Efficacy of commercial lithium-sulphur batteries versus commercially available lithium-ion batteries by proxy of electrochemical comparison

Abstract:

Lithium-sulphur batteries (LSB) have become an area of interest for further improvement to lithium-ion battery (LIB) technology. Supported by its great theoretical specific capacity and resource availability it serves as a potential major step towards a more sustainable battery market. However, this experimental technology is faced with a series of short comings such as higher order sulphuric compound shuttling, low cathode material conductivity and volumetric expansion during discharge. Solutions to these shortcomings have been proposed but remain only experimentally viable. LSB battery cells are therefore currently deemed invalid for commercial use cases.

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Introduction

As the use of wireless technology has increased and become an essential part of humanity's day to day lives, the world of battery technology has skyrocketed in both demand for longevity and efficiency. The modern commercial market has been primarily dominated by lithium ion batteries (LIB) due to their high specific capacities, higher nominal operating voltage, varied composition, as well as their faster charging rates. The purpose of this paper is to compare the electrochemical and chemical qualities of lithium-sulphur batteries (LSB) versus that of other commercially established lithium-ion battery technologies to deem the commercial efficacy of LSB cells. More succinct, this paper aims to answer the question:

Can lithium-sulphur battery technology ameliorate aspects of the commercial market that is now predominantly dominated by other lithium-ion battery technologies?

The addition of the commercial market serves as narrowing the scope to exclude niche markets that would otherwise serve to derail the arguments for each technology. Examples for such being niche transport and research projects or otherwise uncommon usage of battery technologies that may have different requirements than that of the majority battery market. Predominantly discussed in the paper will be cathode related improvements to battery cells.

The modern battery market is today dominated by a series of LIB technologies with the most prominent systems available today being lithium-cobalt oxide (LCO), lithium-nickel-manganese oxide (NMC), lithium-manganese oxide (LMO), lithium-iron-phosphate (LFP).¹⁻³ The wide range of technologies and lack of one dominating cell type is due to the diverse need of the commercial markets. Such markets include battery packs for electric vehicles, to the battery of small electronic devices used in both public and private sectors. With focus on a large capacity, high columbic efficiency, and cheap materials, the LSB technology promises a lucrative step forward within battery cell technology, that few other technologies can.⁴

Numerous of studies concerning LSB cells have concluded that the greatest hinderance for commercial adaptation is the shuttle effect of poly-sulfuric compounds dissolving across the electrolyte solution of the cell.⁴⁻⁷ This effect impedes the capacity, cycle life and internal resistance within the electrochemical system.^{4, 8} Other cell technologies have however had similar yet non-identical issues with cathode material solubility, such as the LMO cathode material. Solutions to the cathode material solubility problem have been proposed and proven effective in rectifying issues that otherwise would make the LMO cell unviable for commercial use. This legitimises the idea that solutions for the LSB

cathode solubility are feasible and some are already being proposed. Included in these proposals are the integration of carbon coatings, copolymerization with graphene structures⁶ and the addition of solid state electrolyte.⁹

Given the wide range of users that battery technology now concern, safety is a pillar of what deems a viable technology in the commercial market. Demonstrated by the exploding "galaxy 7" smartphone battery¹⁰, The grounding of all Boeing model 787 aircrafts in 2013 due to thermal runaway within onboard LCO batteries³, an adherence to not only the greatest battery specification, but safety are fundamental in the success of any battery technology. Established by previous safety analysis of established LIBs the prominent source of safety concern is the internal heat formation through cell resistance.¹ Safe handling of waste material post battery life cycle must also be considered due to risk of environmental pollution.¹¹ These aspects serve as standards for the acceptable safety of LSB cells and must be considered for commercial feasibility.

The pressing state of the climate is in the ever-growing interest for not only the academic world but also that of the public eye. The sustainability of a given battery technology must be reflected in both its components as well as its longevity. The most detrimental part of most secondary batteries in today's market is the overconsumption of cobalt. Cobalt mines are located in some of the most sociopolitical and economically vulnerable regions, and mining practices have faced a great deal of scrutiny.^{1, 12} LSBs are therefore of great potential value due to their lack of cobalt in their electrode material, as the access to sulphur is far greater than that of cobalt, and more readily available in regions less affected by unstable working conditions⁵.

This paper will present the theory behind LSB technology and delving deeper into the current problems the technology has adapting to the commercial market. Throughout, the focus will be to compare the viability of the technology with respect to the aforementioned battery technologies that are predominant in today's market. Focusing on specifications related to specific capacity, nominal voltage, health and safety, columbic effect, and environmental impact. The paper will primarily involve cathode material of the given battery technology and discuss issues regarding other battery components such as the electrolyte, anode, and conductors, only when relevant and specific to a chosen cathode material. Finally, the paper will present paths forward in the improvement and commercial adaptation of LSB batteries, pointing out research that provide findings remedying problems the technology possesses, and whether the technology has any foothold in the commercial market today.

