A Critical Technology Implementation of Sodium Solid-state Battery as the Secure Long-Duration Energy Storage toward the Terra-Watt Grid Projects

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Abstract—The current lithium-ion battery (LIB) has become a vital technology for realizing a highly-productive society. The current system can be found easily in every personal electronic device, such as smartphones, laptops, smartwatches, and digital cameras. However, the future of LIBs is questionable due to the scarcity and security issues. The common electrolytes in this system are highly flammable, toxic, and easy to leak. Thus, inherit them to be applied for more mass-reliable energy sources, the terra-watt projects. Therefore, the development of an all-solid-state battery based on earth-abundant and cost-effective processing should be carried out immediately to dominate the market and for future civilization. Herein, we promoted a Sodium solid-state battery (SSB) that potentially be a key in energy storage technology due to its mechanical properties, electrochemical stability, high ion conductivity, and robust cyclic performance. Furthermore, a five-year direct implementation strategy of SSB was also presented, constructed from sodium and chromium electrodes.

Keywords— Secure energy storage; Sodium solid-state battery; Terra-watt projects.

1. INTRODUCTION

Modern society always requires advanced technology evolutions, that is already happening for decades. The world develops in amazing ways when people start driving cars instead of wagons, replacing pigeons with the internet to instantly send a message, or emerging a cloud system only to store any type of document. Unfortunately, the energy sector is likely to be the same. Although energy always has a vital role in society, even in this 21st century, we are still burning things to keep the work going. In 2020, 1.5 x 10¹⁴ kWh of energy has been consumed, with more than 83% coming from fossil fuels [1]. In detail, renewable energy contributes only 31.71 EJ (~5.7%), which makes the net zero emission by 2050 still a long way off. Fig. 1 presents global energy consumption in 2020 based on the British Petroleum (BP) Energy Outlook.

One of the brightest options to be taken is to effectively harvest electricity from the sun, which potentially provides the world with 40.000 EJ of energy per year [2]. Therefore, the photovoltaic technology market should be fully encouraged in terms of the policies, core technologies, and supporting systems. Especially for the latter aspect, batteries, as the particularly suitable energy storage to be integrated into solar devices, have taken a major step. Since Sony launched its first commercial rechargeable lithium-ion battery (LIB) in 1991, the world has always relied on the LIB to date. There is $53.6 billion global market size, dominated by lithium iron phosphate (LFP) and lithium cobalt oxide (LCO) for around 22.6% and 32.3% shares, respectively [3]. Thanks to the high capacity and reliability [4]. Thus, the promising market is predicted to grow significantly, levelling $216.5 billion of revenue forecast by 2028.

Fig. 1. Global energy consumption by resources in 2020, presented based on BP Energy outlook 2022 [1].
However, the extraction of Lithium is a costly effort and unsafety. Furthermore, combined with their electrolytes, LIBs are relatively highly flammable, easy to explode, and quite toxic [5]. In addition, since LIBs must be built in a package with a protection circuit to sustain the harmless operation, it hinders the enhancement of the total capacity [6]. This basic requirement makes it nearly impossible to size more reliable and socially-crucial energy resources such as a terra-watt project. Moreover, the beginning of the electric vehicles (EVs) era undoubtedly will create more challenges and opportunities in the business. Although some types of EVs seem to operate smoothly, the need for novel battery technology will remain to exist, if it is about safety and high-performance vehicles. In the concern of safety, the explosion of EVs tends to occur easily due to liquid leaks. Therefore, more effective development and technological implementation on a novel battery system, which is relatively inexpensive, much safer, environmentally friendly, and highly trustworthy, is a straightforward strategy for the near future.

Herein we present the severe potential of sodium-based solid-state batteries as a secure, reliable, and higher energy density system to realize terra-watt projects. This article focuses on two-main parts of a battery, electrolytes and electrodes, and compare their properties among current technologies. In addition, a straightforward strategy is also described carefully to assess its implementation for a better energy storage system.

