechanisms to prevent the escalation of such events.

Table 2: Flame retardants with commonly used in lithium-ion batteries and preferred shells

| Flame retardant | Microcapsule type | Delivery method | Reference |
|-----------------------------------------------------------------------------------------|------------------------|-------------------------------------------------------------------------------|-----------|
| 1,1,1,2,2,3,4,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane (DMTP) | PMMA | PMMA microcapsules embedded on separator | 58 |
| Perfluoro(2-methyl-3-pentanone) | N-H based microcapsule | N-H based microcapsules embedded on separator | 59 |
| Heptafluoro-cyclopentane | N-H based microcapsule | N-H based microcapsules embedded on separator | 59 |
| Tri(2-chloroethyl-phosphate) | PUF | PUF microcapsules in electrolyte | 53 |
| Ammonium polyphosphate | Melamine-formaldehyde | Composite phase change material on graphite electrode | 60 |
| Ammonium polyphosphate and zinc oxide | Polysiloxane | Polysiloxane microcapsules were incorporated into the polypropylene separator | 61 |
| Triphenyl phosphate (TPP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) | PUF | PUF microcapsules incorporated in cathode slurries | 62 |

**Figure 11:** Microcapsules mode of action

Firstly, microcapsules can be placed on electrodes and the additive acts as physical barrier when a thermal event occurs, effectively preventing short circuiting on the electrode. Moreover, within the microcapsules, additives are strategically contained to also react with the electrolyte in the event of a thermal incident. This reaction serves to reduce the flammability of the electrolyte, thereby mitigating the potential for combustion and further escalation of the thermal event. Additives within microcapsules can impede ionic transport during thermal runaway. By containing materials that hinder the movement of ions, they effectively slow down the propagation of the thermal event, providing crucial time for mitigation measures to be implemented and reducing the overall severity of the situation.

Yim et al. (2015)⁵⁸ demonstrated the use of (1,1,1,2,2,3,4,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)-pentane) (DMTP) as a flame retardant that was encapsulated in a polymethyl methacrylate shell (PMMA) suspended and placed in the cell separator. The results showed that the flame retardant in a LIB which is highly endothermic can easily suppress the exponential temperature increases during thermal runaway processes.⁵⁸ With the aid of a cross-linking agent, an oil-in-water emulsion-based polymerization reaction was used to safely enclose a fire-extinguishing agent inside a hard-polymeric shell. Direct contact between the extinguishing agent and the electrolyte was avoided by the capping of DMTP with a cross-linked PMMA shell, which also provided the electrolyte with high structural stability. A typical nail penetration test revealed that there was a reduction in the increase in cell temperature rate in the LIB that was tested with the encapsulated additive.

Lou et al. (2022)⁵⁹ reported the use of a N-H microcapsule embedded on the separator material to aid in the increased electrolyte uptake due to the presence of the N-H groups. The reported microcapsule contained a mixture of perfluoro(2-methyl-3-pentanone) and heptafluoro-cyclopentane as core materials which showed good endothermic activity at high temperatures. This would then suppress the exponential temperature increases during the thermal runaway event. Bagniska et al. (2018)⁵³ studied the effect of directly placing a flame-retardant tri(2-chloroethyl-phosphate) into the LIB electrolyte chemistry versus the use of the same encapsulated flame-retardant. They showed that the un-encapsulated flame retardant reduced the ionic conductivity of the electrolyte while the encapsulated additive had little effect on the battery electrochemistry.⁵³

Ammonium polyphosphate (APP) is another flame retardant that is used in LIBs due to its ability to undergo endothermic decomposition when exposed to high temperatures. Xu et al (2023)⁶⁰ reported on experiments that involved the incorporation of a flame retardant (ammonium phosphate) into a solid-solid phase change material (normally used for thermal management) made up of polyethylene glycol and N,N'-Methylnebisacrylamide. Melamine-formaldehyde was the capsule shell of choice for this experiment and further electrochemical studies showed that 19% w/w of microcapsules in the phase change material was enough to provide good thermomechanical

properties without compromising its flame retardancy. APP, alongside zinc oxide, served as an intumescent flame retardant. These components were encapsulated with silicon, forming shells that were subsequently embedded onto a polypropylene separator, thereby enhancing its mechanical stability. It was found that the silicon microcapsules with APP and zinc oxide significantly decreased heat generated during thermal runaway.⁶¹

Ma et al (2022)⁶³ explored the option of coating ammonium phosphate with ammonium hydroxide followed by their encapsulation using a polyurea formaldehyde shell. The capsules were applied onto the electrode of a LIB cell and the results showed that the addition of the capsules improved the thermal stability and that all additions with less than 20% w/w ratio still had cell capacity retention of not less than 94% after 100 cycles.⁶³

