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Recent Progress and Emerging Application Areas for Lithium-Sulfur Battery Technology

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Abstract

Electrification is progressing significantly within the present and future vehicle sectors such as large commercial vehicles (e. g. trucks and busses), high altitude long endurance (HALE), high altitude pseudo satellites (HAPS), and electric vertical take-off and landing (eVTOL). The battery systems performance requirements differ across these applications in terms of power, cycle life, system cost, etc. However, the need for high gravimetric energy density, 400 Wh kg^{-1} and beyond, is common across them all, since it will enable vehicles to achieve extended range, longer mission duration, lighter weight or increased payload. The system level requirements of these emerging applications can be broken down into the component level developments required to integrate Li-S technology as the power system of choice. In order to adapt the batteries' properties, such as energy and power density, to the respective application, the academic research community has a key role to play in component level development. However, materials and component research must be conducted within the context of a viable Li-S cell system. Herein, the key performance benefits, limitations, modelling and recent progress of the Li-S battery technology and its adaption towards real world application are discussed.

1. Introduction

With the ever-increasing need for electrification across many application sectors, the development of new energy storage technologies is of increasing relevance and critical importance. Electrification is progressing significantly within the traditional transportation sectors such as: electric bikes, cars, buses, and other commercial vehicles, enabled by continued cell development and Gigafactory-scale mass production of Li-ion battery technology. However, two key factors are starting to drive the need for new solutions to be found: One factor is the secure supply of key elements - mainly cobalt and nickel - used in most of the

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conventional Li-ion cells are becoming increasingly critical. The other being the performance requirements of desirable emerging application areas are beyond the capabilities of traditional Li-ion battery technology. Examples include large commercial vehicles, [1] high altitude long endurance (HALE), high altitude pseudo satellites (HAPS), electric vertical take-off and landing (eVTOL) [2] and electric passenger aircraft. The weight of the battery system is an especially critical factor for these aviation applications. The battery systems performance requirements differ across these applications: power, cycle life, system cost, etc. However, the need for high gravimetric energy density, 400 Wh kg^{-1} and beyond, is common across them all. Higher energy battery systems will enable these vehicles to achieve extended range, longer mission duration, lighter vehicle weight or increased payload. In the following, key advantages, limitations and progress made to extend cycle life, energy, power, and safety of Li-S battery systems (BMS) are described. Further, recent advances regarding modelling, battery system management and the integration of Li-S batteries into present as well as future real world applications are summarized.

2. Lithium-Sulfur Battery Technology

2.1. Advantages

Li-ion battery systems are the current technology of choice for many applications, however, the achievable specific energy reaches a maximum at around 240-300 Wh kg^{-1} at the cell level. [3] Emerging higher energy battery systems include advanced Li-ion technology (e.g. Silicon-NMC), [4] Li metal–NMC (especially with high-nickel ternary cathodes), [5] Li-S (Lithium-Sulfur), [6,7], and Li-O_2 (Lithium-Air).[6] In addition to that, solid-state technology is recently considered as a focus topic in the battery research and industry. As far as exciting and promising these technologies are, the Technology Readiness Level (TRL) should be strongly taken into account when comparing different technologies, as some of them may not be ready for some time yet.

According to the EU Integrated Strategic Energy Technology Plan (SET-Plan) Action 7 for 2030 [8], Li-air or rather Li-O2 batteries have so far the lowest TRL level. Solid-State batteries, despite the tremendous attention they have gained, still remain mainly in the laboratory in the form of a small pouch cells at best. A full scale solid-state prototype is being envisaged by Toyota for 2025 [9], but Panasonic claims that this technology is more likely to be available in the next decade. First results on Li metal–NMC are very promising [10], but the issue of the availability of the raw materials cobalt and nickel cannot be neglected. Also in terms of safety, high-nickel ternary cathodes in combination with lithium still have to be optimized [11].

Among these next-generation battery technologies, Li-S is attracting increasing attention driven by the significant advantages the chemistry can offer combined with the demonstrated technology performance and promising progress made in terms of its technology readiness level (TRL) in the recent years. [12,13,14,15]

Lithium is the lightest metal and displays a very low standard reduction potential (-3.04 V). These attributes produce an ideal negative electrode which possesses a low operating voltage and high specific capacity. Sulfur is a solid lightweight stable electronegative element that can achieve a high theoretical capacity of 1672 mA h g^{-1} (S) when fully reduced to Li_2S. When combined in an electrochemical cell with lithium, the formation of one of the highest energy material couples is achieved. Sulfur is also an abundant element which enables the possibility for low cost and environmentally compatible battery manufacturing. [16] In addition, Li-S technology does not rely on a supply of materials involved in geopolitical or social issues (such as cobalt). [17] This factor will become even more important in the nearest future when the demand for energy storage will increase exponentially. Li-S technology has also been reported to be more environmentally friendly than commercially available NMC-Graphite, if taking into account CO_2 eq km^{-1} being generated. [18] Furthermore, sulfur based electrodes can be prepared using water-based processes, reducing the need of energy intense toxic solvents commonly used

when processing NMC electrodes. In addition, a dry-transfer film process without using any solvents has been developed. [19]

Today, there are still only very few academic institutions or companies which have demonstrated Li-S battery technology at a TRL (Technology Readiness Level) greater than 5. [20–26] BASF and SION power had worked on Li-S pouch cells [27], but have not published any results for several years. LG Chem recently published a press release on a drone powered by Li-S pouch cells with specific energy as high as 410 Wh kg^{-1}, and stated that commercial cell production is expected to begin in 2025 [28]. The drone, called EAV-3, was co-developed with Korea Aerospace Research Institute (KARI). A pouch cell with a specific energy as high as 470 Wh kg^{-1} was reported by Beijing Institute of Technology [20]. Pacific Northwestern National Laboratory has published work on Lithium-Sulfur prototype pouch cells in order to bridge the gap between academic and industrial research [29]. Dalian University published a Li-S pouch cell with $LiNO_3$ free electrolyte, a specific energy of 350 Wh kg^{-1} and specific power of 60 W kg^{-1} [24]. Tsinghua University in Beijing [30] and Gebze Technical University [31] have built multi-layered pouch cells and investigated the critical parameters for the transfer of research findings from coin to pouch cell level. OXIS Energy Ltd are a company dedicated to the development of Li-S battery technology and are currently expanding beyond its pilot scale production capability at its facilities in Culham, Oxford, UK [32]. At these facilities, high capacity (>15 Ah) Li-S pouch cells are routinely produced which exceed 400 Wh kg^{-1} at a TRL/MRL level of 7-8. The Li-S cells are produced in several form factors, with cell design and components tailored to meet the demands of customers, enabling evaluation of Li-S technology in a wide range of real world application areas (Figure 1a,b). OXIS Energy' Li-S technology is under continuous development enabling the expectation that production of high energy Li-S cells of 500 to 600 Wh kg^{-1} will become possible in the next few years. [33] OXIS Energy and CODEMGE recently signed a lease agreement to build the world's first Li-S

manufacturing plant. [32] In addition, plans by the company Morrow to build lithium-sulfur Gigafactories in Norway are underway. [34]

