Synergy

Lithium-Sulfur Batteries for Commercial Applications

Lithium-sulfur (Li-S) batteries hold great promise as energy storage systems because of their low cost and high theoretical energy density. Here, we evaluate Li-S batteries at a system level for the current most critical and challenging applications.

Battery technologies play key roles in transforming societal development in a more sustainable way. As highly efficient energy storage systems, batteries are participating in an energy-ecological evolution through their expanded applications spanning from portable electronics to electric vehicles (EVs) to grid-scale energy storage. Through the transition from internal combustion engines (ICEs), which burn nonrenewable gasoline and diesel, to the purely electricity driven, the consumption of fossil fuels and the emission of greenhouse gases by road transportation can both be significantly reduced. Such a transition has become a global trend, given that many countries (including Norway, the Netherlands, and the UK) have announced their prohibition of the sale of fuel-based vehicles by the middle of 21st century, and various automobile manufacturers have successively echoed this sentiment with their plans for automobile electrification. Beyond that, battery technologies also significantly affect global energy markets. Given the variable and intermittent nature of solar and wind energy, battery technologies serve as a powerful means of bringing these clean and cost-effective energy sources to everyday use by storing and integrating renewable generation into the electricity grid, which helps to liberate us from our heavy reliance on fossil fuels and move toward energy sustainability. Notably, both the electrification of road transportation and grid-scale energy storage strongly rely on breakthroughs in battery technologies.

Lithium-ion batteries (LIBs) have dominated the electrical market for the past few decades and continue to outperform the competition for EV applications. However, as LIBs approach their theoretical limits with a stubbornly high cost, both academic and industrial communities are seeking new battery chemistries that go beyond lithium-ion intercalation in response to the ever-growing energy demand. In this context, lithium-sulfur (Li-S) batteries based on a conversion mechanism hold great promise. The coupling of metallic lithium and elemental sulfur enables a theoretical energy density of 2,500 Wh/kg, which is nearly four times more than LIBs can currently achieve. In addition, the natural abundance, excellent geographic distribution, and environmental benignity of sulfur make Li-S batteries a green and low-cost alternative. More importantly, the closed Li-S system, similar to that of LIBs, favors an easier and cost-effective transition from LIBs to Li-S batteries in terms of battery manufacture and thus makes it more commercially viable than the open lithium-air system. Recent advances in Li-S batteries are beginning to make their commercialization possible, yet it remains unclear whether Li-S batteries are ready to enter the electricity market to compete with mainstream LIBs. Here, we evaluate Li-S batteries at a system level with regard to the current most critical and challenging energy storage applications, i.e., automotive and stationary energy storage batteries (AESBs and SESBs, respectively) (Figure 1).
Energy Density

Regarding automobiles, although many manufacturers, including Tesla, Nissan, and BYD, have already started their EV mass production based on LIBs, it is worth noting that LIBs store only one-hundredth the energy of gasoline in an equivalent mass,\textsuperscript{4} which precludes EVs from reaching a driving range (usually fewer than 100 miles) comparable to that of conventional ICE automobiles (over 400 miles). Therefore, energy density is one of the first-class technical criterions for AESBs. In this regard, Li-S batteries give good results because of their intrinsically high energy density. Here, we calculated the difference in energy density between LIBs and Li-S batteries at a system level to allow a more practical evaluation of their implementation as AESBs. We adopted the LiCoO$_2$-graphite configuration to represent LIBs and based the calculation on several assumptions: (1) the mass and volume of the separator, current collector, binder, and package are excluded; (2) the densities of electrolytes are 1 g/cm$^3$; (3) the space for sulfur volume variation (80%) is reserved for the cathode, and there is no volume variation for LiCoO$_2$; (4) the sulfur/carbon weight ratio is 4:1, and there is no carbon additive for LiCoO$_2$; (5) the electrolyte/sulfur weight ratio is 3:1, and the electrolyte/LiCoO$_2$ ratio is 1/3; (6) lithium and graphite excesses are 50% and 10%, respectively; (7) the average voltages are 2.15 and 3.8 V for Li-S and LiCoO$_2$-graphite, respectively; and (8) the specific capacities are 1,675 mAh/g for sulfur, 3,860 mAh/g for lithium, 140 mAh/g for LiCoO$_2$, and 350 mAh/g for graphite.