Theory

Intercalation in LIBs and lithium-cobalt oxide cells (LCO)

The basis of most lithium-ion battery (LIB) technologies lie in the concept of intercalation. Intercalation is a reversible insertion of an ion or molecule into a layered structure, such as the insertion of lithium ions into graphite layers in LCOs². This storage of lithium ions in layered structures serves as an intermediate storage space between the charge and discharge cycle of the cell. One of the most fundamental LIB cells is the Lithium Cobalt Oxide battery cell (LCO), whose popularity in the early 2000s dominated the battery market². As seen in figure 1, this cell uses the intercalation of lithium ions inside of a lithium-cobalt oxide electrode and a graphite electrode as reversible storage for lithium ions.



Figure 1: Simple illustration of an LCO battery cell with a graphite anode and the metal oxide LiCoO₂ as the cathode. All the components within the battery are submerged in the electrolyte solution. Reprinted with permission of B. Goodenough et. al.¹³ copyright 2013, American chemical society.

During the process of discharging the battery, the redox reaction and intercalation from the graphite anode to the $LiCoO_2$ cathode is powered by the difference in electrode potential between that of the anode and cathode.

$$nLiC_6 \rightarrow nLi^+ + nC_6 + ne^- \tag{1}$$

$$nLi^{+} + Li_{1-n}CoO_2 \rightarrow LiCoO_2 \tag{2}$$

Equation I & II follow the reaction path for the battery at discharge, the reaction is however reversible through applying electrical power back into the cell's electrodes greater than the sum of the two electrode potentials. As depicted in figure 3, the overlapping band of $\text{Co}^{3+/4+}$ with respect to the O²:2p band result in the release of oxygen from the LiCoO₂ lattice. This, despite higher theoretical capacity, leads to a practical specific capacity of ~140 mAh/g permanently limited by the loss of oxygen¹⁴. Furthermore, the LCO suffer from the most thermal runaway of comparable commercially available battery cells¹.

Solid electrolyte interface (SEI)

Due to the reactive nature of electrode material, hindrances for adverse electrolyte reactions are important through a battery's life cycle. In the case for most LIB cells, the SEI layer serves to limit these unwanted reactions.¹⁵ During the charge/discharge cycle of LIBs, the electrolyte of the given cell reacts with the oxidized compounds produced primarily by cathode activity, forming a solid phase between the electrodes and the electrolyte. This layer serves as a lithium ion permeable separator between the electrode and the electrolyte¹⁵. The layer of oxidized electrolyte compound is what has been aptly named the solid electrolyte interface and is a vital part in the health of some battery cells. Electrolyte shielding is achieved through the oxidized electrolyte compounds forming between the electrode material and electrolyte phase. This placement allows the SEI to mechanically hinder oxidization reactions through decreasing surface area of direct electrolyte contact.

During the battery life cycle however, the further reaction of electrolyte salts produce growth of SEI compounds, leading to clogged electrode material, incapable of intercalating lithium ions. Furthermore, the reactions forming the SEI consumes lithium ions, forming irreversible bonds. This in turn leads to a decrease in battery capacity and increase in internal resistance within the battery.¹⁶ This "double edged sword" effect of the SEI is why the choice of electrolyte is important in battery cells as the accelerated formation of SEI compounds severely inhibits battery functionality¹⁵.

Lithium-nickel-manganese cobalt oxide battery (NMC)

The NMC cell uses the same layered intercalation of lithium ions in between crystalline structures as the LCO cell. The difference between the two is in the addition of a more diverse species of transition metals composed of Ni, Mn and Co as seen in figure 2.



Figure 2: a) Bulk formation of the crystalline structure of LiNiMnCoO² 1:1:1 b) top down representation of crystalline structure of LiNiMnCoO² 1:1:1. Reprinted with permission from Garcia et. al.¹⁷ Copyright 2017 American Chemical Society.

The addition of numerous transitional metals serves to combine benefits of each transitional metal, whilst letting the adjacent species compensate for individual shortcomings. This compromise of translation metal ion qualities serves to increase capacity, structural stability, and nominal voltage. Structural stabilization of ions occurs as the synthesis of Mn³⁺ to Mn⁴⁺ reduces the lower energy band of Ni³⁺, as seen in figure X, to stable Ni^{2+2, 14}.