2.2. Limitations

The main challenges to resolve are the cycle life and rate capability. The relatively short cycle life, compared with conventional Li-ion technology, has its source in use of a lithium metal based negative electrode, especially in combination with the highly reactive polysulfides [30]. The electrolyte according to the state of the art dissolves a high amount of highly reactive polysulfides that indirectly stress the anode. It is known that $LiNO_3$ in combination with the lithium polysulfides play an important role to passivate the lithium anode [35,36]. This depends on the sulfur loading in the cathode [37].Below a certain threshold of concentration of sulfur species, polysulfides can have a beneficial effect. Above a certain sulfur amount, the current density is increased [38] causing dendrite formation or mossy lithium growth is accelerated [8,23]. The development of a stable and reversible lithium metal electrode is of utmost importance for high energy battery research [39,40] and it provides the greatest opportunity to improve the performance of Li-S battery technology. It is noteworthy that the generic development of this component is also required for other next generation battery systems including Li metal-NMC systems and high-energy solid-state battery systems. [26,41] Electrolyte depletion, caused by electrolyte consumption at the anode/electrolyte interface, is the major cause of the low cycle life of Li-S technology. [42] Improving the cycle life of Li-S battery systems is an important metric for all applications. The rate of electrolyte depletion within Li-S systems drives the need for excess electrolyte and lithium to be added to cells, [26,43,44] both of which reduce the gravimetric and volumetric energy density of the system.

Li-S technology has made significant progress in the area of specific energy together with power performance. [7,30,45–47] However, the limited volumetric energy density resulting from

the use of low density and highly porous cathode structures combined with the intrinsic low density of the active material sulfur is still a road block for the implementation of Li-S technology in EV other than trucks and busses. The difference in developing a cell suitable for high energy applications compared to a cell designed for high power applications includes system design and cell design modification, however, enabling a significant development in performance comes down to the design of the cell components, such as the structure of the cathode, and fundamental materials properties such as electrolyte system development. [29] Within the battery research community, significant efforts have been made to improve the performance of the cell components and material used within Li-S batteries. [25,40,48,49,50] The list below briefly summarizes selected examples.

- In regard to cathode adaption, a variety of carbons /sulfur composite materials has been synthesized and evaluated over the last decade. The intrinsic carbon porosity has been adapted by using various templates and precursors. Also, different carbon morphologies (CNT, graphene) have been employed [7,45]. However, the impact of the secondary macroporosity created by the interspace between particles and binders has often been neglected, but is about to be addressed in more details [23,42,51,52].
- In regard to the lithium anode, promising material concepts such as conductive or in-conductive frameworks, ionically conductive coatings, spacer concepts and in-situ SEIs by special electrolyte additives have been developed and analyzed [8,46,53]. In order to bring these material concepts into prototype cells, dead volume and additional inactive material weight or volume need consideration. Coatings should be ionically conductive and maintain a certain mechanical flexibility. Metal-Lithium alloys are also an interesting concept but might lower the cell voltage, overall cell energy and should be stable versus the highly reactive polysulfides.

- In terms of electrolytes, ether based electrolytes are still promising candidates [54]. The concept of sparingly polysulfide solvating electrolytes which intrinsically hamper the polysulfide dissolution and minimize the shuttle effect is promising and allow functioning of the cell without the common $LiNO_3$ additive which has been reported to lead to gas formation. However, the mass density and kinetic limitation of these electrolyte systems needs to be addressed. Solid electrolytes [55], especially the glass ceramic ones, can also inhibit the polysulfide shuttle. However, the cathode tortuosity and processing needs to be strongly adapted since intimate contact between solid electrolyte and sulfur-carbon composite is crucial. Polymeric electrolytes are easier to process, but need to be run at elevated temperature leading to a partial dissolution of polysulfides and a charge/discharge behavior which is known from state of the art of ether electrolytes [56].

Further developments are, however, still required to enable Li-S technology to fulfil its potential. With respect to the cell level limitations, one important consideration is the geometry of commercially available lithium foil (minimum thickness of 50 µm and maximum width of 10 cm [57]) which limits the overall cell geometry and optimization of the ratio between active to inactive component mass. Consequently, nickel tabs need to be adapted for these electrode geometries and for each application (high power vs. high energy, see section 2.3) as these tabs usually play a key role in cell cooling [58] as well as transfer the current.

Another limitation is the pouch cell as a cell type, as some applications prefer cylindrical cells with a stainless steel casing. As Li-S cells are normally subjected to a drastic volume change, winding and employing the lithium anode and sulfur cathodes into rigid cylindrical housings can be detrimental. In addition, the steel housing limits the overall energy density [59].

In order to tackle the limitation in terms of volumetric energy, thinner than 50 µm lithium foils are required, ideally without current collector such as nickel or copper as these have a

detrimental impact on the gravimetric energy density. Lithium as an anode is ductile, hence the flexural stiffness is limited as well. Further approach to minimize inactive mass is to employ perforated aluminum current collectors on cathode side. This require a free-standing active cathode layer, such as dry film coatings or buckypaper. The scale up of these films has definitely improved over the last decade, but is still limited when considering Gigafactory scale.

To facilitate focused and high value materials research it is suggested that the scientific community should regard a Li-S cell in its entirety and consider the interplay of components and electrolyte on the cell level performance, possible approaches will be detailed below.[15,23,60]

2.3. Approaches to improve the Cycle life, Energy, Power and Safety of Li-S technology

Cycle life

So far, the most promising approaches to improve the anode/electrolyte interface have been the development of stable electrolyte systems [25,61] and the use of solid-state electrolyte coatings. [46,48,62] The realization of a stable lithium anode is crucial to extend the cycle life but it also provides the opportunity for improvements to specific energy, energy density, power performance, and safety. OXIS Energy are actively developing scalable lithium metal protection concepts to stabilize the lithium metal electrolyte interface within Li-S batteries and enable isolation of lithium metal from the electrolyte component in prototype cells. An example of a protected lithium electrode produced by OXIS Energy is presented in Figure 2, where the SEM image highlights the ability to plate dense lithium metal beneath a protection layer. Cell design is a critical parameter for conducting materials level research into lithium-based anodes, the use of small pouch cells has been of significant benefit to enable the use of realistic electrolyte volumes and stack pressure. For electrochemical testing, especially of lithium half cells, a minimum charge passed per step of 3 mA h cm^{-2}, with a minimum current density of 0.3 mA cm^{-2} should be implemented, with current densities >1.5 mA cm^{-2} targeted. The

electrolyte loading (E/S ratio) should also be minimized and kept below 2.0 µL mAh^{-1} of charge passed per step. Under these conditions the true impact of materials level developments can be clearly identified.

Energy (gravimetric vs. volumetric)

A careful and holistic cell design is the key to achieve high values of the gravimetric (Wh kg^{-1}) and volumetric energy density (Wh L^{-1}). [7,23,43,45] The energy density of Li-S technology is a key development metric, especially required for applications in which space is limited such as electric vehicles (EV). There are three main approaches to increase the energy density (Figure 2):

First (i), increasing the cathode density. Due to the low intrinsic density of both carbon and sulfur, the current electrode tap densities range approximately between 0.4 – 0.6 g cm^{-3}. Increasing this density values to > 0.7 g cm^{-3} while maintaining areal capacities higher than 4 mAh cm^{-2} enable an increase of energy per volume. Cathode densification will however significantly reduce the volume available for the uptake of electrolyte and might kinetically hamper the conversion mechanism, especially in electrolyte with high lithium polysulfide (LiPS) solubility. [23,63] Hence, the cathode density needs to be tailored in conjunction with the electrolyte development.

