Advanced Lithium-Sulfur Batteries Based on Lyten 3D Graphene™

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Abstract

Li-S batteries promise significant advantages over Li-ion batteries but have been hampered by poor cycle life caused by polysulfide shuttle. Lyten, an advanced materials company, has developed new 3D Graphene™ material with mechanically flexible and electrically conductive framework, and hierarchical porous structure designed for potentially confining sulfur and polysulfides and mitigate polysulfide shuttle. Lyten 3D Graphene™ materials have shown enhanced sulfur utilization in Li-S cells far superior to the commercial nanocarbons, and upon integration with Lyten's new protected Li anodes, advanced electrolytes, and multi-functional separators have resulted in Li-S cells with specific energy comparable to current Li-ion cells (~250 -275 Wh/kg). The cycle life is, however, relatively modest with 300 cycles @ 100% DOD, C/3 in coin cells, and 150 cycles@100% DOD and over one thousand cycles @ 50% DOD in multi-layer pouch cells and 18650 cylindrical cells. There is a steady growth in both these categories enabled by further tuning of 3D graphene and advances in other materials. Preliminary safety tests performed on early prototype cells have yielded surprisingly good results for the Li-S cells containing Li metal anode.

Keywords

Lithium-sulfur cells; 3D graphene; polysulfide shuttle; abuse tolerance; specific energy; high-capacity sulfur cathode; multi-layer pouch cells; 18650 Li-S cells, green technology; abundant and inexpensive raw materials.

Introduction

With the projected need for a large number of Li-ion batteries (LIB) to support rapidly expanding EVs, there are serious challenges from the availability and supply of key materials (e.g., Co and Ni), which are exacerbated by the relentless control of Asian countries on the processing of these critical materials, and their overwhelming dominance in battery manufacturing. It is expected that these issues will impact critical DoD applications that require high energy batteries, making it strategically disadvantageous for the US government. Additionally, the future EVs and DoD applications demand battery technologies with higher specific energy and energy density, beyond the capabilities of LIB. Lithium - sulfur (Li-S) batteries are the leading candidates among the next generation high energy systems to supplement or supplant LIB. Unlike other high energy systems with NMC cathodes, Li-S chemistry has the distinct advantage of being unaffected by the criticality and scarcity of raw materials (e.g., Co, Ni and Mn), and is benefited by a robust supply chain and stable pricing for the key materials. Li- S cells can potentially offer 2-3-fold higher specific energy compared to LIB at significantly lower cost and have better compliance with environmental regulations and a significantly reduced carbon footprint.[1] Despite their numerous advantages, the implementation of Li-S batteries in practice has been impeded by their classic problem of 'polysulfide (PS) shuttle', which is a result of PS dissolution in liquid electrolyte, and is primarily responsible for poor cycle life.[2]

Lyten, an advanced materials company founded in 2015, has developed Lyten 3D Graphene™ (3DG) from methane cracking that has a flexible, electrically conductive framework and a hierarchical porous structure to accommodate high proportions of sulfur. Lyten's patented[3] reactor technology allows fine tuning of key parameters of 3D graphene such as porosity, surface area, conductivity, surface energy etc., to create a novel host for sulfur cathode that can support facile sulfur reduction and potentially sequester polysulfides within the cathode structure through "nano-capture". Figure 1 shows the nano-phase features of Lyten 3D graphene through a SEM image of a 3D graphene-sulfur cathode made with proprietary post-synthesis processing, lithium infusion and finally casting electrodes using industry-standard fabrication methods and equipment.