The calculation showed that the Li-S configuration holds more than twice the gravimetric energy density of LIBs (734.0 versus 300.0 Wh/kg) but has a lower volumetric energy density (682.3 versus 727.5 Wh/L), which is less than expected. This is because the insulating nature of sulfur forces a certain amount of carbon additive in the cathode, and a considerable lithium excess is also required to mitigate its poor cycling efficiency. More importantly, the large dosage of electrolyte to support the solution-based sulfur electrochemistry significantly increases both the weight and volume of the configuration, thus resulting in unspectacular energy density. Even so, Li-S batteries are still highly competitive as AESBs, particularly in the gravimetric level, although continuous improvements are expected for enhanced volumetric efficiency, which would involve the sparing use of electrolytes and advances in solid-based sulfur electrochemistry.

As for SESBs, Li-S batteries do not seem that advantageous over LIBs in terms of energy density given that stationary energy storage suffers from many fewer mass
and volume constraints. The power stations are generally fixed in a spacious environment with easy access to renewable energy sources and thus do not require excellent gravimetric or volumetric performance. On the bright side, however, the slight volumetric disadvantage of Li-S batteries can be overlooked in such cases, allowing them to still be comparable to LiBs for SESB applications.

Cost
AESBs based on Li-ion intercalation chemistry constitute up to 50% of the cost of EVs and have been stalling the extensive electrification of road transportation over the past years. Although recent progress involving an expanded production scale and optimized production chain might optimistically reduce the price to $110/kWh by the end of 2025, the effect is still limited with respect to the extensive EV affordability. Li-S batteries delivering a different conversion chemistry are expected to ameliorate this problem. Sulfur is one of the most abundant elements on Earth and has an average price of $0.25/kg, which is less than a hundredth of that of LiCoO$_2$ ($40/kg). Meanwhile, it is much more cost effective to recycle sulfur than the metal elements in conventional cathode materials because of sulfur’s easier sublimation and solubilization. These virtues endow Li-S batteries with a tremendous cost advantage over LiBs. However, the relatively higher price of metallic lithium than of a conventional graphite anode ($50/kg versus $12/kg) and the more expensive and widespread use of electrolytes are gnawing away at the cost advantages of Li-S batteries.

As for SESBs, the cost control is even more crucial because of the much larger scale of the devices and energy involved. The accumulation of cost savings in each cell contributes to astonishing economic benefits for the establishment and generalization of SESBs. In this regard, the cost superiority of Li-S chemistry makes the commercialization of SESBs more achievable than that of AESBs after moderate improvements. Future cost control for Li-S batteries could rely on the development of inexpensive electrolytes and their sparing use. Substituting anodes with low-cost alternatives such as silicon and graphite is also helpful but results in reduced battery energy densities to some extent.

Safety
Although LIB-based EVs are qualified by the same road-safety assessments as ICE cars and are legally permitted into the automotive market, many concerns regarding the burning or explosion of EVs still linger, leading to questions about their safety and reliability. However and unfortunately, rather than help this problem, the implementation of Li-S batteries might instead bring about even more safety hazards. The high reactivity of metallic lithium and the formation of lithium dendrites have long been denounced as serious safety loopholes that not only aggravate the side reactions between electrodes and electrolytes but also increase the risk of internal short circuit, making it extremely challenging to control battery temperature and gas. In addition, the widespread use of volatile and flammable electrolytes further weakens the tolerance of Li-S batteries to thermal, mechanical, and chemical impacts.

These safety issues become even more serious for SESBs because far more energy is involved. A safety failure in individual cells can easily spread and trigger severe safety incidents. The safety performance of Li-S batteries warrants serious improvements before they can be implemented in either AESBs or SESBs. The transition from a liquid to a solid configuration seems to be a promising strategy for safer Li-S batteries. Solid-state electrolytes (SSEs) are well reputed for their high thermal,
mechanical, chemical, and electrochemical stabilities, which greatly favor the circumvention of the abovementioned safety hazards. The advances in solid-based sulfur electrochemistry, as well as the ion conduction and cost control in SSEs, are also required to coordinate with the promotion of solid-state Li-S batteries.

**Lifespan**
Although intercalation chemistry is capable of enduring over thousands of cycles, Li-S batteries with a comparable lifespan have barely been reported. The difficulties in prolonging the Li-S lifespan are ascribed to the complicated electrochemistry inside, which involves multi-phase interfacial reactions, polysulfide equilibria and shuttling, and electrolyte decomposition, etc. Under the assumption that an EV with one charge-discharge cycle per day has a typical lifespan of 10 years, AESBs are required to endure 4,000× more cycling, which is hardly achievable for state-of-the-art Li-S batteries. The cyclability of Li-S batteries faces even more critical challenges for SESB applications. The charge-discharge pattern of SESBs is more irregular and complex in order to balance and supply the grid demand, which raises higher demands for battery reliability and lifespan. Thus, state-of-the-art Li-S batteries still long for serious and cost-effective improvements in lifespan to meet the commercial standard for either AESB or SESB applications.