Second (ii), the electrolyte volume needs to be decreased for both gravimetric and volumetric energy density so that the conversion mechanism can take place while polysulfide shuttle and electrolyte depletion is minimized. The total electrolyte volume within a cell must be considered and limited. [24,25] Electrolyte densities can range from 1 – 1.5 g cm^{-3} depending on the conductive salt concentration [64] or if fluorinated solvents [25,61] are used. In order to tackle the issue of a low volumetric energy density (in Wh L^{-1}), the mass density of the electrolyte is less important than for the gravimetric energy density (in Wh kg^{-1}). [49] Reducing the content of

electrolyte from 3 to 1.5 µl or mg per mg of S active material [24] will decrease the weight of electrolyte and the free volume required for its uptake. This is of importance as in all known Li-S cell concepts the electrolyte may take a large fraction of the cell (> 40 % of the cell weight and volume [23,52]). The strategy on electrolyte development consequently involves:

(a) Development of an electrolyte with low polysulfides (PS) solubility [25,49,61,65] or redesign of the cathode/cell and the accompanied process adaption for the employment of solid electrolytes. These concepts have the potential to increase the reversibility of the system and sulfur utilization while reducing the required content of electrolyte as sulfur species mainly exist in the solid state.

(b) Development of a new generation electrolyte for Li-S cell enabling increased average discharge voltage.

(c) Thirdly, the reduction of lithium excess to only 20 % and hence, decrease the thickness of the lithium anode to app. 25 µm (corresponding to 5.15 mAh cm^{-2} usable areal capacity) is another important approach to reach higher values for both energy per mass as well as energy per volume. This can be done by further developing new coating techniques for the application of thin lithium metal films, such as melt-processing or physical vapor deposition (PVD).

Power

Only a few references investigate power capability from a holistic point of view at pouch cell level. It is widely accepted that Li-S technology is not going to compete with the most powerful Li-ion cells (with LTO or LFP chemistries, capable of cycling at very high C-rates). Nevertheless, the specific power (W kg^{-1}) obtained from a carefully designed OXIS Energy Li-S pouch cell [66] dedicated for power applications can be as high as 800 W kg^{-1} (for continuous discharge) or reaching up to 1500 W kg^{-1} at the peak (10 sec discharge at 90% SoC). Specific discharge peak power is strongly dependent on the SoC% and that is closely related with

internal chemistry/electrochemistry taking place in the cell while cycling, and it will be explained in more details further.

In order to increase the power density of a Li-S pouch cell, several components contribute to the internal resistance of a Li-S cell and need to be adapted (Figure 3): thinner electrodes reduce the length of lithium ion transport, an important kinetic factor. In addition, similar to Li-ion batteries (LIB) [67], micro-scale structuring or porosity in the cathode layer can be beneficial for higher power systems. Moreover, carbon additives offering a percolating network of electronic pathways increase power capability. [42,68] Importantly, electrolyte viscosity and Li^+ transfer numbers [69] are crucial parameters that need further development.

In contrast to LIBs, at medium state of charge (SoC), the ether-based standard electrolyte for Li-S batteries changes to a highly viscous gel-like state - caused by a) the increase of the Li-polysulfide (LiPS) concentration Li_2S_8 to 2 Li_2S_4 and b) the aggregation of lithium polysulfides of stoichiometry Li_2S_4 to form dimers and clusters. [70] As a result, the electrolyte resistance increases, and thus, the power density decreases. If the electrolyte content is very low, the formation of sparingly soluble LiPS solvate complexes also sets in. These clog the porosity of the cathode and thus strongly impair the ion transport as well as the power density. Furthermore, the deposition or conversion of the charge or discharge products (S_8 or Li_2S) is kinetically inhibited.[71] It is known that a certain amount of polysulfides is necessary to chemically "activate" the discharge product Li_2S. However, the high solubility of polysulfides in the electrolyte also produces the so-called polysulfide shuttle leading to reduced charging efficiency. [72,73] First promising approaches describe the suppression of polysulfide solubility in the electrolyte by the so-called "solvent-in-salt" concept. [74] In order to improve the insufficient ion transport capacity of the ether/Li-salt complexes, low-viscosity hydrofluoroethers (HFE) were investigated as co-solvents or diluents, since they interact very little with the Li ions.[75] The low solubility and mobility of LiPS in such systems poses new

challenges, since the conversion of the sulfur species is now bound to the surface of the porous cathode structure and does not occur rapidly in the liquid phase. Therefore, the kinetics of the reactions taking place at the phase boundary carbon - sulfur/Li_2S - electrolyte have to be understood and specifically optimized for the application as high performance battery. For example, it has been shown that the saturation of Li_2S_6 in the electrolyte can be drastically reduced compared to the reference system (DME/DOL) by using a sulfolane/fluoroether based solvent system and low conducting salt concentrations of 1.5 M. The electrolyte system has been successfully transferred from coin cells to prototype cells and demonstrated over 200 stable cycles at only 3.5 µL electrolyte per mg sulfur. [25]

It should be mentioned that higher areal currents generally lead to higher dendrite formation for unprotected lithium.[26,76] Consequently, a protected lithium electrode that can operate under high power conditions can significantly alter the cell design. From a prototype pouch cell point of view, tab geometry may also play an important role. In addition, packaging and sealing needs special consideration in regard of their employment in space and maritime environments.

Safety

OXIS Energy Li-S cell technology has been demonstrated to display superior performance to that of traditional of lithium ion technology under a number of safety tests, including nail penetration. [77] However, prototype cells recently produced by Fraunhofer IWS evaluating the stability of new electrolyte systems have found that specific electrolyte formulations designed to reduce the polysulfide solubility can significantly influence the safety characteristics. Safety tests of 5 Ah pouch cells have revealed that thermal stability is deteriorated by the use of the low polysulfide solubility sulfolane/hydrofluorether-based electrolyte [25] when compared with a traditional DME/DOL based electrolyte. Thermal runaway of the cells containing this electrolyte are thought to occur due to the direct and highly-exothermal reaction between elemental sulfur and lithium, the difference in safety of the cell type is due to the fact that less

polysulfides emerge from the cathode, and these are the polysulfide species that are crucial to passivate metallic lithium and prevent direct contact between sulfur and lithium. [37] Above a critical temperature of 125 °C, continuous self-heating may occur in cells containing this low polysulfide solubility electrolyte system. However, the development of a Nafion coated separator concept [78] has been identified as a solution approach and as an additional safety component. In this way, a closed Nafion layer applied on an Al_2O_3/polyolefin hybrid separator can prevent contact between the molten sulfur and the metallic lithium, and thereby increase the safety of emerging Li-S cell concepts employing low polysulfide solubility electrolytes (Figure 2).[79]

3. Integration of Li-S cell technology

In general, the integration of new battery technology to real world applications requires significant development from cell level up to module, pack and control systems according to the so-called validation and verification model (V&V model).[80] It means that the requirements at e. g. aircraft level translate into the system definitions at (sub-)component and prototype level. In addition, a strategy and concept for the integration of the cells or rather cell-packs need to be developed. The integrated cells/cell-packs are then evaluated in functional tests, and certification plus safety assessment are carried out to validate the developed concept and strategy.

