



A RECENT PROGRESS IN SOLID STATE BATTERY TECHNOLOGIES AND ITS COMPARISON WITH LITHIUM-ION BATTERY

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Abstract : Traditional lithium-ion batteries use liquid electrolytes to facilitate the transfer of lithium ions between the cathode and anode of the battery. The automotive and electronics industries have recently become interested in all-solid-state battery technology due to their high safety and high energy density. The main concern with this fact is the commercialization of all-solid-state batteries (SSBs), which allow lithium metal to be used as the anode instead of the carbon anode, which increases the energy density. However, all-solid-state batteries did not meet all the current LIB's latest liquid electrolyte performance indicators. Start with the recent advances in LIB and future all-solid-state battery capabilities with the latest adaptations such as current performance characteristics and commercial cost trends.

IndexTerms – LI-ion Battery, Solid State Battery (SSB), LIM, Solid State Electrolyte (SSE).

I. INTRODUCTION

In recent years, researchers have spent a great deal of effort and developing new ways to save energy consumption. Due to the world's population and technological advances, the demand for energy consumption has increased exponentially each year. Most of this energy is produced by burning fossil fuels such as coal, oil and natural gas. These substances can generate enormous amounts of energy, but they are finite resources and will be completely depleted unless there is a major change in the world's energy consumption. Renewable energies can reduce their dependence on fossil fuels and play a bigger role in relation to environmental issues.[1]. Many researchers have developed PV models and efficient algorithms to extract maximum power from PV power generation systems.[2][3][4][5][6]. Researchers have implemented a variety of technologies to improve the performance quality and voltage profile of fossil fuel-generated electricity in existing power systems and reduce vibrations. This fact has revolutionized renewable energy sources such as hydropower, wind turbines and solar power. These energy sources are theoretically endless, but the energy obtained from them must be stored for later use, which is a potential problem. Batteries, whether fossil fuels or renewable resources, can be used as a device to store power from energy sources until they are needed at some point in the future. Rechargeable batteries, also known as archaically accumulators, are especially popular because of their multiple charge and discharge functions. A conventional all-solid-state battery model is shown in figure 1 [7]

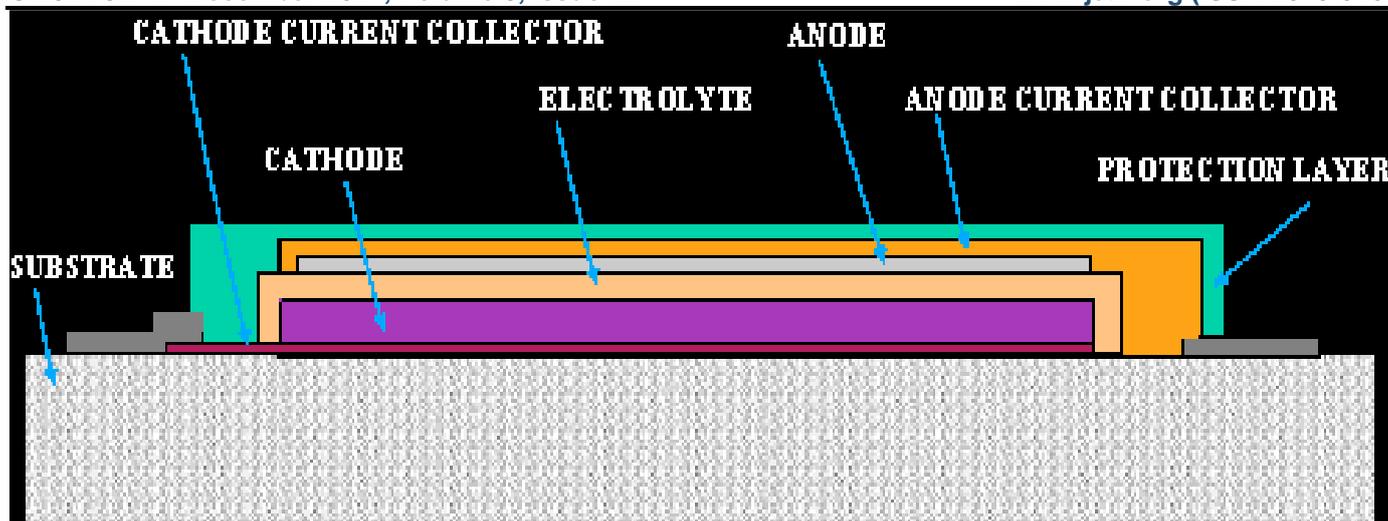


Fig.1 Conventional solid state battery [7]