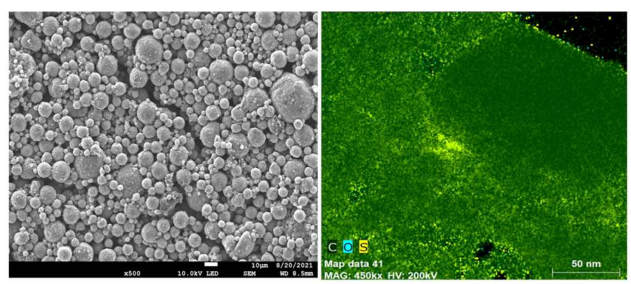


Fig. 1 SEM of Lyten 3D Graphene-sulfur cathode (left) and uniform distribution of sulfur in the cathode from SEM_EDS (right)

Lithium-sulfur chemistry is rather complex not only due to the sulfur cathodes, but due to the challenges from the lithium anode, which include severe morphological changes, dendritic deposition, and continued electrolyte consumption in the form of SEI formation. Lyten's Li-S cell development is thus focused on developing multiple components: i) 3D graphene tuned chemically and for appropriate nano/micro porosity, ii) 3d graphene sulfur composite cathodes with high areal capacity (mAh/cm^2), iii) protected Li anodes for dendrite-free cycling, iv) electrolytes compatible with Li anode and sulfur cathode kinetics, v) multi-functional separators and vi) energy-efficient cell designs, both multi-layer pouch cells and cylindrical 18650 cells.

Tuning of 3D Graphene

The unique morphology, surface characteristics and tunability of Lyten 3D graphene nano carbons have rendered them impressive performance compared to the commercial nano-porous carbons commonly used in Li-S cells (Fig.2).

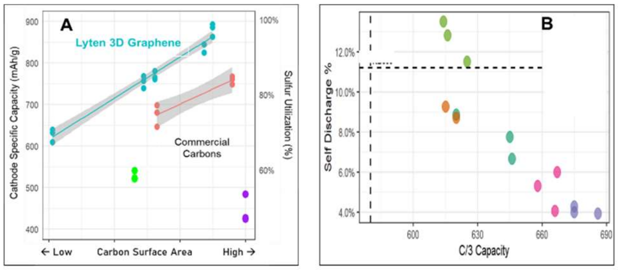


Fig. 2 Superior performance of Lyten 3D graphene-sulfur cathodes compared to the commercial analogs: A) Discharge @ C/20 and B) Self-discharge over one week at 100% State of charge.

As shown in Fig. 2, both sulfur utilization and self-discharge are distinctly superior for Lyten 3D graphenes, with the sulfur utilization improving by 15% and self-discharge decreasing to 30%, compared to the best commercial analog.

Protected Li Anode

Designing a stable Li anode is more challenging in Li-S cells compared to other Li metal batteries due to the adverse effects of polysulfides in forming insulting lithium sulfide films on the anode. Lyten has developed new protected Li anodes incorporating modifications both in the bulk composition and interfacial conditions, which have led to noticeable improvements in the cycle life of Li-S cells. Fig. 3 shows the cycle life of Li-S coin cells with different anodes and high sulfur loading cathodes during 100% DOD cycling at C/3, and the improvement of rate capability with a 3D anode.

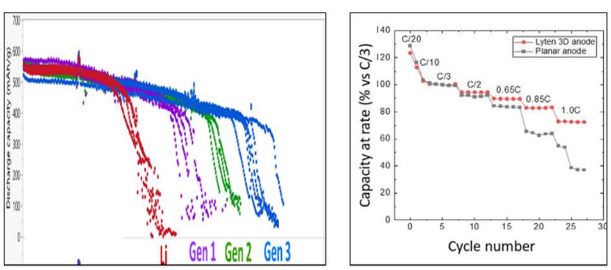


Fig. 3. Various innovative anodes, Gen-1, Gen-2 and Gen -3, displaying progressively increasing cycle life in Li-S coin cell vs. Li anode. The new 3D anode (Right) shows improved high-rate performance (1C)

As shown above, there is progressive improvement in cycle life from Li anode through the various generations of anode, and an improvement in the high-rate performance with our first generation of 3D Li anode.