Lui et al (2021)⁵⁴ coated a polyolefin separator with some ceramic based silica microcapsules. These microcapsules contained a phase change material (molten steric acid) and a flame retardant (triethyl phosphate). The molten steric acid provided an early release of the triethyl phosphate due to its low melting point.⁵⁴

Huang et al.'s (2017)⁶² experiments demonstrated the successful encapsulation of triphenyl phosphate (TPP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) using PUF microcapsules. These microcapsules were integrated into the cathode slurry, leading to improved dispersion. Conversely, when TPP and DOPO were added to the slurry without encapsulation, they tended to aggregate, resulting in decreased conductivity. Their flame retardancy was tested in LiFePO₄ coin cells and was found to have self-extinguishing efficiencies of 32% for TPP and 37% for DOPO.⁶²

CAPACITY DECAY AND MICROCAPSULES

Capacity decay

Capacity decay or the change in the state of health (SoH) of a battery is influenced by several factors that can occur in the battery or its system over the lifetime in application. In a simplistic way, the life expectancy of a battery relates to the number of capacity cycles that can be obtained at a specified depth of discharge (DoD) which is the battery's capacity that has been dissipated over that specific DoD. This is usually done under controlled conditions of a specific current rate and set temperature, which often differs from the battery in application. Some of the more common factors which lead to capacity decay include the changes in the surface area and porosity of the electrodes over time. These include the growth of the solid electrolyte interphase (SEI) primarily at the anode, loss of the active material to current collector interphase, mechanical stresses, lithium plating and electrolyte decay. Watanabe et al. (2014)⁶⁴ reported on some of the main factors that contribute to capacity fading in batteries and are strongly dependent on the temperature, the current rates, and the change in DoD. In their study they reported on the formation of microcracks that formed on the lithium cobalt aluminium oxide (NCA) electrode which affects the amount of surface area available for lithium-ion intercalation to take place. The most common anode material is activated carbon (AC) and Eleri et al. (2023)⁶⁵ work showed the effects of electrolyte degradation on the AC material and how it related to the capacity fading of the cell. Different electrochemical states of AC were studied, and it was shown that the PF₆⁻ anion in the electrolyte would deposit onto the electrode

surface which in turn reduces the available surface area, increasing the internal resistance and hence reduces the lithium-ion intercalation ability and its availability.

Capacity decay and microcapsules

Table 3 summarises some of the more novel microencapsulation techniques used in LIB related applications followed by a brief description of their main features.

Different types of encapsulated materials have been researched to improve the capacity retention of the LIB. For these purposes it is important that the capsules are highly porous to allow for the migration of lithium ions in and out of the shell and to interact with encapsulated active material. Yu et al. (2000)⁶⁶ explored the idea of encapsulating graphite with Nickel composites to prevent irreversible capacity loss during the first few capacity cycling after formation. The results showed that up to 10 wt% of the encapsulated active material improved the initial charge and discharge efficiency from 59% to 84% respectively. Tin as a potential anode additive was investigated by Han et al. (2020)⁵⁶ and they showed that if tin is directly incorporated into the anode material, the cell's discharge and charge capability decreases significantly due to increased volume expansion during the lithiation and de-lithiation reaction process. Their work explored the encapsulation of tin as "nanoflowers" using nanotubes as the shell material. This resulted in a decrease of the capacity decay during cycling where the voids of the microcapsules provided enough space for the volume expansion to occur without damaging the anode active material.⁵⁶

The use of transition metals as possible anode materials in LIB's have shown to have significantly higher theoretical capacities relative to the use carbonaceous anodes. However, the main issue with most transition metal anodes is their large volume expansion that occurs during the lithiation and de-lithiation reaction during the charging and discharging reaction thereby resulting in significant capacity loss during cycling.⁶⁹ Also, most of the transition materials have poorer conductivity when compared to carbonaceous anodes. Alternative synthesis schemes of the active material have been proposed to include some form of novel encapsulation techniques. Liu et al. (2021)⁶⁷ discussed the fabrication of SnS₂ quantum dots as shell material to encapsulate Cu₉S₅ "nanoflowers" using a flow focusing device. The shells produced were highly porous to allow for high electrolyte penetration and the voids were big enough to allow for significant volume expansion without faulting or damaging the anode material. The use of the capsules improved utilization of active material and improved conductivity with an increase in electrochemical capacity. Fe₂O₃ has also been explored as potential anode material but suffers from capacity decay during cycling. Wu et al (2021)⁵⁷ in their research found that encapsulating Fe₂O₃ using Zinc "nanoflowers" allowed the active material to deal with the charge induced stressors due to the porous nature and availability of free space in the capsules. Encapsulating Fe₂O₃ improved both the cycling performance and the conductivity of the active material. The use of phosphorous and nitrogen dual doped nano carbon capsules (PNCCs) have also been shown to improve electrochemical properties of iron-based anodes as they create more active sites for lithium intercalation.⁷⁰ The formed Fe (PNCCs) has a comparatively higher charge and discharge capacity when compared to graphite anodes.⁷⁰ A Ga-Sn liquid