Mn and Co work as diametrically opposed additions to the structure. Mn causes no oxygen release from the crystalline structure as the $Mn^{3+/4+}$ band lie above the O^{2-} band supporting the chemical stability of the structure. However, as illustrated in figure 3, Mn possesses a quality of structural instability through the migration of Mn ions from tetrahedral and octahedral holes within the crystalline structure. $Co^{3+/4+}$ transitional band on the other hand overlaps the O^{2-} band, causing oxygen formation and loss in chemical stability. Co ions are however not prone to octahedral and tetrahedral displacement, adding structural stability within the structure^{2, 14}.



Figure 3: Positioning of redox energies relative to p-bands of the top anion. The larger the gap between Li/Li⁺ the greater the cell voltage. The overlap between metallic ion transition bands over the O²⁻ band increases risk for chemical instability of metal oxide crystal structure².

The division of given transitional metals affect the battery specifications, and as the attempted phasing out of Co content in batteries, the market trend moves towards higher Ni content². The reasoning behind this being to lower the cost of production, lowering Co consumption for reasons discussed further, and to increase capacity. This decrease of Mn content within the cathode material decreases the dislocation of manganese illustrated in figure 4. However, it in turn decreases the chemical stability of the battery, as the Ni ions affinity to react with the oxide ions within the metal oxide structure causes loss of battery capacity and increased thermal runaway. This loss of chemical stability is much lesser than that with increased cobalt concentration. The difference in chemical stability is explained by the lesser overlap of transition band between the Ni^{3+/4+} and O²⁻ ions as depicted in figure 3. Further cell degradation is also due to the cation mixing of Ni²⁺ and Li⁺, due to their similar ionic radii¹².



Figure 4: Displacement of transitional metals in layered metal oxide crystalline structure. Proclivity to occur with low structural stability ions such as the transition metal Mn. Reprinted with permission from K. Kleiner¹⁸, copyright 2018 American Chemical Society.

Lithium-manganese oxide cell (LMO)

Differing from other LIB cells, the LMO cell uses a transitional metal oxide cathode with a spinel crystalline structure of $LiMn_2O_4$ as depicted in figure 5 to intercalate the lithium ions during the discharging of the cell. This serves as an improved 3-D crystalline structure to the previously discussed 2-D layered structure. Where added benefit is caused by Li⁺ ions diffusing between octahedral sites within the structure using intermittent tetrahedral sites to lower the energy requirement for the diffusion¹⁹.



Figure 5: Spinel structure of LiMn₂O₄.¹²

The lithium diffusion within the structure provides faster lithium conductivity than that of the other LIBs and a higher nominal voltage, operating at around $4V^{20}$. This lower internal resistance also allows for faster charging and higher current discharging compared to other LIB cells.

According to C. Zhan²¹, complication with LMO cells arises as the migration of Mn species occur through dissolution into the electrolyte solution. This migration is believed to be due to manganese's reactivity to acid compounds, forming irreversible compounds, breaking down the spinel structure and lowering capacity. Observed by H. Tsunekawa et.al²², the manganese migration also causes the poisoning of the SEI layer, forming metallic manganese on the anode of the battery cell and permanently reducing battery capacity by hindering the active transference of lithium ions.

Lithium-iron-phosphate battery (LFP)

LFP cells uses an intercalation cathode composed of LiFePO₄ in an olivine crystalline structure as depicted in figure 6. Using the polyanion $(PO_4)^{3-}$, A. K. Padhi et. al.²³ found that the redox energy of the Fe²⁺/Fe³⁺ transition can be reduced to redox energies that produce useful discharge voltage of around $3.4V^2$. This lowering in redox energy is done through weakening the covalent bonds of the iron ions within the crystalline structure by creating a polarization of the O²⁻ ion to form stronger covalent bonds with the polyanion (PO₄)³⁻.



Figure 6: Spinel structure of the cathode material LiFePO₄.¹²

This cell possesses greater thermal stability than that of spinel structured cathode materials. This is due to the strong covalent bonds P-O serves as a bonding force, locking oxygen in place and preventing structural degradation. However, sacrificing the specific capacity and volumetric density of spinel and layered LIB cells such as the LCO and NMC cell as seen in table 1.

The LFP cell exhibits lacking electron conductivity due to a separation of the FeO_6 octahedral structure caused by the polyanions. This has been improved upon since its invention by the addition of conductive carbon based compounds coating the cathode material²⁴.

Lithium-sulphur battery (LSB)

Using elemental sulphur as cathode material has been an area of great scientific interest of the later years driven by the high theoretical capacity for a metallic lithium anode, elemental sulphur cathode at 1675 mAh/g^{14, 8, 25, 26}. In contrast to most LIB cathodes, the LSB cathode does not use the intercalation of crystal structures to reversibly store lithium ions. Instead, the storage is carried out through a series of intermediate reactions (eq. 3-13) forming lower order sulphuric compounds, reversibly bonding with lithium ions crossing the electrolyte from the metallic lithium anode during discharge.