Significant progress has been made in this direction for Li-S cell technology, and OXIS Energy has integrated its pouch cells into modules and demonstrator battery packs for evaluation in real-world application scenarios (Figure 1c-e). Development of Li-S modules and battery packs, designed to meet the power requirement profile of a specific application, so-called mission

profile, occurs through a series of stages from cell and system modelling up to bench testing under simulated conditions. OXIS Energy and its partners have developed advanced battery management systems (BMS) incorporating the most advanced State of Health (SoH) and State of Charge (SoC) estimators [73,81] for Li-S battery systems, a critical requirement for integration of Li-S battery technology into applications. [82]

Generally, Li-S technology is receiving increasing levels of research and development with efforts focused on performance aspects including cycle life, power performance, volumetric energy density and safety. [25,36,42,49,51,61–65,83] To meet the varying performance requirements of emerging applications, OXIS Energy has developed two cell product streams, each with optimised performance characteristics (Figure 1a,b). Application requirements can generally be divided into two sectors: 1) high energy focused with low power requirements (High Energy), and 2) moderate energy with the capability for sustained high power (High Power).

4. State-of-the-Art and Recent advances of Li-S Cell Modelling for State Estimation

Modelling for the purpose of battery management and state estimation has particular requirements in terms of execution speed and computational complexity.[84] The modelling techniques which have been developed for Lithium-ion batteries are not applicable for explanation of discharge phenomenon in Li-S cells. The flat open-circuit voltage curve of Li-S battery (illustrated in Figure 4) is a unique characteristic that demonstrates there is a problem in observing the SoC from voltage calculations alone.[85,86] The complex electrochemical pathways which exist in Li-S cell mean that short-term capacity can vary so 'Coulomb counting' is also ineffective for this particular cell chemistry. In response to the aforementioned problem, two families of estimation technique have been proposed for Li-S cell in the literature: (1) techniques derived from control and estimation theory, based on nonlinear variants of the Kalman filter,[81,85] and (2) techniques that come from computer science such as Adaptive

Neuro-Fuzzy Inference Systems (ANFIS) [86] and Long Short-Term Memory Recurrent Neural Networks (LSTM RNN). [87]

Although most of the research published in the literature are focused on Li-S SoC estimation, Li-S cell SoH estimation techniques are also under development from both control theory and computer science. Examples are the general framework describing Li-S cell SoH in terms of capacity fade and resistance growth which has been presented in [7], and the SoH estimation technique presented in. [88] Looking at the literature, Li-S cell degradation mechanism has been investigated by electrochemists in a number of studies; however, the literature suffers from lack of studies where Li-S cell SoH estimation is investigated for BMS application. Although an insight into understanding of the degradation mechanism in Li-S cells by using electrochemical models is quite helpful, but those models are hardly useable in real-time applications mainly due to their complexity. In online applications, quick models/estimators are required to generate 'good enough' results by providing a proper trade-off between accuracy and speed [89]. In fact, many details related to the electrochemical reactions taking place inside a cell, are not required to be analyzed in a real-time application. A couple of studies in the literature where Li-S cell degradation has been investigated by considering the practical application limitations are presented in [90] and [91].

All the aforementioned online state estimation techniques (both SoC and SoH) rely on equivalent circuit network (ECN) models. ECN model parameterization for a Li-S cell was performed in [82] and [92] for the first time. Since the aim of modeling in those studies was to implement the model in a real-time BMS, quick identification techniques were applied to extract the ECN model parameters. The identification results are then used for Li-S cell state estimation. For example in [86], the simplest form of an electric circuit battery model (i.e. internal resistance model) is parameterized and its parameters are used for SoC estimation. In that study, three inputs including open-circuit voltage (V_{OC}), ohmic resistance (R_O), and the

derivative of resistance with respect to SoC (dR_O/dS_{OC}) are used for SoC estimation using ANFIS method. As another example in [85], the Thevenin ECN model is parameterized and used in Kalman-variant estimators for Li-S cell SoC estimation.

5. Current and Future Applications for Li-S Battery technology

Among the future applications requiring high specific energy battery systems, a few examples are presented in Figure 5 and Table 1, where Li-S technology has the potential to play a significant role in enabling these applications to be successful.[14] Principally, the applications can be divided into few segments strongly depending on the technology adaption timing and power requirements.

5.1. Current and Future Application Demands

The current performance of Li-S cell technology is already sufficient for a number of emerging applications which require relatively low power and limited cycle life. There are a number of applications which, apart from demanding high specific energy, also have an increased demand for power. The power requirement is specific to the application and can depend on many factors such as system level requirements, battery configuration, energy of the battery pack, usage of the vehicle etc. A number of key applications areas for future battery technology are discussed in further subsections, starting with applications whose requirements are close to be fulfilled by the current Li-S technology and its TRL/MRL levels, and moving further, describing the applications which require further development of Li-S technology (in terms of power, safety, etc.) are stated. The latter are expected to incorporate Li-S batteries in the further future. Generally, for the implementation of batteries in drones or aircrafts, the design of the drone, the space for take-off and landing, and the respective flight modes need to be addressed. As for fixed-wing aircrafts/drones, more space for take-off and landing is required and the power

requirements are lower compared to rotor blade-based drones. The latter require higher power, but need less space for take-off/landing or rather hovering. So-called tilt-rotor blade allow both flight modes in one drone.[93]

5.1.1. Aerospace

A growing number of organizations around the world are developing HAPS/HALE aircraft, with a number of systems having already completed successful test flights. This emerging application requires high specific energy batteries to enable maintenance of high altitude flight at mid-high latitudes. HAPS aircraft are designed to circles in the stratosphere, approx. 20 km above the ground, in contrast to satellites, i.e. GEO (geostationary earth orbit) satellites which are in orbit about 36000 km away from earth and LEO (low earth orbit) satellites which are about 1200 km away [94] Thanks to that the launch and maintenance costs are much lower. Stratosphere offers mild weather conditions with little change in windspeed, which result in a stable flight. In addition, due to closer proximity to earth (compared to satellites) and greater compatibility with drones and other aircrafts in the stratosphere, it can be greatly beneficial for the next generation telecom system. [95]

For this application it has been suggested by HAPS vehicle designers that a high specific energy (> 400 Wh kg^{-1}), low to moderate charge & discharge rates (<C/5), and low to moderate cycle life (60-400) are required. The pack also requires low pressure tolerance (approximately 50 mbar) given its high altitude environment. [7] Significant progress has been made in the development of Li-S battery systems for HAPS/HALE applications, the Airbus Zephyr 7 aircraft utilized Li-S batteries produced by Sion power. Recently Airbus has announced that it is utilizing Amprius' silicon nanowire anode lithium ion battery technology for its Zephyr S and T models. [96] OXIS Energy is currently integrating its Li-S technology into HAPS vehicles. To maximize the benefit of high specific energy cells, the design of performant but lightweight

pack enclosures and control systems must also be considered. OXIS Energy has recently developed a high energy HAPS module at 380 Wh kg^{-1}, which achieves a 95% specific energy retention when moving from cell to module level.

