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The promise beyond lithium-ion technology: Dream vs. reality

In the quest for a sustainable and green future, renewable energy storage systems emerge as a ray of hope to fulfill the future energy needs while also addressing the climate change concerns. The awareness about limited inventory of fossil fuel-based energy resources has catalyzed a global shift towards the exploration of alternative sustainable energy storage systems. The revolutionary era of electrochemical energy storage gained momentum with the commercialization of lithium-ion batteries (LIBs) by Sony corporation [1]. With its continuous material innovations, LIBs transformed the whole energy sector by enabling grid storage solutions and facilitating the widespread adoption of electric vehicles. This field got further exciting by the 2019 Noble prize awarded to S. Whittingham, A. Yoshino, and J.B. Goodenough for their pioneering work on lithium-ion batteries [2].

Electrification of transportation systems necessitates high power and high energy density (driving range >300 miles per charge), low cost and high safety. The surging interest in electric vehicles leads to accelerating consumption of the key transition metals used in LIBs like lithium, nickel, and cobalt. All major automotive manufacturers are now heavily investing in their battery R&D. Lithium metal supply is unevenly distributed and localized in specific regions and is prone to cost variability. Currently, as an example, Tesla motors employ lithium nickel cobalt aluminum oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NCA) as cathode of choice while many other automotive companies use lithium nickel manganese cobalt oxide ($LiNi_xCoyMn_zO_2$, MNC). Nickel- and cobalt-based cathodes offer higher energy density than the non-cobalt containing cathodes such as olivine $LiFePO_4$ [3]. This mandates cobalt (Co) and nickel (Ni) supply along with lithium metal. Cobalt scarcity is well studied in the literature [4]; similarly, battery grade nickel is also difficult to source. Fig. 1 shows the abundance and cost metric of the essential elements used in LIBs. Gauging the popularity of EVs and bolstering efforts by various governmental and environmental agencies, it is likely that all the Li, Co, and Ni resources will be predominately consumed by the automobile industry, hence allowing very little space for other sustainable applications. This makes exploration of “beyond Li ion technology” imperative to meet future non-EV energy demands.

The advent of beyond lithium ion or post lithium ion technology has garnered enormous attention due to its potential to achieve high energy densities along with high safety. These futuristic energy storage systems explore alternative electrochemistries that aim to reduce material cost and to enhance safety while also trying to achieve high energy density (>500 Wh·Kg^{-1}). Some of the promising candidates include solid-state batteries, lithium sulfur batteries and non-lithium-based batteries such as sodium, potassium, and magnesium batteries. This article aims to give a brief overview of these emerging technologies, underscoring their theoretical advantages, prevailing challenges and future perspectives.

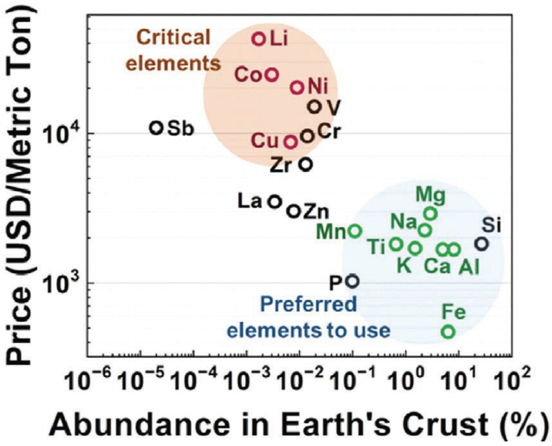

Fig. 1: Abundance vs price of metal resources (reproduced with permission from Ref. [3]).

Solid-state lithium metal batteries

The legacy lithium-ion batteries work on the concept of intercalation chemistry where Li^+-ions from lithium salt dissolved in an organic non-aqueous solvent reversibly shuttles between a graphite anode and a lithium transition metal oxide cathode. The electrolyte is one of the crucial components in a battery system since it provides the pathway for the Li^+-ions migration between anode and cathode. Liquid electrolytes used in conventional LIBs are both flammable and prone to leakage, which presents safety concerns like fire hazards. Some of the infamous examples of these hazards are 2013 Boeing 787 Dreamliner [5] and 2013 Tesla Model S Fire [6]. Thus, a significant amount is usually invested in a battery management system for a Li ion battery pack to reduce the risk of fire accidents.