According to the electrochemical study of poly-sulphuric compound scission by Kawase et. al. ²⁵ the scission occurs in 4 separate stages. In the first stage scission, denoted by eq. 3-7 the S₈ molecular ring is reduced to $Li_2S_x^{2-}$ ($4 \le x \le 8$).

$$S_8 + 2e^- \to S_8^{2-}$$
 (3)

$$S_8 + 4e^- \rightarrow S_7^{2-} + S^{2-}$$
 (4)

$$S_8 + 4e^- \rightarrow S_6^{2-} + S_2^{2-}$$
 (5)

$$S_8 + 4e^- \rightarrow S_5^{2-} + S_3^{2-}$$
 (6)

$$S_8 + 4e^- \rightarrow 2S_4^{2-} \tag{7}$$

In the second stage of the scission the further reduction of sulphuric compounds, denoted in eq. 8-12, $Li_2S_x^{2-}$ $(1 \le x \le 3)$ is formed.

$$S_8^{2-} + 2e^- \rightarrow S_6^{2-} + S_2^{2-}$$
 (8)

$$S_8^{2-} + 2e^- \to S_5^{2-} + S_3^{2-} \tag{9}$$

$$S_8^{2-} + 2e^- \to 2S_4^{2-} \tag{10}$$

$$S_7^{2-} + 2e^- \to S_4^{2-} + S_3^{2-} \tag{11}$$

$$S_6^{2-} + 2e^- \to 2S_3^{2-} \tag{12}$$

$$S_5^{2-} + 2e^- \to S_3^{2-} + S_2^{2-} \tag{13}$$

$$S_8^{2-} + 2e^- \to 2S_2^{2-} \tag{12}$$

In the third stage, denoted in eq. 13, the Li_2S_3 formed in the previous stages is further reduced to Li_2S_2 and Li_2S .

$$S_3^{2-} + 2e^- \to S_2^{2-} + S^{2-} \tag{13}$$

Finally, in the fourth stage, the reduction of S_2^{2-} into S^{2-} takes place. According to Kawase et. al.²⁵ the ¹H NMR results of LSB discharge suggests that the conversion into Li_2S is not complete and the majority of Li_2S_2 remain intact. During the

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charging of the LIB cell the reverse reaction occurs, however is complicated by the solubility of polysulfides that form^{2, 25}.

Polysulfide shuttle effect formation

As mentioned above, a multi-step scission reaction of higher order sulphuric compounds occurs during the discharge of the cell^{4, 5, 25}. These higher order compounds have a high affinity towards commonplace electrolytes in common LIB cells such as the solvent 1,2-dimetheoxy (DME) and 1,3-dioxolane (DOL)^{5, 8}. This increased electrolyte affinity lead to a solid/liquid/solid transition of the different sulfuric compounds as seen in figure 7.



Figure 7: Cell diagram of graphene additive and polymer binder sulphur cathode. Presence of shuttle effect illustrated by the polysulfide compounds present in the electrolyte phase. Reprinted with permission from T. Li⁵. Copyright 2014, American Chemical Society.

This transition means as the elemental sulphur breaks down upon discharge the higher order sulphuric compounds $\text{Li}_2S_x \ 3 \le x \le 8$ predominantly $6 \le x \le 8$, will dissolve into the electrolyte solution and diffuse to the lithium anode, creating low order sulphuric compounds. From there, upon the charging of the cell, the low order sulphuric compounds will diffuse back to the sulphur cathode and form higher order sulphuric compounds^{4, 5, 8}. This "shuttling effect" can cause a failing cycling stability, leading to loss in columbic effect and capacity throughout the battery's cycle life.

Volume expansion

Volume differential on the cathode side during lithiation (discharge) of the battery as the reaction proceeds from $S_8 - Li_2S$ leads to volumetric expansion of the cathode material and mechanical instability of the system. Porous systems of carbon compounds such as 3-D graphene structures²⁷ and doped graphene sheet copolymerization²⁸ have been suggested to mitigate the volumetric expansion as well as limit the shuttle effect by mechanically trapping polysulfides in the pores of the given structures as documented by Helen et. al²⁷ and Xu et all.

Low conductivity

Elemental sulphur on its own is an isolative material, meaning poor transfer of electrons from the sulphur cathode of LSB. To increase the conductivity of the sulphur cathode numerous methods have been suggested. 3-D graphene structures have been mixed into the sulphur cathode by Xu et. al.²⁶ and Helen et. al.²⁷ with promising results, enabling high-rate charge/discharge by decreasing the internal resistance of the cathode compound and in turn decrease internal temperature increase during the charge/discharge cycle. As found by Xu et. al.²⁶ however, in relation to reliable specific capacity over cycle life, this cell performed at ~600 mAh/g over 100 cycles, dropping from a starting specific capacity of ~1300 mAh/g.