5.1.2. Maritime

Autonomous underwater vehicles (AUVs) are a growing market and application area for high energy battery systems. AUVs are self-propelled, unmanned, underwater vehicles can be used for different purposes, such as survey platform to map the seafloor, to observe oceanographic fields, to name few. [97] The key requirements of this application are well aligned with Li-S technology today; high specific energy (> 400 Wh kg^{-1}) combined with low to moderate power requirements. The battery system must also operate at low temperatures (4 °C) and needs to be adapted to withstand high pressures (45 MPa eq. to 6000 m depth). AUVs usually aim to achieve neutral buoyancy, a recent study has identified that significant benefits to the overall system level performance can be achieved via the use of Li-S battery technology.[98]

5.1.3. Aviation

Depending on the drone, during take-off and hovering, high-power density is required. However, relatively low or moderate power is needed during cruise. The mission profile and system level requirements for flying applications vary significantly depending on the mission distance and altitude. Hence, mission profile specific testing of cells and battery systems must be carried out to gain valuable insight into system level performance. Generally, high specific energies (> 300 Wh kg^{-1}) and moderate power requirements (peak discharge at 1-2 C) are needed. Hybrid battery concepts comprising both a high power and high energy battery are possible as well. [99] Li-S technology may be incorporated into concepts in which a Lithium-

Polymer batteries are used for take-off & hover-mode and a Li-S battery operates as a range extender. [100]

5.1.4. Heavy Electric Vehicles

The major benefit of the use of Li-S technology for future eTrucks and eBuses applications is the ability for much lighter battery packs. Reduced battery weight can enable both extended range and increase payload, enabling greater distances between charging, especially important for locations where installation of significant charging infrastructure may not be viable. Future long range/high payload eBuses and eTrucks will have similar performance demands; a high specific energy (> 400 Wh kg^{-1}) at moderate continuous discharge C-rates 0.5-0.2 C and pulses of power in the range of 1-2 C. Energy density (Wh L^{-1}) is less important for this type of EV when compared to common passenger cars [101–104]. OXIS Energy has conducted mission profile specific testing of its cells and battery systems to gain valuable insight into system level performance of Li-S batteries for eBuses, with more details presented in section 5.2.

5.1.5. Future Urban Air Transport

At the extreme end of energy and power requirements lies the eVTOL (electric powered vertical take-off and landing) aircraft application, an application which demands >400 Wh kg^{-1} at sustained discharge rates of around 1-2 C along with peak power requirements of up to 4-5 C.[2] With the development of high energy and high power battery systems for this urban, manned application, safety is of critical importance. The development of Li-S cell technology to meet the demands of this future application sector is a key area of development for OXIS Energy.

5.2. Application case-study: Li-S battery for an electric city bus

Various works [105] have been carried out regarding the modelling of the Li-S cell chemistry within the past years. Continuous shuttle current measurement method for Lithium Sulfur Cells was developed by TU Munich in collaboration with Daimler AG in 2020 [106]. A simple analytical model of capacity fading for Lithium-Sulfur cells was published by Brno University of Technology in collaboration with OXIS Energy [107]. Three-dimensional image based modelling of transport parameters in lithium-sulfur batteries was carried out by UCL [108]. Electrochemical Impedance spectroscopy-based electric circuit modelling of Lithium-Sulfur Batteries during discharging was evaluated by Aalbourg University [109].

In a recently reported case-study [110], the application of a 19 Ah prototype Li-S pouch cell in an electric city bus was investigated. In that study, a Li-S battery pack was designed as an alternative for the existing Li-ion battery pack in a London city bus. Maximum power demand, required energy on board, weight and other required features of the Li-S battery pack were extracted from the existing electric bus. [101] Two existing Li-ion battery technologies were considered to be compared with Li-S: (i) $LiFePO_4$, and (ii) $Li_xNi_yMn_zCoO_2$.[102] Based on the Irizar electric city bus battery pack's specifications [103], there is 282 kWh energy on board when the battery is fully charged. The sizing of the Li-S battery pack was then performed in a way to have same amount of energy. Consequently, the number of Li-S cells in series and parallel were calculated and after that, the pack was simulated to investigate its performance in such an application. Millbrook London Transport Bus (MLTB) cycle [104] was used in the simulations as a standard test procedure. Figure 6 shows a case-study where the proposed Li-S battery pack was simulated in an electric bus. In that figure, battery SoC, current and terminal voltage are shown during MLTB simulation. [110]

Figure 7 shows the range of an electric city bus over the MLTB cycle [104] using different battery technologies. In that figure, all battery packs had same amount of energy (kWh) but they were different in weight depending on the cell's energy density. As shown in Figure 7, the EVs range

will increase remarkably when Li-S battery technology will be used instead of the existing Li-ion battery technologies just because of battery light-weighting. [110] This result can become even better because the Li-S prototype cell that was used herein had only a moderate energy density of 290 Wh kg^{-1} whereas this number is expected to increase to 400-600 Wh kg^{-1} in the next generations of Li-S cell.

The results presented in [110], is not just about simulation; a 19Ah Li-S cell was actually tested under MLTB driving cycle condition. Although the whole Li-S battery pack was not built/tested, scaled-down tests were conducted on single cells under conditions representing the real-word driving cycles. Figure 8 illustrates current profile and cell's terminal voltage measurement during MLTB test, performed on a 19Ah Li-S cell. Regenerative braking was also considered in the real tests by applying both charge-discharge current values (the negative current demand in Figure 8 represents regenerative charging).

6. Outlook and Conclusion

Looking forward to the evolution of electric powertrains, new generations of battery technology are currently being developed to meet the requirements of emerging applications in terms of cycle life, safety, power, and scalability. Further material level developments are required to realize the full potential of Li-S technology and the academic research community has a key role to play in achieving this. However, materials level research must be conducted within the context of a viable Li-S cell system. Li-S technology has the potential to offer cell level specific energy of up to 600 Wh kg^{-1} and thereby enable key performance benefits such as extended range and payload for emerging applications.[1] When these key performance benefits are considered together with the low cost, availability of materials, stability of supply chains and demonstrated high TRL/MRL, it is unsurprising that Li-S battery systems have been identified

both by academics and industry leaders as a key enabling technology for future electric vehicle applications. [12,15,23,33]

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Figures



(b)

Cell Type	High Energy Cell	High Power Cell
Cell Part Number	POA000412	POA000343
Gravimetric Energy Density	400 Wh/kg	300 Wh/kg
Nominal Capacity	16 Ah	19 Ah
Max. Discharge Rate (Continous)	1C	3C
Capacity Retention at 1C (% of nominal)	44%	79%
Dimensions (W x L x T)	78 x 145 x 10 mm	118 x 151 x 10.7 mm
Weight	85 g	141 g
Targeted markets	HAPS	aviation, eBus, eTruck, eVTOL