2. THE BATTERIES DEVELOPMENT

Compared to LIB, Sodium-Ion batteries (SIB) are getting the spotlight due to their abundance (20 ppm vs 23,000 ppm for sodium availability in the crust), low-cost extraction process, and obviously the security side [7,8]. Even though the cell voltage is lower than typical 3.5V on the LIB, the SIB still has reasonable values (~2.5V). Interestingly, they recorded a 150 Wh/kg of specific energy and 375 Wh/L energy density of 18650 size of cell. This is comparable to the typical lithium-ion battery, which has a specific energy and energy density of 126 Wh/kg and 325 Wh/L, respectively, with the same cell size [6]. Combined with the aforementioned properties, SIBs are more competitive to be developed as a large-scale power grid than current LIB technology.

However, the employment of a conventional organic-liquid electrolyte to provide conductivity between the electrodes and the external environment, in which ions can diffuse, still limits its scalability. Because of flammability and the probability of leakage, the use of the liquid environment should be avoided. Consequently, the sodium solid-state battery (SSB) is the answer for the future energy storage systems. Removing the electrolyte and separator in conservative SIBs, SSB uses a non-flammable solid-state electrolyte (SE), exceptional thermal stability, and lack of leakage [9,10]. Obviously, integrating with the Na metal, the use of SEs will drastically reduce the size, resulting in energy density improvement [11]. In addition, the formation of dendrites, which is the major obstacle in prolonged lifespan, is expected to be prevented when using the SEs, thus the battery will last longer [12]. A brief comparison between commonly used liquid-based electrolyte battery and all-solid-state battery system is presented in Fig. 2.

![Fig. 2. The schematic diagram of comparison between conventional liquid-based electrolyte and solid-state electrolyte systems. The illustration is modified from ref [14].](image)

To provide a practical robust SSB, we should focus on the SEs development because it has many opportunities and challenges. As the vital components in SSB, SEs suffer from the low ionic conductivity at room temperature (RT), poor stability, and the electrode/electrolyte interfacial compatibility [15]. Numerous studies indicate that high electrochemical stability, reasonable ionic conductivity, good interfacial and mechanical characteristics are the minimum requirements to produce high performance SEs with the RT working environment [13,14,15]. To date, there are three types of SEs based on inorganic-ceramic (ISE), solid polymer (SPE), and a combination of polymer and inorganic, namely the hybrid solid electrolyte (SHE). Their remarkable results from these milestones are also reported here. Since the discovery of Na-β-alumina (Na3O·11Al2O3) in the 60s, many studies have been conducted in ISE to make SSB commercially available due to the highest recorded ionic conductivity of 0.1 S cm−1 at the RT operations [16]. However, it should be noted that over 1200 °C sintering with the complexity preparation is applied to obtain perfectly confined single crystallinity, which makes industrialization dreadful. Nowadays, researchers have developed some facile procedures with a reasonable result, or have shifted to other materials like sodium superionic conductors (NASICON). A noticeable work has been reported by Noguchi et al. in 2013, in which they use SSB-symmetrical battery with Na2Zr2Si2P2O12 (NASICON type) and confirm a rechargeable 1.7 V plateau with 50 mAh g−1 at the RT [17]. Furthermore, some ionic conductivities in RT of 10−3 S cm−1 have been published by introducing Na+ vacancies.
[18] and Ca$^{2+}$ doping [19]. The later strategy improves cycling performance due to the grain-boundary modification as well. In addition, the Na$^+$ diffusion has been simulated using density functional theory (DFT) molecular dynamics (MD) demonstrating that a minimum of 10$^{-3}$ S cm$^{-1}$ conductivity can be reached by Ca-doped on NaPSi. SE [20]. It worth noted that the DFT calculation is a strong and reliable first principal method, not only for designing the molecules but also for calculating the time-dependent molecular activities [21,22]. In a recent study by Payandeh et al., [23] a stable mixed boron hydride has successfully improved the electrochemical stability window of 3V SSB. Based on the intrinsic properties, ISEs reveal an excellent thermal and chemical stability, and ionic conductivity due to the direct use of metallic bonding within the system. However, such a system still renders huge interfacial resistance [24].