Discussion

The need for a battery technology to meet the demands of future technology is apparent and of great commercial value. As continued strides in the fields of electric vehicles (EVs), renewable energies and consumer electronics are made, the need for safe, reliable, high-capacity batteries grow more apparent. In this field, LSB are of great interest and show potential due to their large theoretical specific capacity and simple, inexpensive ingredients.

It is clear the most used forms of LIBs have been thoroughly improved upon over time, as is apparent in the increased battery life of commercial electronics and the increased production and longevity of electric vehicles. However, the rapid optimization of these technologies has led to growing concerns within the industrial sector as to whether battery technologies can keep up with the growing demand for higher power density and capacity in the future. In the case of the mentioned LFP and LMO technologies, these are battery cells with already commercially a specific capacities of 170 mAh/g and 148 mAh/g respectively²⁹, and as seen in table 1, the approach of this theoretical ceiling will leave the technology obsolete in the future. Therefore, the demand within electrochemical studies for new battery technologies with greater theoretical ceilings has increased. In this field the LSB excel, with a theoretical specific capacity of 1672 mAh/g and an experimental cell constructed by Xu et. al⁶. achieved a specific capacity of 1022 mAh/g.

Table 1: Structural, specific theoretical/experimental/commercial* gravimetric and volumetric capacities, and nominal voltage of each LIB cell technology^{3, 7, 12}.

	LCO	NMC (1:1:1)	LMO	LFP	LSB
Structure	Layered	Layered	Spinel	Olivine	Conversion
Nominal Voltage [V]	3.8	3.7	4.1	3.4	$1-3^{5, 6, 26}$
Stability	Good	Varying	Good	Very good	Poor
Specific capacity [mAh/g]*	274/148/145	280/160/170	148/120	170/165	$1672/1022-880^{**6, 7}$
Specific volumetric capacity [mAh/cm^3]*	1363/550	1333/600	596	487	***

** experimental values not proven reliably reproducible over multiple battery cycles, decreasing between 10 - 30% over a 100 charge/discharge cycles.

*** Volumetric capacity not available due to the volume expansion of sulphur cathodes during discharging process of 79% of elemental sulphur

The reliability for batteries to perform over several charge/discharge cycles without loss of capacity is gaining further relevance as the increased usage of EVs demand batteries capable of lasting 5-10 years without dramatic shift in battery capacity. The shuttle effect of higher order sulphuric compounds remains the most prominent issue with LSB cells. The practical cycle life of the cell, documented at 10-30% capacity loss over just 100 cycles⁷, remains too unreliable for commercial uses.

Proposed solutions to the shuttle effect are the addition of a graphene layer containing polysulfide-scission reagents in between the elemental sulphur cathode and the electrolyte³⁰. This was demonstrated by Hua et. al.³⁰ where a LSB cell consisting of porous carbon nanotube, elemental sulphur mix cathode and a graphene/dithiothreitol (DDT) interlayer, performed at a capacity of ~880 mAh/g with 88.3% capacity retention over 400 charge cycles. This proved a promising result. However, the experimental cell utilizes LiNO₃ as an electrolyte, which is an oxidising agent that could cause health and safety risks at higher working temperatures^{6, 30}. Furthermore, the use of CNT increase complexity in production and high costs²⁷.

Xu. et. al.⁶ also reported severe limiting of the shuttling effect using sulfhydrylfunctionalized graphene oxide sheets (GSH), copolymerized with an open S_8 ring to form S-GSH. This copolymer, achieving promising results as it does not require the use of LiNO₃ as an electrolyte. This is due to the scission of any long-chained poly-sulfuric compounds takes place within the GSH structure and is centred at the cathode material. This allows for a wider range of electrolyte options for safer and thermically stable operation.

Commercially available LMO cells also possessed a similar degradation problem of manganese through acidic compounds in the electrolyte solution. A demonstrated solution proved to be the doping of LiMn_2O_4 with small amounts of transition metal cations³¹ which stabilized the volumetric changes within the crystal lattice of the cathode compound and by proxy, increased structural stability. This solution demonstrates that similar issues have been overcome with other cell technologies.