Solid-state electrolytes (SSE) came forth as a potential alternative in response to the issues of safety hazards, and the auxiliary cost involved in battery management systems in traditional lithium-ion batteries. Broad categories of solid-state electrolytes are polymer-based solid-state electrolytes, ceramic-based sol-

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id-state electrolytes or composite solid-state electrolytes. SSEs offer enhanced safety, mitigating the Li-dendrite formation while also enabling the use of lithium metal anode to achieve higher energy density. Despite all these attractive features, the practical implementation of SSEs is gated due to various challenges. The benchmark for polymer-based SSEs is based on a polyether oxide (PEO) -Li salt complex. Li^+-ions form coordination bonds with the ether oxygen atom, ionic conduction in polymer-based electrolytes occurs in the amorphous regions where the ions hop by complete ligand exchange [7]. Despite its attractive safety features, polymer-based SSEs suffer from low room temperature ionic conductivity due to the presence of crystalline moieties in their structure. Various efforts have been made to increase the ionic conductivity in polymer-based SSEs like incorporation of plasticizers or inorganic fillers, side chain branching or incorporation of copolymers to lower the glass transition temperature [8-10]. An emerging class of polymer-based gel electrolytes are single ion conducting (SIC) electrolytes, which offer a Li^+-transference number close to 1 and offer superionic conductivity when swollen with liquid electrolyte [11]. However, most of these electrolyte systems are only analyzed in laboratory settings and will require additional development and significant scale up before they can be commercialized. Inorganic ceramic-based SSEs have gained popularity in the era of SSEs as well, they are mostly composed of Li-rich oxides or sulfides such as LiSICON (Lithium-Super Ionic-Conductor), Garnet type $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO), or Thio-LiSICON $Li_{10}GeP_2S_{12}$ (LGPS) [12, 13]. These SSEs offer high room temperature ionic conductivity but suffer from poor adhesion to electrode forming a poor interface with electrodes. Thio-based ceramic SSEs are also extremely moisture-sensitive and require an extremely inert environment for processing. The synthesis of these SSEs has high Li-resource requirements, which hikes the cost of this technology and beats the purpose of addressing the lithium scarcity for future development. A forward-looking outlook for the success of solid-state electrolytes will be an integration of an organic polymer and an inorganic ceramic electrolyte that can synergistically resolve the current challenges of a poor electrode interface while also offering superionic room temperature ionic conductivity and chemical stability. It is also important to explore the compatibility of fabrication of these electrolytes on a scalable platform like roll-to-roll processing to make this usage viable for industry.

Lithium sulfur batteries

Another emerging post Li ion technology is lithium sulfur (Li-S) batteries: Li-S holds an extremely high theoretical energy density of 2600 Wh kg^{-1} (approximately five times that of commercial lithium-ion batteries) [14]. Sulfur is also one of the cheapest and abundant raw materials produced as a byproduct of desulfurization of crude oil and natural gas. Unlike intercalation chemistry involved in LIB, Li-S operates on alternative conversion chemistry. The operation of Li-S encompasses a complex electrochemical reaction where, during discharge, Li^+-ions from the lithium anode migrate through the electrolyte solution to the sulfur cathode, whereas a reduction reaction takes place on the cathode side yielding Li_2S. However, the redox reaction is complex, and it goes through multiple intermediate steps forming high order polysulfides that shuttle between the cathode and anode and cause continued loss of active materials leading to capacity fading and poor cyclability. This is commonly known as “Polysulfide shuttle effect” and is a major roadblock in the realization of Li-S batteries. Sulfur is an insulator and offers poor electronic conductivity that overall affects battery performance. Various attempts have been made towards an optimization of cathode design for Li-S batteries, one of the most rewarding ones is the use of porous carbon material as cathode host that can entrap the soluble polysulfides, additionally graphitic carbon also enhances the overall electronic conductivity of the cathode [15]. Various research groups demonstrated that introducing polarity via heteroatom doping facilitates immobilization of lithium polysulfides in the cathode materials [16, 17]. Apart from the cathode side, an electrolyte design compatible with Li-S electrochemistry also plays a crucial role in determining the battery performance. To sum up, Li-S battery technology is still in its infancy due to various existing material challenges that hinder its practical battery applications. Given the promise of high energy density offered by these batteries in theory, it is worth exploring novel electrodes as well as electrolyte materials.