On the other sides, the SPEs commonly involve sodium salts in the polymer matrix. In this typical system, the salts act as a sodium source, whereas the polymer matrix becomes the host transporter for Na$^+$ ions. Since the sodium cations are conducted by the migration of polymer chains in the amorphous regions, the number of free ions and mobility of the chains, significantly affect the transport capacity in the SPEs, which directly affects the performance of the battery [25]. Foremost efforts have been made in this type of SE due to their high Na-salt solubility, good contact for the electrode, flexibility, and producibility. Poly(ethylene oxide)-based electrolytes (PEO) is one of the reliable SPEs that has been massively developed since 1988 because of its interesting characteristics that potentially support large-scale projects. A remarkable result has been shown by Ma et al. in 2017 [26], when their NAFNFSI PEO exhibit 3.36 × 10$^{-3}$ S cm$^{-1}$ at 80 °C via a simple solution casting method of fabrication. Another interesting work has been shown by Zhou et al. developing the poly(vinyl ethylene carbonate) as the PVEC-based SPEs through in situ polymerization resulting 2.1 × 10$^{-3}$ S cm$^{-1}$ conductivity under RT conditions [27]. Moreover, a crosslinked poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP) demonstrated by Shi et al. showing a better interface stability toward metal anode and recording 0.81 × 10$^{-3}$ S cm$^{-1}$ ionic conductivity [28]. In general, PSEs provide a possible approach to be a future option based on their relatively simple procedure, lightweight, and large operational window, but commonly exhibit relatively low ionic conductivity due to their large polarization. A schematic diagram of the SEs design is presented in Fig. 3, with the focus in atomic scale and interface chemistry.

Combining the advantages of ISE and SPE without being affected by each deficiency is the master mind behind the HSEs development [29]. Therefore, a system that demonstrates high mechanical properties, such in ISE with no interface problem like in the SPE is highly desirable through an additional layer, sufficient doping, and synthesize of ceramic/polymer composites. A great example is shown by Chen et al. revealing the effective interactions between GO and PVD-F-HFP-PEO polymer via hydrogen bonding [30]. This effect leads to a double ionic conductivity compared with the polymer-only reference. Thus 2.1 × 10$^{-3}$ S cm$^{-1}$ conductivity is recorded during the work. To further increase the mechanical properties, the advantage of inorganic nanoparticles is introduced to the system to enhance cell capacity and ion diffusion pathways.

Accordingly, Song et al. and Ma et al. have demonstrated a meaningful improvement when they employ SiO$_2$ and Carbon Quantum Dots (QDs) on the polymer interface, respectively [31,32]. Recently, the doping strategy has shown a potential pathway, which is revealed by a study on Ga-doped NZTO reached 10$^{-3}$ S cm$^{-1}$ ionic conductivity due to supressed polymer crystallization [33]. In general, the comparative properties between electrolytes are presented in Table 1.

According to intensive studies described previously, it is well noted that high Na$^+$ conductivity (<10$^{-3}$ S cm$^{-1}$) in operating temperature, that usually around RT, is a key factor. Additionally, a fundamentally strong

**Table 1. Comparative Properties Between Current Electrolytes Technology**

<table>
<thead>
<tr>
<th>Electrolytes Type</th>
<th>Ionic Conductivity</th>
<th>Interfacial Compatibility</th>
<th>Electrochemical Stability</th>
<th>Mechanical Strength</th>
<th>Cost Investment</th>
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<td>Liquids</td>
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electrode design with sufficiently large voltage without distressing the interface and its performance is a crucial step as well. In turn, highly secure, cost-effective and compatible batteries for enormous capacity will be ready for the market by the SSB technology.

3. REALIZING SODIUM SOLID-STATE BATTERY

Adaptability is a crucial factor to emphasize a novel technology. Therefore, the current high-performance and stable lithium metal oxide cathode, LiMO$_x$, are modified by replacing Li atom with Na, then chemically synthesizing the NaCrO$_2$ as a cathode. In 2015, Yu et al. has provided a reproducible synthesis route for layered O$_3$-type NaCrO$_2$ with surface modification by carbon to obtain extremely high electrical conductivity [34]. In addition, a study shows 250 mAhg$^{-1}$ theoretical capacity and practical reversible capacity of nearly 110 mAhg$^{-1}$ when cycled between 2 and 3.6 V [35] making it reasonable for application in the prospective SSB system.