Battery cells use easily combustible and reactive material that can serve as their own source of oxygen within the combustion mechanism.^{1, 3} This self-fuelling mechanism of LIB combustion is in large part why fires within a cell are difficult to extinguish and pose a safety risk. The most prominent source of such a reaction is the internal heat formation within the battery. This takes place during extreme use or environment factors, leading to production of evaporated liquid electrolyte, oxygen formation and finally short-circuiting. These safety issues are especially relevant to LCO and NMC, where the self-heating of LCO and NMC is large part due to their oxygen formation from metallic oxide crystalline cathode.¹

LFP and LMO have been proven safer and more thermically stable due to their lack of formation of oxygen gas in the decomposition of the cathode material^{1, 2}. In the case of the LFP cell, it has proven the safest out of the technologies presented, passing numerous extreme safety test for thermal runaway¹. The low thermal runaway is due to the strong covalent bonding of P⁵⁺ ion with the oxygen in the octahedral FeO₆ structure explained in the theory. In the case of the LMO cell, the chemical stability of Mn as discussed in the theory of NMC cells, provide a lesser formation of oxygen gas. This makes the LMO cell significantly more thermally stable than that of LCO and NMC cells.

Comparing the safety standards of the commercially available LIB mentioned, the LSB cell falls short. Safety concerns regarding LSBs are mostly caused by the metallic lithium anode material. Solid lithium anodes have demonstrated formation of lithium dendrites through the dissolving and reformation of metallic lithium throughout the battery cycle.^{1, 5, 27} These dendrites provide pathways for short-circuiting extending across the electrolyte.^{1, 5} Potential solutions to this problem have been demonstrated by Solid State Electrolyte solutions. Using solid electrolyte (SE), the formation of dendrites is reduced as the SE provide a solid barrier between the electrodes and is harder to penetrate comparative to liquid electrolytes.⁹ Furthermore, with the eventual establishment of SE, the problems of evaporation and eventual degradation in liquid electrolytes are lessened significantly, and the thermal stability of the cell increases correspondingly.⁹

The major environmental concern of modern battery cells is the consumption of cobalt in the cathode material of the LIB.^{1, 32} Cobalt is a scarce resource in the natural environment and the available reserves are in socio-political unstable regions, where approx. 60% of the world cobalt supply is originating from the democratic republic of Congo where no other country supplies more than 6%³². In recent years the market trend of phasing out the use of LCO is partly due to being outcompeted by the NMC cell, the unsustainability of high cobalt content cathode material and price of the high cobalt use. Even in NMC technology, the newer battery cells tend towards higher concentration of nickel to decrease pricing and decrease cobalt usage. LSBs are made up of readily available materials such as elemental sulphur, graphite or other cheap anode material, and electrolyte solution composing of common and readily available organic solvents and lithium salts⁵. This factor of sustainability is one of the key arguments for the further study of LSB technology, as with cobalt being not only damaging for the environment through mining, but also toxic. This in turn can lead to unproperly disposed of battery cells contaminating natural habitats and posing health risk to natural resource supplies.

Conclusion

The large theoretical benefits of LSB gives the technology great merit for commercial use as its specific capacity and experimentally demonstrated high coulombic effect is one not matched by any of the other available LIB cells. Comparing available, highest capacity LIBs on the markets today, LSB shows a capacity numbering anywhere from 638-594% higher than that of any other high capacity technologies specified in this paper. Its consumption of cathode materials that are low cost and high abundance further resonates its benefits in wide scale adaptation of the technology, only being outshined by the LFP battery regarding its resource availability.

Concerning its downsides, the LSB remains lacking in reliable cycling life in comparison to other LIBs, with few earlier adaptations of the technology managing 100 life cycles without suffering between 10-50% decrease in battery capacity. Demonstrating further the shuttle problem to be one of LSB largest hindrance for wide scale use. Material conductivity persists to be a pressing issue as well, as elemental sulphur serves as an insulating material, creating inadequate nominal voltage throughout its operation. This high internal resistance within the battery material is also prone to creating thermal runaway within the battery, spawning possible safety hazards in cell operation. The use of metallic lithium as anode material poses further safety concerns. This is due to the proclivity towards dendrite formation and short circuiting, leading to extreme, uncontrolled reactions within the cell and resulting in explosion or fire. Furthermore, due to it using metal bond formation instead of widely adapted intercalation, the discharge of the cell results in a scission reaction of long chain poly-sulfuric compounds into LiS and LiS₂. This formation of smaller sulfuric compounds in turn results in a volume expansion of ~80% of initial volume. Such an extreme expansion proceeds to destroy cathode material and make the practical construction of a battery cell that accounts for material expansion pose a difficulty no other cell technology currently requires.

Accounting for all factors mentioned, a wide adaptation of LSB technology is deemed unviable in today's market, as more reliable options are readily available and with established production methods. For the LSB cell to be a viable commercial option in the future, the previous shortcomings must be accounted for and optimized. Proposed solutions for the conductivity and cathode material expansion are the addition of 3-D graphene structures. This porous structure functionally operates as a sponge for the simpler sulphuric compounds formed during the discharge of the cell and can account for the excess volume. In addition, the porous structure serves as a physical barrier between the cathode material and the electrolyte solution, preventing the dissolving of higher order sulphuric compounds and shuttle effect formation. Finally, the higher conductivity of graphene also ameliorates the low conductivity of elemental sulphur, improving coulombic efficiency and internal heat generation.