II Methods & Data

All thin film solid state battery technology removes the various difficulties and offer high energy densities. Thin film Solid State battery technology is shown in fig 2. In this technique we use alternate layers of active electrolyte lithium garnet component (Li Al La Zr O , or LLZO) with layers of lithium nitride (Li N). These layers are formed like a wafer cookie by using pulsed laser deposition process at about 300°C (572 degrees Fahrenheit). Then they are heated to 660°C and by cooling it slowly, which is known as annealing process. In particular, the LiCoO_2 (LCO) cathode and its transition metal oxide successors (notably $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ - NCA and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ – NMC_{xyz} with $x+y+z=1$) coupled with the carbon (C) anode and a liquid electrolyte with additives has been incredibly successful since the early 1990s. Schematic traditional solid state One obvious change to the oxide cathode/C anode paradigm is to replace the C anode with Li metal (Lim). In past few years rechargeable batteries are dominant in consumer electronics market of Energy storage sources, automotive industries, and other energy requirements. However, non-uniform stripping and Lim deposition takes place due to repeated charging and discharging cycles and finally dendrites are formed. These dendrites may connect the anode to cathode through the separator. (Fig. 3), which develops easy conduction for electron transport (electron flow will no longer in external circuit) leading to high self-discharge currents that may lead to electrolyte ignition, resulting in explosions/fire. This occurred when Lim was used as an anode in Moli Energy cells in the early 1990s and also in cells that were researched by Exxon around the same time [9][10][11][12][13].

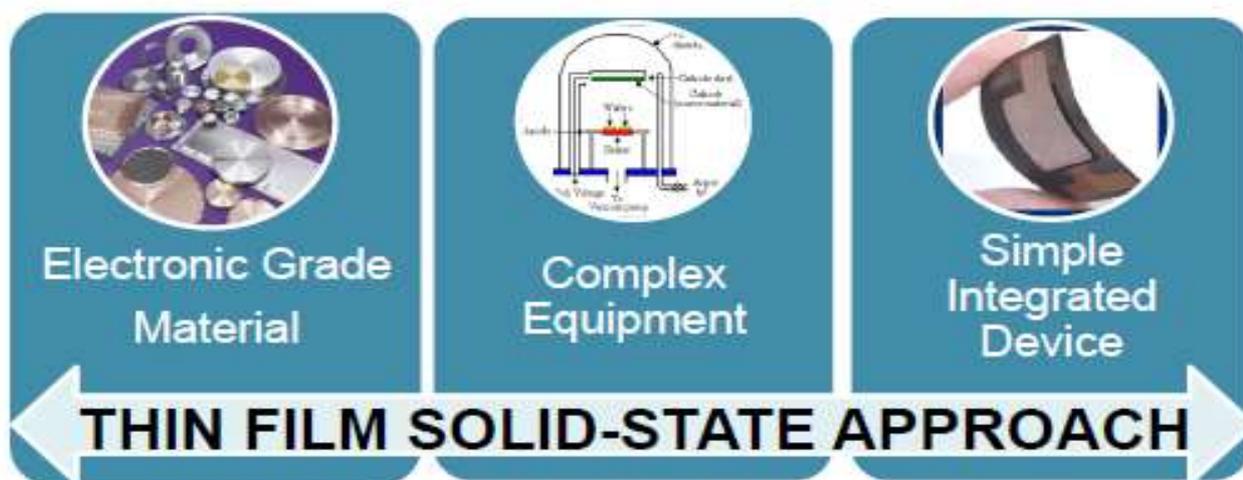


Fig.2 Thin film Solid State battery Technology[8]