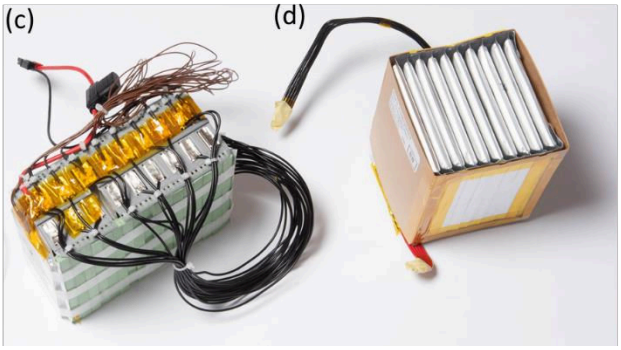




Figure 1. Picture of OXIS Energy Li-S Pouch cells available in different form factors (a) and more detailed characteristics of High Energy and High Power prototypes (b). Pictures of representative modules assembled from High Energy (c) and High Power cells (d) along with an example of a prototype battery pack (e).

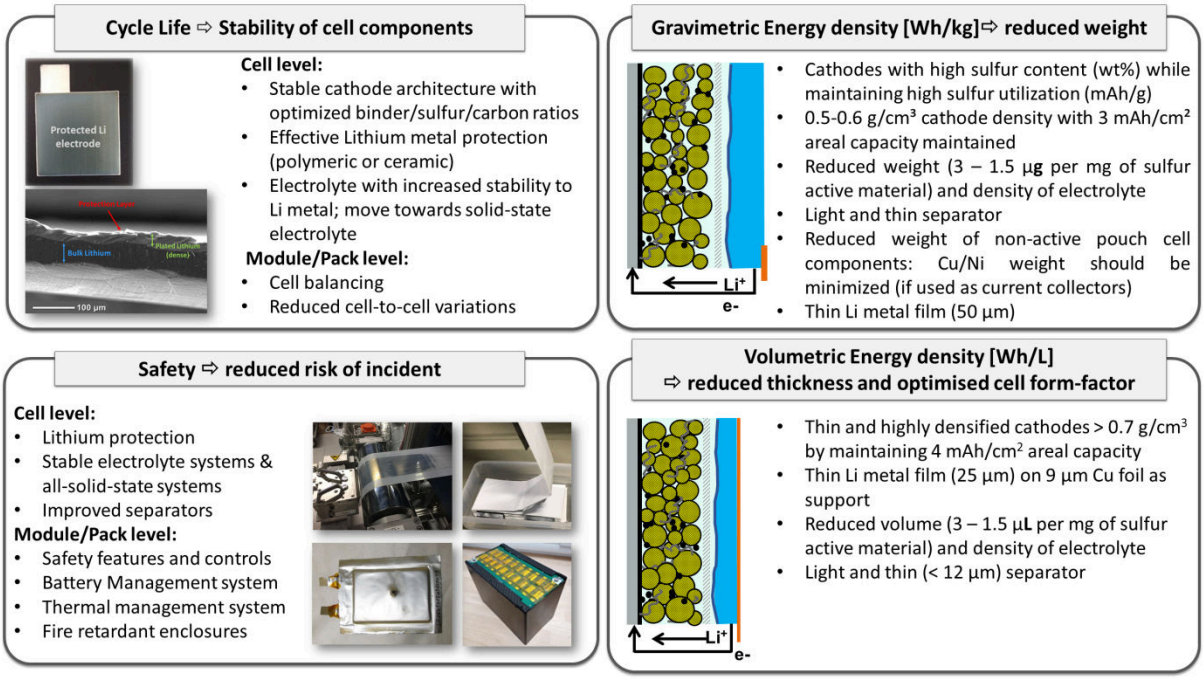


Figure 2. Key factors affecting the main performance characteristics of Li-S pouch cell technology, from materials to system level.

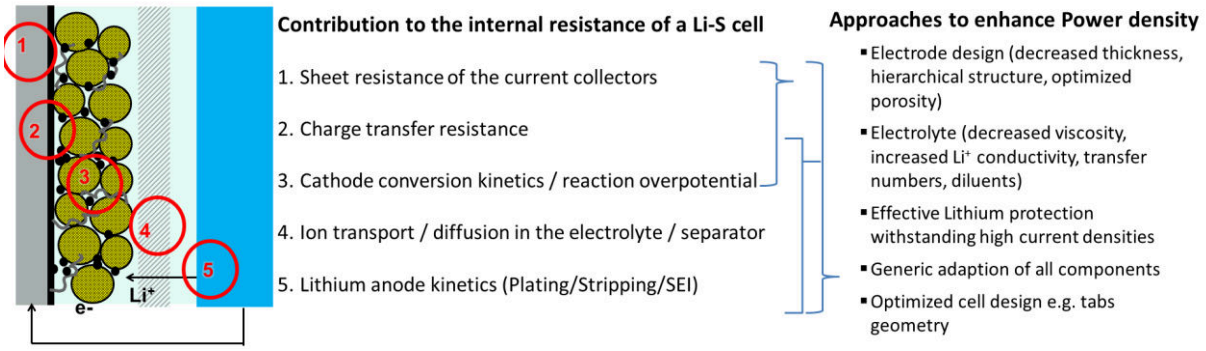


Figure 3: Illustration of which Li-S cell components the internal resistance should be reduced in order to achieve higher power densities

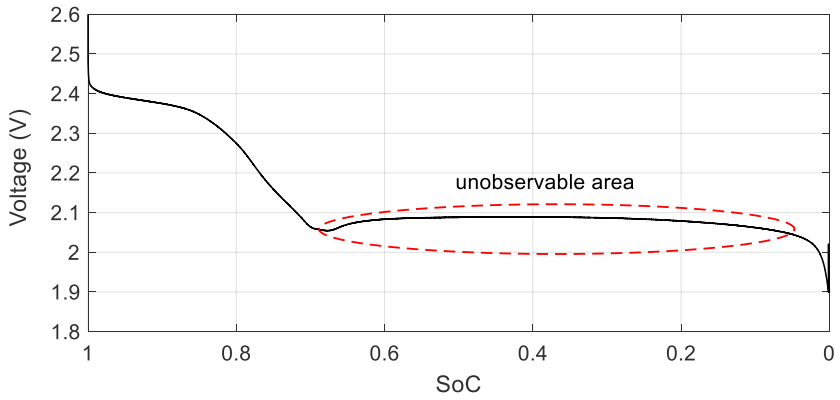


Figure 4. Flat voltage encountered in discharge. This is an example of one of the key differences between many present-day technologies and Li-S. It is hard to determine state of charge from voltage alone because this curve is relatively flat.