To provide a maximum number of ion diffusion, Na metal is employed as the anode, since it has a high theoretical capacity, 1166 mAhg$^{-1}$ and low redox potential -2.71 V, lead to larger working voltage and energy density compare to lithium. Therefore, the chemical redox reaction within the system will be:

Anode: Na $\Leftrightarrow$ Na$^+$ + e$^-$

Cathode: Na$^+$ + e$^- +$ CrO$_2$ $\Leftrightarrow$ NaCrO$_2$

Overall: CrO$_2$ + Na $\Leftrightarrow$ NaCrO$_2$

Nevertheless, to directly use sodium metal as the anode might present some problems due to its high chemical reactivity. Thus, to overcome the Na dendrite growth and instability of interface issue, coupling it with tin to make Na-Sn (with various compositions) composites is a promising strategy. To further increase the conductivity and reduce the contact loss, acetylene black is also employed.

More than 50% of the projects will be dedicated to designing high-performance and stable SE, which will focus on the hybrid-type. Firstly, a polymer electrolyte should be synthesized, which is based on NaClO$_4$ as the sodium source, and then dispersed to poly(ethylene glycol) diacrylate (PEGDA) monomer under the action of a thermal initiator within the glass fiber matrix and will be further polymerized. To increase the surface wetting property, the residual pores of glass fiber matrix are then filled with Polyethylene glycol (PEG) [36]. In addition, sodium salt is also added during the polymerization of PEGDA and the PEG filling process. A schematic HSE filling is presented in Fig. 4.

To increase the conductivity, a small amount of zirconium can be doped to the polymer and the interface modification with the SiO$_2$ can also be applied. The small Zr$^{4+}$ doping in the polymer is predicted to construct a low dopant level, to further increase the Na$^+$ diffusion ability via controlled defect formation [37]. In addition, SiO$_2$ can play as the passivation agent for the surface, enhance ion diffusion from the interface, and support the mechanical stability of the solid electrolyte.

Finally, a compact and highly efficient SSB constructed from Na-Sn/SiO$_2$-Zr/PEGDA/NaCrO$_2$ should be delivered within 3 years, with an additional 2 years for market testing and research which already critically reported in other reviews [38, 39, 40]. As presented in Fig. 5, this all-new solid-state battery is the main key to the net zero emissions by facilitating a robust and

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**Fig. 4.** Schematic HSE coating, start from glass fiber membrane, coated with PEGDA, adding the Na salt, and finally filled with the PEG. The graphic modified from ref. [36].

**Fig. 5.** Schematic diagram of realizing terra-watt power-grid using SSB as the safe Long-Duration Energy Storage (LDES).
highly secure energy storage system to provide long-duration energy storage (LDES) integrated with ultra-large photovoltaic farms, wind-powered turbine, natural gas plant, and stable transmission system.

Furthermore, this dense, compact, and again, strictly safer battery compared to the current Li battery will become a new trend for electric vehicles. In spite of the fact that all-solid-state battery technologies are still in development stage, recent studies have recorded cycle lifetimes of over 10,000 cycles at 90% capacity retention [41,42,43]. Thus, we believe, with a high intention on this development, our society will definitely live in a cleaner and brighter world.

4. CONCLUSION

The global campaign for battery application had reached a rapid development phase, necessitating the immediate development of energy storage technologies with high specific energy, high energy density, and safety. Although several additives had been produced to increase the electrochemical performance and safety of liquid electrolytes, the energy density of commercial LIBs was limited due to their flammable liquid organic solvent electrolytes, and the practical application process had revealed numerous security issues, especially for large-scale energy storage systems. This enhancement was insufficient to meet demand. Currently, solid-state batteries with high energy density and good security qualities had received worldwide interest, particularly those that substitute sodium for lithium as the prime electrode because it was more environmentally friendly. In this perspective, the current status of SSE technology and the intentionally promoted SSB as the near future technology superstar, and how to realize it in less than decades had been described. The SSB constructed of Na-Sn/SiO2-Zr/PEGDA/NaCrO2 should be started to be developed at worldly. Thus, the actual implementation could come sooner.

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CONFLICT OF INTEREST

We declared that there is no conflict of interest among authors.

AUTHOR CONTRIBUTIONS

TK and FA conducted the literatures review, gathered all information needed, and wrote the manuscripts under the direct supervision of NN. NN and MF designed the strategy, evaluated the technological implementation, TK, MF, FA, and NN reanalysed, revised, and wrote the manuscript.

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