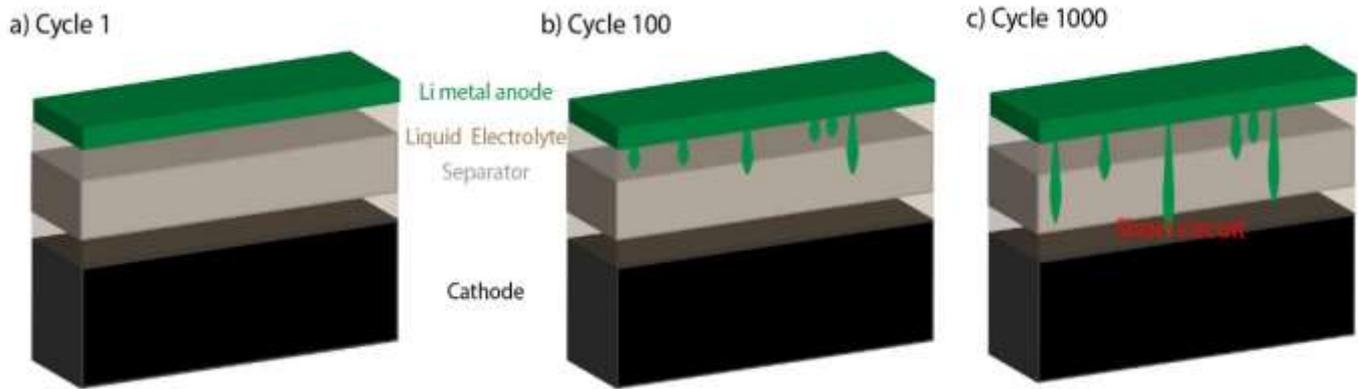


Fig 3 Lithium Dendrite formation after various charge and discharge cycles [14]

As a result, C has replaced the commercial cell Lim as researchers continue to look for ways to solve the dendrite problem. The Li-dendrite formation scheme shown in Figure 1 repeats the charge and discharge cycles, resulting in a short circuit and ignition of the flammable electrolyte. Due to repeated deposition / stripping, the Li metal begins to form dendrites and travels through the separator. If the dendrite reaches the cathode while connected to the anode, a short circuit will occur, leading to a rapid discharge and potential ignition of the flammable liquid electrolyte. Theoretically, solid electrolytes prevent dendrites from reaching the cathode by physically blocking the cathode. In fact, some solid electrolytes allow the growth of dendrites through grain boundaries. Several other methods, including electrolyte additives and nano structuring, have also shown the potential to eliminate dendrite growth in the presence of liquid electrolytes [11]. Specific power and energy for different types of batteries is shown in fig 4