Advanced Electrolyte

Since sulfur undergoes solid-liquid-solid reaction in our current design with liquid electrolytes, the choice of electrolyte is very crucial not only in achieving adequate stability at the anode, but also to support sulfur reduction kinetics at the moderate to high discharge rates ($\geq$C/3). Another requirement for the electrolyte is that it needs to enable the cells to operate with low electrolyte quantity i.e., electrolyte to sulfur ratio (E/S), which is crucial in realizing high specific energy. Unlike Li-ion cells, electrolyte indeed contributes to ~50% of the cell mass and it is a challenge to bring it down, especially with cathodes with high sulfur-loadings. Lyten has investigated hundreds of binary and ternary formulations with different salts and additives and identified a family of electrolyte formulations that outperform the electrolyte formulations commonly used in the literature. Fig. 4 shows the performance of some of these electrolytes in coin cells with the Li anode, and in pouch cells with Gen-1 or Gen-2 anodes containing low E/S.

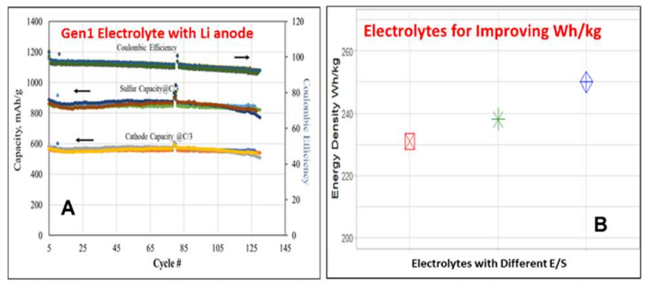


Fig. 4. Performance of Lyten's advanced electrolytes in Li-S cells: A) In coin cells with Li anode, B) In pouch cells enabling low E/S for improving specific energy.

Multi-layer Pouch (MLP) and Cylindrical 18650 Cells

Lyten has developed high-energy cell designs in both cylindrical and pouch format. Two key design parameters to realize high specific energy in a Li-S cell are: i) low E/S and ii) high sulfur loadings (Fig.5)[4], both of which pose challenges for achieving long cycle life.

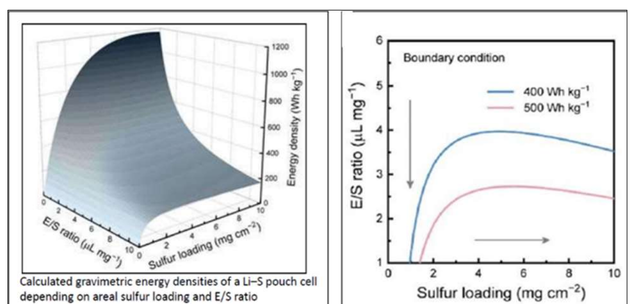


Fig. 5.High specific energy of a Li-S cell dictated by low electrolyte content (E/S) and high sulfur loading (Yang et al., Electrochemical Energy Reviews (2018) 1, 239-293.

Lyten has developed 3D graphene-sulfur cathodes with new binders in smaller proportions, high sulfur loadings and high areal capacities (mAh/g), and high-energy cell designs with minimal excess anode capacity (low N:P ratio) and low quantities of electrolyte (low E/S ratio). These advances have culminated in Lyten Li-S cells with high specific energy (275 Wh/kg), on par with current Li-ion cells. The cycle life in MLP and 18650 cells is currently shorter, at ~150 cycles at 100% DOD, in contrast to the 300 cycles realized in coin cells, and improvements are underway to close this gap.

Partial DOD Cycling

Similar to other battery chemistries, e.g., aqueous Ni rechargeable batteries or LIB, Li-S cells also provide longer cycle life at partials DODs. Partial DOD cycling is adopted in several applications, especially satellites to extend the cycle life and operational life of batteries. Our early version prototype cells that have lower specific energy have demonstrated ~600 cycles at 40% DOD and ~1200 cycles at 20%. We have been able to achieve similar benefit from partial DOD cycling in our recent high-energy cell designs (Fig. 6).