Table 3: Summary of microcapsules used to aid in capacity decay.

| Electrode material | Microcapsule type | Reference |
|--------------------------------------------|---------------------------------------------------------------------------------------|-----------|
| Graphite | Nickel composites | 66 |
| Tin nanoflowers | Nanotubes | 56 |
| Cu ₉ S ₅ nanoflowers | SnS ₂ quantum dots | 67 |
| Fe ₂ O ₃ | Zinc nanoflowers and Phosphorous and nitrogen dual doped nano carbon capsules (PNCCs) | 57 |
| Silicon | Mesoporous carbon nanoparticles | 68 |

encapsulated alloy was shown to improve the self-healing capabilities of the active material in a cell.⁵⁰ Similarly, urea capsules were used to encapsulate Ga-Sn liquid alloy material that accommodated the volume expansion without altering the anode material properties and exhibited a capacity of 711.6 mAhg⁻¹ after 500 cycles.⁵⁰ Silicon, like the transition metals, has a high theoretical capacity when used in LIBs. However, it suffers from poor electrical conductivity, short life-cycling and capacity decay because of the large volume expansion during lithiation and de-lithiation reactions.⁶⁸ The material can be effectively used as an anode material with the aid of encapsulation to optimise its performance. Yang et al (2015)⁶⁸ explored the option of encapsulating silicon with carbon to counter the volume expansion problem. The capsules formed were porous enough to allow the free transport of lithium ions in and out of the shell and showed that after 400 cycles the cells still had 78.6% capacity retention. Similar to the carbon encapsulated silicon, Si-Al/Al-MOF was used where MOF was a molecular organic framework of aluminium capsules that reduced the effects of volume expansion during lithiation and de-lithiation reactions. The work by Wang et al (2019)⁷¹ showed that these capsules also increased the conductivity of the active material and showed a capacity retention of 79% after 500 cycles. In other studies, zeolitic imidazole frameworks 90 with a coating of a covalent-organic framework were explored to encapsulate silicon. The porous cages that formed improved the electrical conductivity on the surface of the microcapsules and showed a coulombic efficiency of more than 99%.⁷² Yang et al. (2018)⁶ reported a 92.4% capacity retention after 200 cycles while Ma et al (2018)⁷⁵ and Lou et al (2022)⁶⁶ reported 93% and 95% capacity retention after 200 and 100 cycles respectively.

CONCLUSION

This review paper gave a brief “snapshot” on the advancements made in a fast emerging and commercial relevant field of improving the safety and performance of lithium-ion batteries by using microencapsulation technology. Even though microencapsulation has been around for many years and is extensively used in a range of industries, their application in improving the functionality, safety, and durability of the lithium-ion batteries has only taken off over the last 10 years. This is based on the large increase in research articles that were published over the same period and are in line with the more recent high adoption of consumer technologies that make use of portable and stationary energy storage systems. These would typically be electronics, such as cell phones and computers, e-mobility such as e-bikes, scooters and BEVs, and stand-by or electrical grid support systems where there is also a noticeable increase in thermal events that are typically reported in the media.

Hence it is possible to microencapsulate active ingredients that can be incorporated into the cell chemistry that would otherwise interfere with the normal functioning of the electrochemistry, or in some cases even enhance their electro-performance in specific applications. This allows for addition of multiple additives with each having their unique role that can upon certain triggers, be it a thermal or within specific material degradation conditions, be allowed to activate and then ensure for a safe shut-down or induce a type of self-healing effect to extend the life in application. These novel technologies could open opportunities for the battery to be used in often challenging conditions where temperature, long cycle life and safety are crucial. These could include applications for large-scale air-travel, underground mining, robotics and remote sensor or telecom systems near arctic or desert locations.

Even though the addition of perceived electro-neutral chemicals to the lithium-ion battery chemistry might increase the overall cell weight, their advantage might be able to off-set the additional cost and weight that comes from the additional complexity of the accompanying BMS and battery housing for a battery pack.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest with regards to the content published in this article.

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