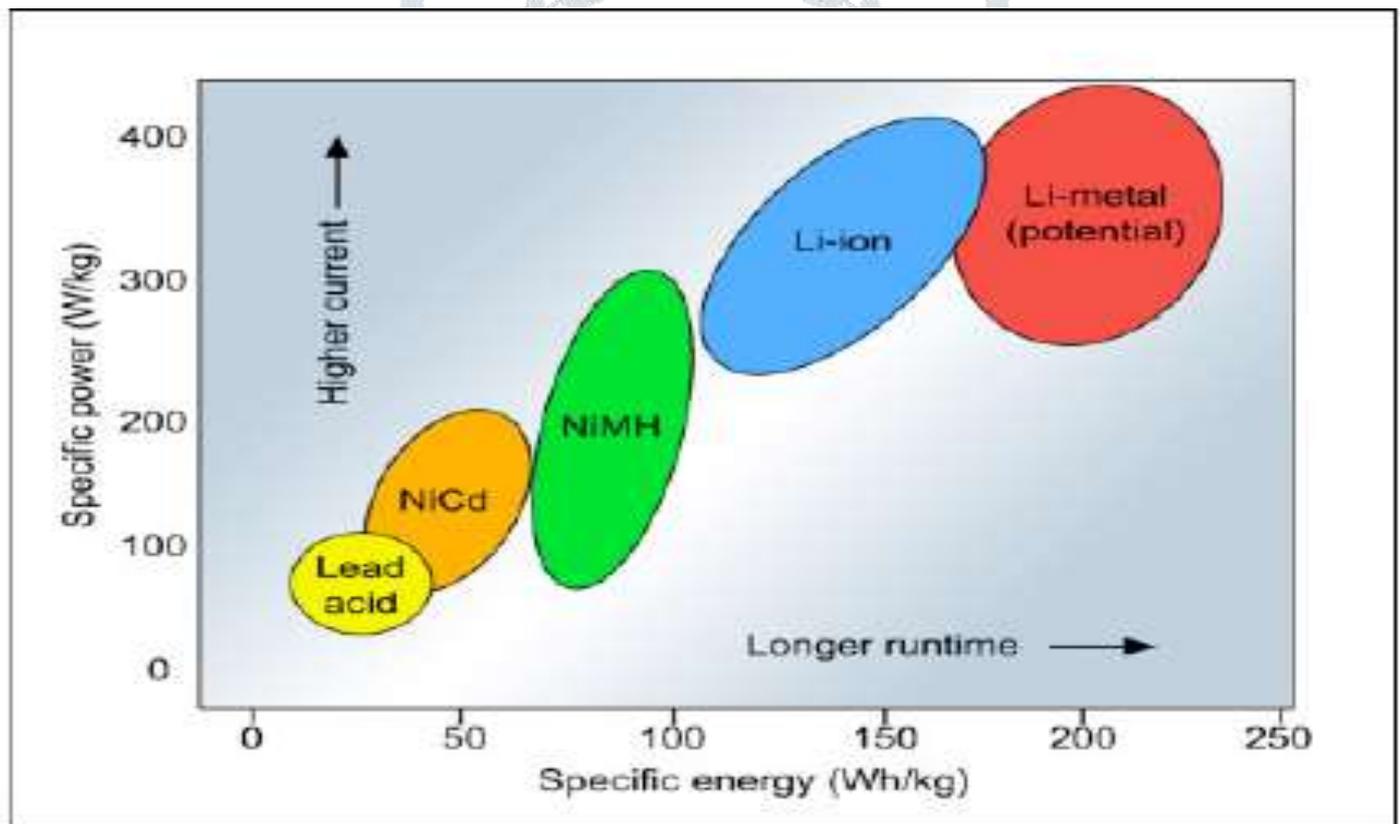


Fig 4 Specific power vs Energy in different battery types [15]

Solid-state electrolytes (SSEs) are one of many approaches to solving Lim dendrites. In this approach, SSE replaces the liquid electrolyte and acts as a physical barrier to dendrite penetration.