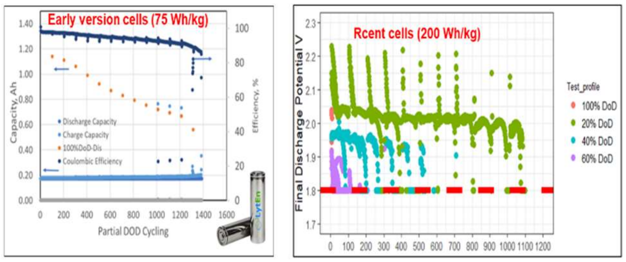


Fig. 6 Cycling of Lyten's early version 18650 Li-S cells at 20% DOD (left) and of recent high energy cells at variuos DODs.

Based on the extrapolation from the Wohler curve between cycle life and DOD, we expect to get >1000 cycles at 50% DOD and >2000 cycles at shallower DOD in our recent high-energy cells.

Safety of Lyten Li-S cells

Another notable advantage of Lyten Li-S cells is their superior abuse tolerance, compared to LIB, during electrical, mechanical, and thermal abuse. Though Li-S cells, like other Li metal batteries, are suspected to be less safe due to metallic Li, the safety of Lyten Li-S (1.5 Ah) multi-layer pouch and 18650 cylindrical cells has been surprisingly good as demonstrated in our preliminary abuse tests: nail penetration simulating internal short, external short, overcharge, over-discharge, and mechanical crush test (Fig. 7, only nail penetration and overcharge are shown).

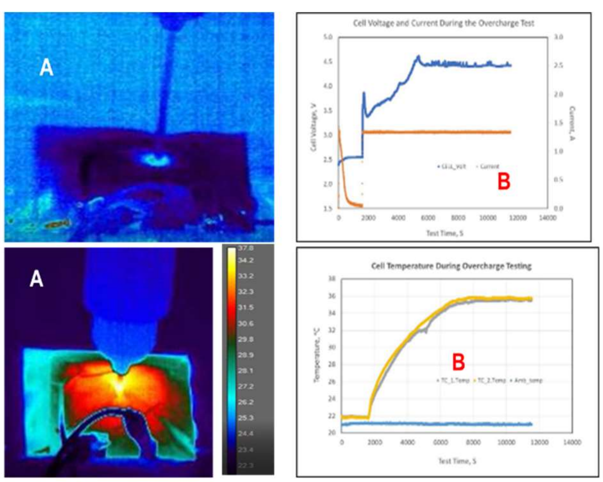


Fig. 7 Safety tests on Lyten Li-S cells (1.5 Ah): A) Nail penetration and B) Overcharge

There is no flame, smoke, charring, rupture, or thermal runaway in any of these abuse tests, underlining the innate safety of Lyten Li-S cells. This behavior is consistent with previous studies in literature. For example, nail penetration tests conducted on Oxis's MLP Li-S cells by Offer et al[4] reveal that the cells could survive nail penetration well, while also maintaining the cell voltage. This is possibly due to the non-conductive reaction products such as Li_2S_2 and Li_2S formed locally at the penetration site during high current events, which insulate the short circuit and allow the cell to behave normally. Alternately the soluble polysulfides formed locally may make the electrolyte viscous, less conducting and limit the reaction. The overcharge tolerance of Li-S is also consistent with the studies by Huang et al.[5] and is attributed to the disproportionation reaction of long-chain lithium polysulfides and the absence of oxygen evolution from the cathode. Fig. 8 summarizes the results of various safety tests performed on MLP and 18650 cells.

Electrical	External Short	Rapid drop to 0V	pouch	1.90 Ah	No damage/fire, T_{max} = 26 °C
			18650	1.03 Ah	No damage/fire, T_{max} = 37 °C
	Over charge	1C Charge until > 200% SoC	pouch	1.87 Ah	No damage/fire, T_{max} = 32 °C
			18650	1.36 Ah	No damage/fire, T_{max} = 93 °C
	Over discharge	1C Discharge	pouch	1.85 Ah	No damage/fire, T_{max} = 26 °C
			18650	1.24 Ah	No damage/fire, T_{max} = 37 °C
Mechanical	Nail Penetration	3 mm Nail puncture at 10 mm s^{-1}	pouch	1.86 Ah	No damage/fire, T_{max} = 35 °C
			18650	1.43 Ah	No damage/fire, T_{max} = 62 °C
	Ball Crush	51 mm Sphere at 2 mm s^{-1}	pouch	1.75 Ah	No damage/fire, T_{max} = 27 °C

Fig. 8. Summary of abuse test results on Li-S MLP/18650 cells.