Presently, the solution with greatest promise is the use of r-GO sheets to form copolymers with the intermediate high order sulphuric compounds. This greatly reduces the shuttle effect and allows the uses of a wider ranges of electrolytes, as the negation of solubility is not dependent on the electrolyte itself. Furthermore, the r-GO sheet structure possesses similar porous qualities of 3-D graphene structures, minimising cathode material expansion and induce higher conductivity within the cathode material, similar to that of the 3-D graphene structures.

References

1. Mauger, A.; Julien, C. M., Critical review on lithium-ion batteries: are they safe? Sustainable? *Ionics* **2017**, *23* (8), 1933-1938, 1946.

2. Manthiram, A., A reflection on lithium-ion battery cathode chemistry. *Nature communications* **2020**, *11* (1), 1-9.

3. Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G., Li-ion battery materials: present and future. *Materials today (Kidlington, England)* **2015**, *18* (5), 257-260.

4. Ren, W.; Ma, W.; Zhang, S.; Tang, B., Recent advances in shuttle effect inhibition for lithium sulfur batteries. *Energy Storage Materials* **2019**, *23*, 707-732.

5. Li, T.; Bai, X.; Gulzar, U.; Bai, Y. J.; Capiglia, C.; Deng, W.; Zhou, X.; Liu, Z.; Feng, Z.; Proietti Zaccaria, R., A comprehensive understanding of lithium–sulfur battery technology. *Advanced Functional Materials* **2019**, *29* (32), 1-12.

6. Xu, N.; Qian, T.; Liu, X.; Liu, J.; Chen, Y.; Yan, C., Greatly Suppressed Shuttle Effect for Improved Lithium Sulfur Battery Performance through Short Chain Intermediates. *Nano Lett* **2017**, *17* (1), 538-543.

7. Xiao, L.; Cao, Y.; Xiao, J.; Schwenzer, B.; Engelhard, M. H.; Saraf, L. V.; Nie, Z.; Exarhos, G. J.; Liu, J., A soft approach to encapsulate sulfur: polyaniline nanotubes for lithium-sulfur batteries with long cycle life. *Advanced materials* **2012**, *24* (9), 1176,1178-1179.

8. Evers, S.; Nazar, L. F., New approaches for high energy density lithium–sulfur battery cathodes. *Accounts of chemical research* **2013**, *46* (5), 1135-1143.

9. Chen, R.; Yao, C.; Yang, Q.; Pan, H.; Yu, X.; Zhang, K.; Li, H., Enhancing the Thermal Stability of NASICON Solid Electrolyte Pellets against Metallic Lithium by Defect Modification. *ACS Appl. Mater. Interfaces* **2021**, *13* (16), 18743-18747.

10. Apitanawit, M., Influence of the Samsung Galaxy Note 7's Battery Problem on Consumer Perception and Intention to Purchase Samsung Smartphone in the Future. *Master Science Program in Marketing, Thammasat University* **2016**.

11. Rarotra, S.; Sahu, S.; Kumar, P.; Kim, K. H.; Tsang, Y. F.; Kumar, V.; Kumar, P.; Srinivasan, M.; Veksha, A.; Lisak, G., Progress and Challenges on Battery Waste Management :A Critical Review. *ChemistrySelect (Weinheim)* **2020**, *5* (20), 6190-6191.

12. Kwon, S.-J.; Lee, S.-E.; Lim, J.-H.; Choi, J.; Kim, J., Performance and life degradation characteristics analysis of NCM LIB for bess. *Electronics (Basel)* **2018**, 7 (12), 406.

13. Goodenough, J. B.; Park, K.-S., The Li-ion rechargeable battery: a perspective. *Journal of the American Chemical Society* **2013**, *135* (4), 1167-1176.

14. Chebiam, R. V.; Kannan, A. M.; Prado, F.; Manthiram, A., Comparison of the chemical stability of the high energy density cathodes of lithium-ion batteries. *Electrochemistry communications* **2001**, *3* (11), 624.

15. An, S. J.; Li, J.; Daniel, C.; Mohanty, D.; Nagpure, S.; Wood III, D. L., The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon* **2016**, *105*, 53-58.

16. Tsubouchi, S.; Domi, Y.; Doi, T.; Ochida, M.; Nakagawa, H.; Yamanaka, T.; Abe, T.; Ogumi, Z., Spectroscopic characterization of surface films formed on edge plane graphite in ethylene carbonate-based electrolytes containing film-forming additives. *Journal of The Electrochemical Society* **2012**, *159* (11), A1786.