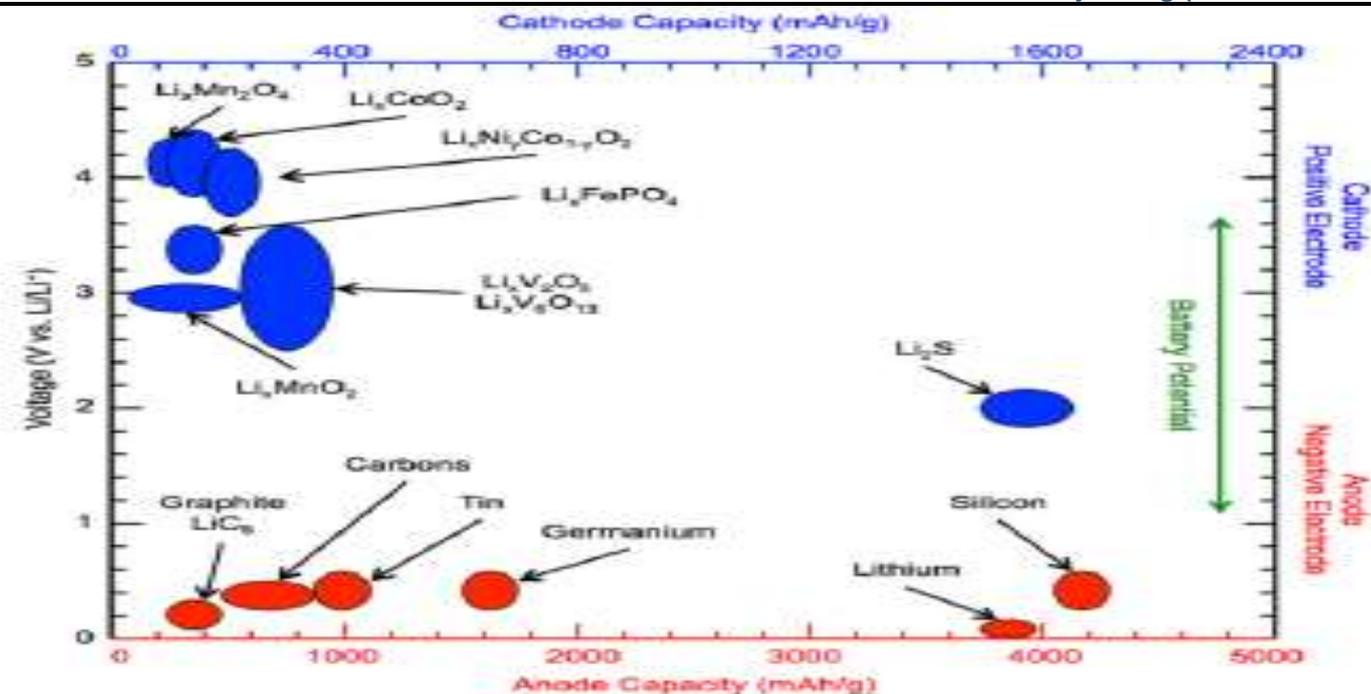


Fig. 5 Capacities and voltage window comparison of various types of cathode and Anode[16]

However, keep in mind that some studies have shown that dendrites permeate along the grain boundaries of the SSE. In addition, SSEs are generally less flammable than liquid electrolytes and are therefore safer in the event of a dendrite short circuit [17]. While promising in this regard, SSEs generally transport Li ions slowly because ion diffusion in solids tends to be orders of magnitude slower than ion diffusion in liquids. Therefore, it is difficult to build a circulating battery with proper rate function. This paradigm was recently changed by the discovery of SSE (from the thioLISICON family), which has higher conductivity than standard LIB liquid electrolytes. Figure 5 shows a comparison of the capacitance and voltage windows of the different types of cathodes and anodes [16]. It focuses on recent reports on all-solid-state batteries (SSBs) in operation and how they are compared to current commercial LIBs. Researchers have developed a new pulsed laser deposition technique to make lithium electrolyte thinner with less heat. This can result in faster charging of lithium-ion solid-state batteries and higher voltage. Figure 6 shows a comparison of the ionic conductivity of various lithium-ion battery electrolytes [18].