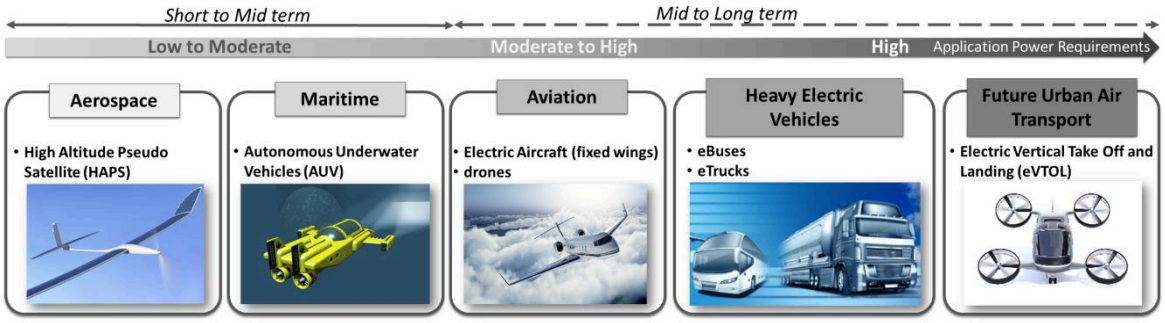


Figure 5. Illustrative schematic demonstrating main markets suitable for Li-S technology now and in the future.

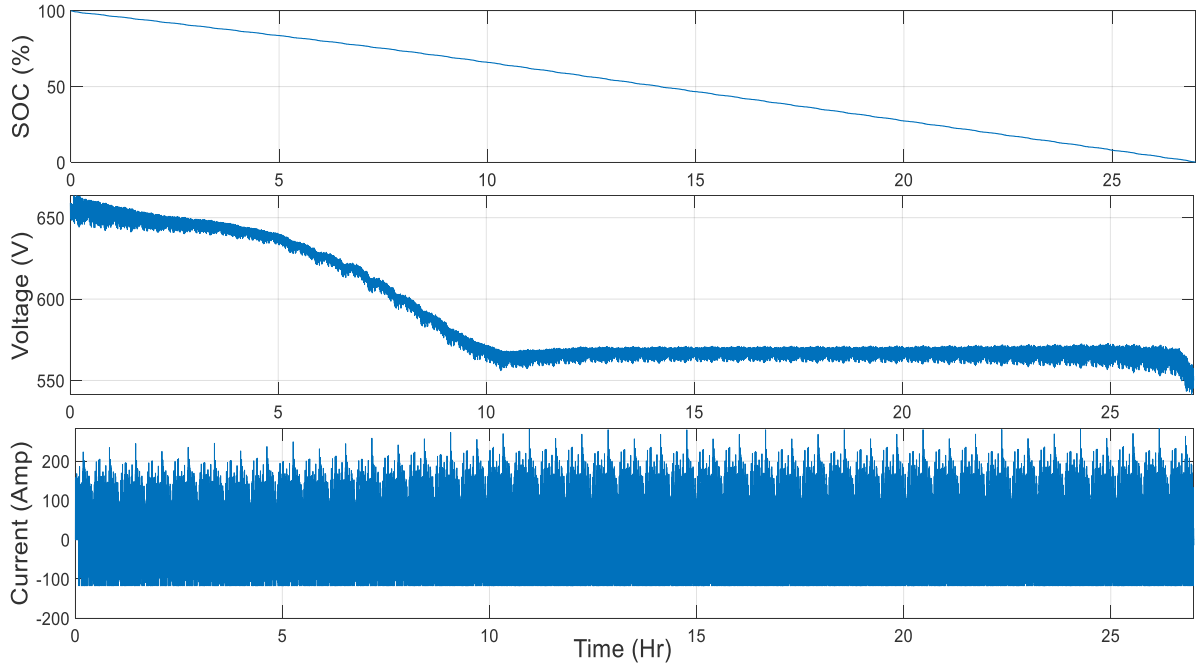


Figure 6. Li-S battery pack SoC, current and terminal voltage during MLTB simulation case-study [110]

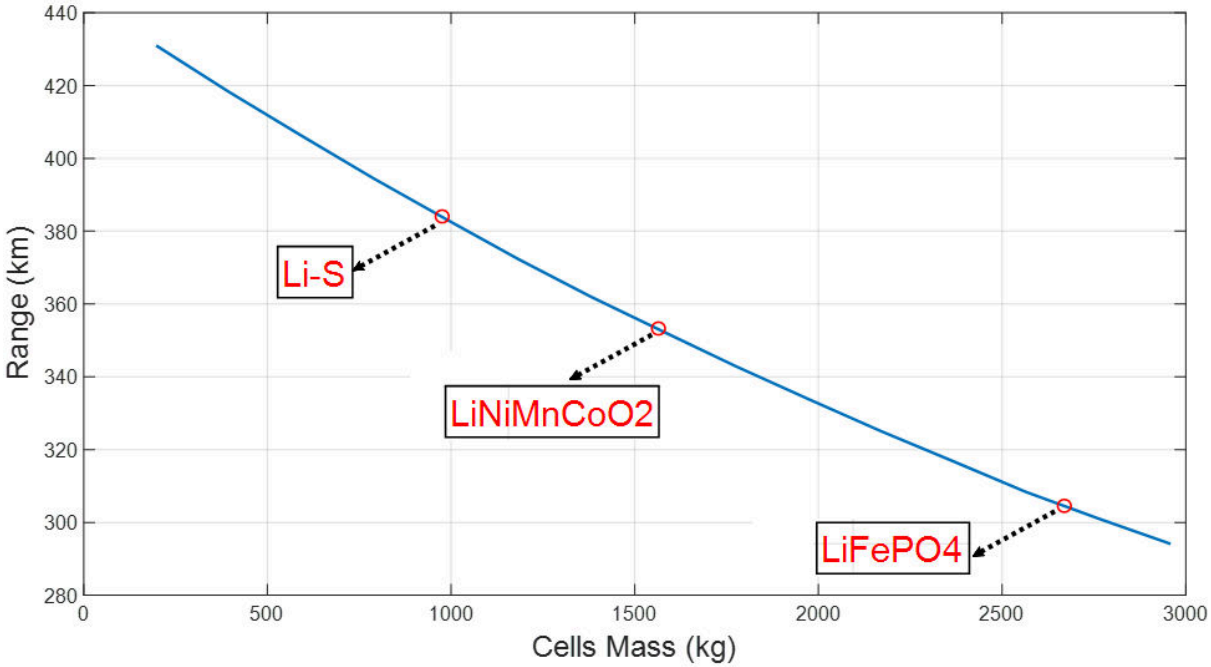


Figure 7. Range of an electric city bus over repeating MLTB cycle using different battery technologies – all battery packs have same amount of energy (kWh) but they are different in weight depending on the cell's energy density [110]