**Self-Discharge**
Li-S batteries suffer from more serious self-discharge than LIBs as a result of the polysulfide shuttling mechanism, which leads to poor energy efficiency and reduced mileage in AESB applications. The self-discharge issue could become more disastrous in SESB applications. Stationary energy storage is supposed to store solar and wind energy to support grid or backup use. It is inefficient and wasteful when the stored energy dwindles significantly by itself. Therefore, self-discharge behaviors need to be well constrained for both AESBs and SESBs to enhance the energy efficiency. Future improvements could rely on rational structural designs that manage the migration of sulfur species in Li-S batteries well. Solid configuration is also highly effective at eliminating self-discharge by fundamentally bypassing the dissolution and shuttling behaviors of the polysulfides in Li-S batteries.

**Environmental Tolerance**
Good tolerance of harsh environments is also important to AESBs, given that the batteries must always be available to support road transportation. Low-temperature performance is a typical example. Batteries generally undergo a considerable performance decay under low temperatures as a result of the retarded ion mobility and sluggish reaction kinetics. Unfortunately, Li-S batteries perform even worse in this respect because of the originally poor kinetics of sulfur electrochemistry, as well as the heavy dependence of sulfur solubility and ion mobility on temperature. Although an onboard temperature conditioner could ameliorate this problem, it would consume extra energy that is already limited in EVs. More fundamentally, electrolyte optimization and exploration of faster reaction pathways could lead to better results. By contrast, it seems easier and more cost effective to handle this problem in stationary energy storage. Given that SESBs are generally large scale, highly united, and centrally managed, an integrated conditioner is able to overcome the poor performance under harsh environments, which considerably facilitates the SESB application of Li-S batteries.

**Conclusions**
The potential applications of Li-S batteries as AESBs and SESBs have both advantages and challenges. Some of the attractiveness of Li-S coupling is lost...
when evaluated more practically. However, it might be a stretch to achieve a “per-
fect” battery system before it is tested in practical applications. Moderate
advances could transform the electrical market by choosing a direction for Li-S
batteries and making targeted improvements to meet the specific demands of the
intended application. An emphasis on targeted research could promote the
commercialization of Li-S batteries in a more efficient way.

ACKNOWLEDGMENTS

G.L. and Z.C. want to acknowledge the support provided by the Natural Sciences
and Engineering Research Council of Canada and by the University of Waterloo
and the Waterloo Institute for Nanotechnology. J.L. gratefully acknowledges
support from the Assistant Secretary for Energy Efficiency and Renewable Energy
of the US Department of Energy (DOE) Office of Vehicle Technologies through the
Advanced Battery Materials Research Program (Battery500 Consortium). The
Argonne National Laboratory is operated for the DOE Office of Science by
UChicago Argonne LLC under contract number DE-AC02-06CH11357.

Gaoran Li,1 Zhongwei Chen,1,* and Jun Lu2,*
1Department of Chemical Engineering, Waterloo Institutes for Nanotechnology and Sustainable
Energy, University of Waterloo, Waterloo, ON, Canada
2Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA
*Correspondence: zhwchen@uwaterloo.ca (Z.C.), junlu@anl.gov (J.L.)

https://doi.org/10.1016/j.chempr.2017.12.012

announcing plans to phase out petrol and diesel

2. Manthiram, A., Fu, Y., Chung, S.H., Zu, C., and
Su, Y.S. (2014). Rechargeable lithium-sulfur

3. Sapunkov, O., Pande, V., Khetan, A.,
Highly efficient and low cost friction method for
producing 2D nanomaterials on poly(ethylene
terephthalate) and their applications for
commercial flexible electronics. Transl. Mater.
Res. 2, 045002.

4. Schlachter, F. (2012). Has the battery bubble

5. Soulopoulos, N. (2017). When will electric
vehicles be cheaper than conventional

6. Li, Z., Pan, M.S., Su, L., Tsai, P.C., Badel, A.F.,
Valle, J.M., Eiler, S.L., Xiang, K., Brushett, F.R.,
aqueous sulfur flow battery for ultralow-cost

lithium metal anode for high-energy batteries.

Lithium battery chemistries enabled by solid-