Sodium/Potassium/Magnesium/Calcium-ion batteries

Recent surge in interest in non-Li based energy storage systems stems from the low abundance and uneven distribution of Li metal. Na-ion (SIB) Batteries have been a topic of discussion since the early 1980s. Analogous to LIBs, SIBs operate on the reversible intercalation chemistry in layered oxides making SIBs a cost-effective alternative to LIBs. However, the energy density attainable by SIB is lower than LIBs due to the electrode potential of sodium (-2.71 V vs. SHE) being slightly more positive than that of lithium (-3.04 V vs SHE) [18]. Another intriguing but comparatively less researched alkali metal is potassium (K). The energy density of a practical K-ion battery (PIB) is expected to be equivalent to a Li-ion battery, but this technology is underdeveloped due to a lack of compatible electrode and electrolyte materials. The material costs of SIB and PIB are considerably lower not only due to the higher abundances of sodium and potassium, but also since, they are compatible with aluminum (Al) current collectors that eliminates the need for expensive copper (Cu) current collectors, which reduces the overall costs significantly [3]. Divalent magnesium ion energy storage possesses several advantages over LIBs including almost double volumetric capacity (3833 mAh/mL vs 2062 mAh/mL for lithium), low cost and improved safety due to low risk of dendrite formation [19]. Regarding the limitations of MIBs, Mg-ions carry double the charge as compared to a monovalent Li ion, leading to a high charge density rendering magnesium cations highly reactive and forming nonreversible bonds with metal oxides which limits the cycle life; in addition, magnesium metal also forms a non-Mg ion passivating layer on the metallic surface that needs additional surface treatment [20]. Lack in material design and cell engineering makes MIBs less attractive in battery applications but its utilization in electric double-layer capacitors (EDLC) has received considerable attention. In fact, as part of my graduate studies, we worked on a magnesium ion conducting solid polymer electrolyte for EDLC devices where we demonstrated cyclic stability of over 11,200 charge-discharge cycles [21]. Despite its attractive features, calcium ion energy storage is still in its nascent stage and has not been explored enough compared to other alternative systems with e.g. Na-ions and Mg-ions. By far, Na-ion batteries are considered the closest to commercialization. They are fitting the energy needs in grid storage and other non-EV or mid-range EV applications. Overall, the future success of these technologies hinges on addressing their current challenges and optimizing performance for tailored use cases.

In summary, investigation of "beyond lithium ion" is an encouraging era to reshape the future energy demands as well as to achieve long-term sustainability goals; however, they face significant challenges that require a collaborative effort from researchers and industry stakeholders to overcome. Undoubtedly, to date, Li-ion batteries remain the gold standard for high performance and high range EV market. Meanwhile the frontrunners among these post Li-ion technologies can still penetrate other energy storage applications where affordability takes precedence over energy density.

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Spotlight on

Post-lithium batteries

Current electrochemistry research focusses on identifying new concepts and materials for post-lithium batteries, as also described in the contribution by M. Trivedi in this issue (p. 201). To develop new cell concepts for post-lithium batteries, a wide range of different mobile ions and corresponding materials has to be investigated, including both organic and inorganic materials and substances ranging from inorganic solids via polymers to liquids. This topic is also a major interest in the Cluster of Excellence POLiS (Post-lithium storage), connecting researchers at the Universities of Ulm, Karlsruhe, and Gießen. In the group of J. Janek (JLU Gießen), solid electrolytes and electrode materials are investigated with the aim to develop, characterize, and optimize new battery concepts. For example, the group developed metal-air batteries with potential replacement of Li by Na. For this, it is important to provide in-depth investigations on e.g. electrode kinetics in solid ion conductors as well as of structural characterizations of newly developed materials of potential interest, also under operating conditions. The properties of alkali metal electrodes are a subject of particular interest, as metal anodes hold the promise of very high specific capacity, and solid-state concepts will be required to enable their stable operation. The knowledge of structural changes during battery operation is crucial to maximize the number of life cycles of a specific battery type. These structural changes cause critical ageing processes that can result in a reduction of the batteries' capacity – an important factor to be optimized before post-lithium batteries can enter into applications.

[https://www.postlithiumstorage.org/en/]
[https://www.uni-giessen.de/de/fbz/fb08/Inst/physchem/janek]

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