As shown above, there is no flame, smoke, charring, rupture, or thermal runaway or any damage except for a small rise in temperature, in any of these abuse tests. More recently, thermal runaway tests performed on similar Oxis cells show the absence of runaway behavior during thermal ramp tests even up to 300ºC, especially in cells with lean electrolyte.[6] We are planning to perform a full suite of safety testing including ARC (Accelerated Rate Calorimetry) on larger prototype cells (4-5 Ah) to be fabricated in-house.

Prototype Cell Manufacturing

Concurrent with the on-going material and cell development for enhanced performance and safety demonstration, semi-automatic cell assembly lines have been installed and are being commissioned to manufacture prototype cells at a rate of about 100k/y cells of both cylindrical (18650/2170/ 26650) and pouch cells of 10 Ah. The pilot scale assembly lines have a projected total capacity of 2.4 MWh/y) (Fig. 9).

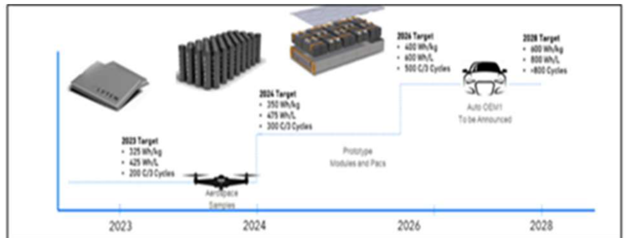
Fig. 9. Pilot lines for assembling MLP (10Ah) and 18650/ 2170/ 26650 cylindrical Li-S cells

Cell fabrication processes of Li-S cells are similar to LIB, and involve the standard processes of electrode coating, electrolyte filling and cell sealing, which allowed us to adopt conventional equipment used for the assembly of LIB cells in our pilot cell assembly lines. Additionally, multiple battery tester units (Maccor and Arbin) with >3000 test channels have been set up for cell formation and cycling.

Lyten's Li-S Roadmap

Subsequent to a successful manufacturing of prototype cells on the in-house pilot scale assembly lines for MLP and cylindrical cells, Lyten is planning to set up a mini-GW plant, which will enable us provide samples to various boutique customers, e.g., aerospace and niche DoD applications, such as drones, UAVs, CubeSats and Smallsats. Lyten plans to infuse their Li-S battery technology into various civilian and commercial applications, which will supplement or drive additional production volumes in domestic markets, as the performance levels match the requirements of these applications. As the technology is matured for large-scale implementation in commercial (EV) and a range of DoD applications, one or two GW factories will be planned within US at strategic locations. Detailed lists of BOM and assured and redundant suppliers are being established for the materials and components. Fig. 10 shows the roadmap, both for technology and production, for Lyten Li-S batteries over the next few years.

Lyten's Li-S technology will alleviate supply chain challenges, sole source dependency concerns, variable procurement practices, and prohibitive costs associated with the current battery technologies. Being a domestic manufacturer, Lyten will be a reliable and robust source of rechargeable batteries, which is critical importance to the US defense industrial base.



Scale	Low volume	Low volume San Jose semi-auto pilot line (2MWh)	Medium volume production Small Gigafactory (1-2 GWh)	High volume production First Large Gigafactory
TRL	3 - 4	5 – 6	7 – 8	8 - 9
Customers	Commercial samples Auto OEM A-sample	Select commercial Samples Auto OEM A, B-sample Commercial aerospace samples	Targeted commercial customers Auto OEM A, B, & C-samples EVTOL customers	Targeted customers Auto OEM customers EVTOL customers

Fig. 10. Lyten Li-S Cell performance and production roadmap

Acknowledgements

The authors acknowledge the US Space Force and DIU for partially funding part of this work.

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