17. Garcia, J. C.; Bareño, J.; Yan, J.; Chen, G.; Hauser, A.; Croy, J. R.; Iddir, H., Surface structure, morphology, and stability of Li (Ni1/3Mn1/3Co1/3) O2 cathode material. *The Journal of Physical Chemistry C* **2017**, *121* (15), 8290-8299.

18. Kleiner, K.; Strehle, B.; Baker, A. R.; Day, S. J.; Tang, C. C.; Buchberger, I.; Chesneau, F.-F.; Gasteiger, H. A.; Piana, M., Origin of high capacity and poor cycling stability of Li-rich layered oxides: a long-duration in situ synchrotron powder diffraction study. *Chemistry of Materials* **2018**, *30* (11), 3656-3667.

19. Thackeray, M.; David, W.; Bruce, P.; Goodenough, J., Lithium insertion into manganese spinels. *Materials Research Bulletin* **1983**, *18* (4), 461-472.

20. Gummow, R.; De Kock, A.; Thackeray, M., Improved capacity retention in rechargeable 4 V lithium/lithium-manganese oxide (spinel) cells. *Solid State Ionics* **1994**, *69* (1), 59-60.

21. Zhan, C.; Lu, J.; Kropf, A. J.; Wu, T.; Jansen, A. N.; Sun, Y.-K.; Qiu, X.; Amine, K., Mn (II) deposition on anodes and its effects on capacity fade in spinel lithium manganate–carbon systems. *Nature communications* **2013**, *4* (1), 1.

22. Tsunekawa, H.; Tanimoto, S.; Marubayashi, R.; Fujita, M.; Kifune, K.; Sano, M., Capacity fading of graphite electrodes due to the deposition of manganese ions on them in Li-Ion batteries. *Journal of the Electrochemical Society* **2002**, *149* (10), A1326-A1331.

23. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *Journal of the Electrochemical Society* **1997**, *144* (4), 1189-1191.

24. Prosini, P. P.; Zane, D.; Pasquali, M., Improved electrochemical performance of a LiFePO4-based composite cathode. *Electrochimica acta* **2001**, *46* (23), 3517-3523.

25. Kawase, A.; Shirai, S.; Yamoto, Y.; Arakawa, R.; Takata, T., Electrochemical reactions of lithium–sulfur batteries: an analytical study using the organic conversion technique. *Physical Chemistry Chemical Physics* **2014**, *16* (20), 9344-9350.

26. Xu, C.; Wu, Y.; Zhao, X.; Wang, X.; Du, G.; Zhang, J.; Tu, J., Sulfur/threedimensional graphene composite for high performance lithium–sulfur batteries. *Journal of Power Sources* **2015**, *275*, 22-25.

27. Helen, M.; Reddy, M. A.; Diemant, T.; Golla-Schindler, U.; Behm, R. J.; Kaiser, U.; Fichtner, M., Single step transformation of sulphur to Li2S2/Li2S in Li-S batteries. *Sci Rep* **2015**, *5* (1), 12146-12146.

28. Lin, C.; Niu, C.; Xu, X.; Li, K.; Cai, Z.; Zhang, Y.; Wang, X.; Qu, L.; Xu, Y.; Mai, L., A facile synthesis of three dimensional graphene sponge composited with sulfur nanoparticles for flexible Li-S cathodes. *Phys Chem Chem Phys* **2016**, *18* (32), 22146-22153.

29. Lee, S.; Yoon, G.; Jeong, M.; Lee, M. J.; Kang, K.; Cho, J., Hierarchical Surface Atomic Structure of a Manganese-Based Spinel Cathode for Lithium-Ion Batteries. *Angewandte Chemie* **2015**, *127* (4), 1169-1174.

30. Hua, W.; Yang, Z.; Nie, H.; Li, Z.; Yang, J.; Guo, Z.; Ruan, C.; Chen, X. a.; Huang, S., Polysulfide-scission reagents for the suppression of the shuttle effect in lithium–sulfur batteries. *ACS nano* **2017**, *11* (2), 2209-2210, 2216.

31. Kanevskii, L.; Dubasova, V., Degradation of lithium-ion batteries and how to fight it: A review. *Russian Journal of Electrochemistry* **2005**, *41* (1), 1-16.

32. Banza Lubaba Nkulu, C.; Casas, L.; Haufroid, V.; De Putter, T.; Saenen, N. D.; Kayembe-Kitenge, T.; Musa Obadia, P.; Kyanika Wa Mukoma, D.; Lunda Ilunga, J.-M.; Nawrot, T. S.; Luboya Numbi, O.; Smolders, E.; Nemery, B., Sustainability of artisanal mining of cobalt in DR Congo. *Nat Sustain* **2018**, *1* (9), 495-504.