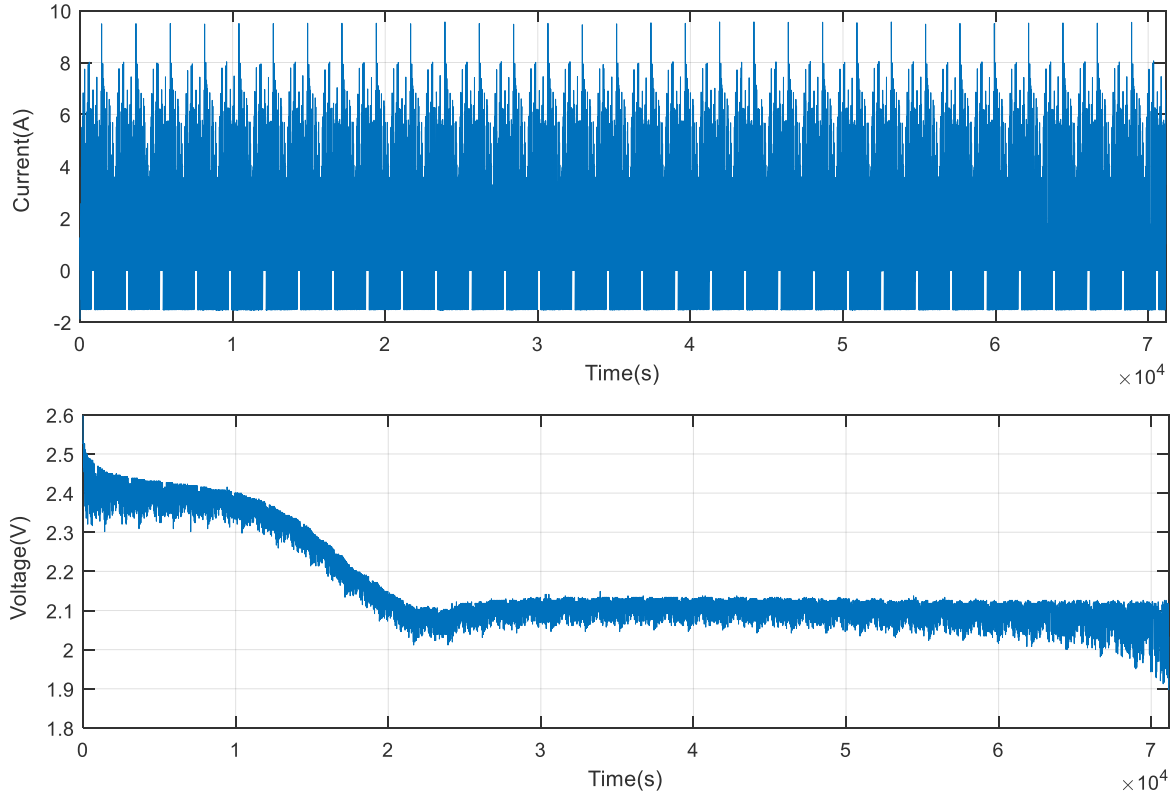


Figure 8. Current profile and cell's terminal voltage measurement during MLTB test, performed on a 19Ah Li-S cell [110]

Table 1. Illustrative schematic demonstrating main markets suitable for Li-S technology now and in the future with the required values for specific energy, C-rate, cycle life, environment, and remaining challenges

[21](Future) commercial vehicle	Aerospace	Maritime	Aviation	Heavy Electric vehicles	Future Urban Air Transport
Examples	High altitude pseudo satellites (HAPS)	Autonomous underwater vehicles (AUV) 2	Electric aircrafts (fixed wing) drones	eBuses eTrucks 4	Electric vertical Take Off and Landing (eVTOL)
Required E_{grav}	> 400 Wh kg^{-1}	> 400 Wh kg^{-1}	> 300 Wh kg^{-1}	> 400 Wh kg^{-1}	> 400 Wh kg^{-1}
Required continuous discharge rate	<*C*/5	~ C/10 – 1 *C*	Peak discharge at ~ 1 – 2 *C*	Peak discharge at ~ 1 – 2 *C*	4 – 5 *C* for take-off / landing ~ 1 – 2 *C* during cruise
Cycle life	60-200 cycles	60-200 cycles	200-500 cycles	1000 cycles	500 cycles
Environmental requirements	10-40 °C Low pressure (50 mbar)	Low temperature (4 °C) High pressure (45 MPa)	-10 – 60 °C	-10 – 60 °C	-10 – 60 °C
Main remaining challenges	-	-	Cycle life (> 500) Safety regulations	Cycle life (> 1000) Safety regulations	Fast discharge (4-5 *C*) whilst retaining 400 Wh kg^{-1} Fast charge (1-2 *C*) Cycle life (> 500) Safety regulations Enhanced thermal management



Dr. Susanne Dörfler studied chemistry and received her Ph. D. in the field of vertical aligned carbon nanotubes for supercap and lithium sulfur battery electrodes from the University of Technology Dresden in 2013. She then led a junior research group financed by the European Social Fund in the field of LiS batteries. Since 2016, she has been working as a group manager "Battery and Electrochemistry" at the Fraunhofer Institute for Material and Beam Technology in Dresden. Her main research topics are material development, establishing structure-property relations between the respective materials, electrolytes, and their electrochemical performance.



Dr. Jacob Locke received his Ph. D. in the field of silicon nanowire-based negative electrodes for high energy lithium-ion batteries from the University of Southampton in 2015. Since joining OXIS Energy in 2015, he has been involved with a number of Innovate UK funded projects developing electrolyte and negative electrode materials for future generation Li-S cell technologies. He currently leads the anode development team at OXIS Energy Ltd as a principal scientist.



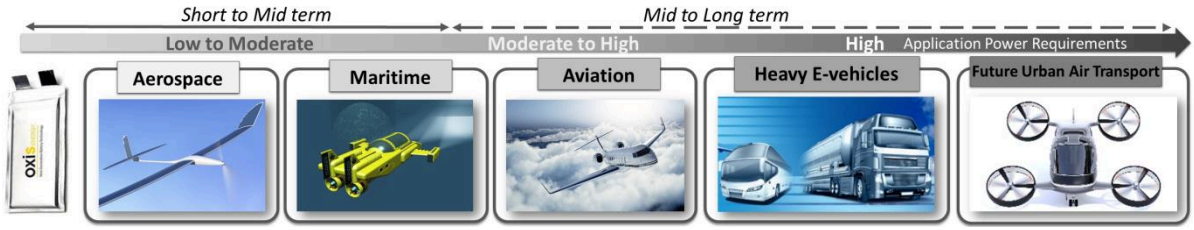
Dr. Abbas Fotouhi is a lecturer (assistant professor) in Advanced Vehicle Engineering Centre at Cranfield University. His expertise are dynamical systems modelling, simulation, optimization, and control. He has also extensive practical and algorithmic experience of applying AI and Machine Learning techniques in engineering problems. His current research is focused on electrified powertrain systems, energy storage technologies, intelligent cars and transportation systems. His total writing portfolio lists over 40 articles. Dr Fotouhi is an editorial board member of Neural Computing and Applications Journal and he is a fellow of the UK Higher Education Academy.

Herein, the advantages, limitations and progress of Li-S batteries are described. Approaches to extend cycle life, energy, power, and safety are further discussed. In addition, recent advances regarding modelling and battery management of Li-S batteries are summarized, and the requirements for as well as the integration of Li-S batteries in present and future real world applications is elaborated.

Keyword: Lithium sulfur battery applications

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Progress on Major Application Areas for Lithium-Sulfur Battery Technology



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Recent progress and emerging application areas for lithium-sulfur battery technology

Dörfler, Susanne; Walus, Sylwia; Locke, Jacob; Fotouhi, Abbas; Auger, Daniel J. ...

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