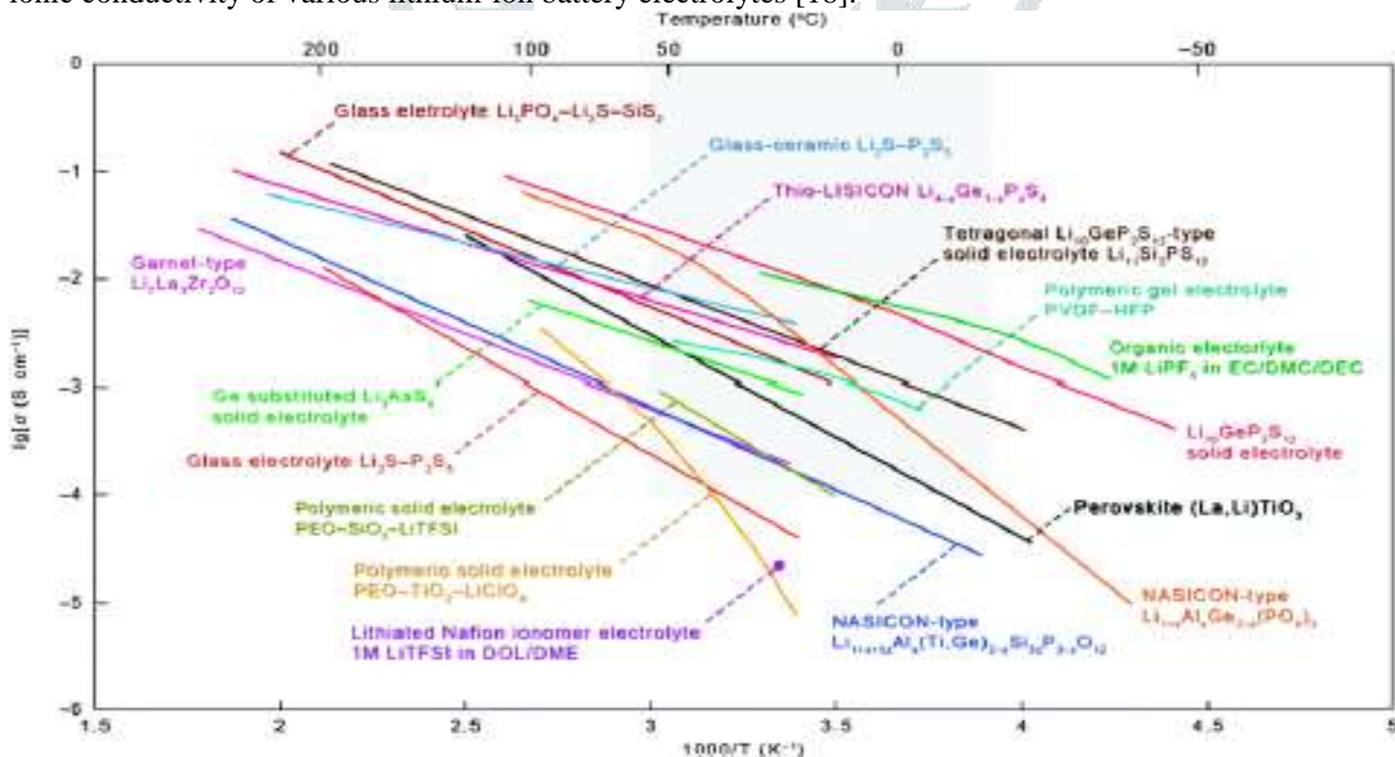


Fig. 6 Ion conductivity comparison of various lithium ion battery [18]

Cost reductions are driven by a variety of factors, including improved cell production methods, learning rates for package integration, and achieving economies of scale (Giga factories). It is important to note that with current technology, the cost of a gasoline vehicle is likely to be achieved within five years. I can't explain the commercial factors driving cost savings, but I'll explain how close the energy density of the current cell is to the basic limits of the chemicals selected. Then compare these limits with the SSB limits. State-of-the-art LIB contains oxide cathodes (especially NMC and NCA) 31, liquid electrolyte 22-24 with additives to improve Coulomb efficiency, and 35% silicon added to improve energy density. Use a carbon anode.[19][10][20][21]. A typical construction of a battery stack is shown schematically in Fig. 7.

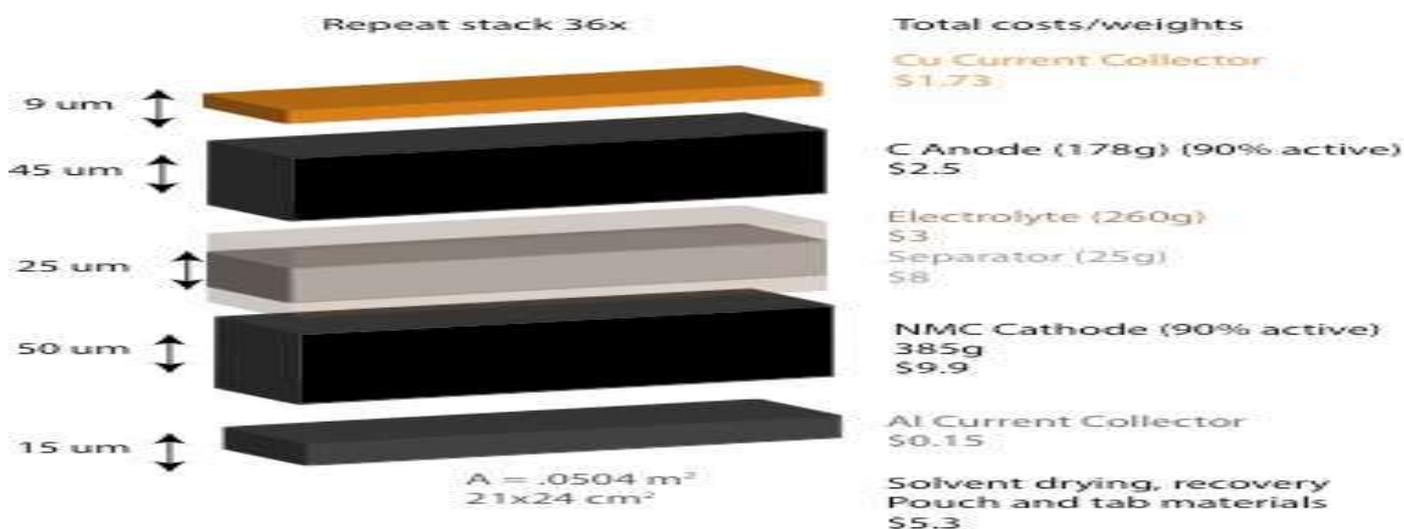


Fig. 7 A 52 Ah pouch stack of cell with costs and weights[22] [23]

The total cost was estimated using the cost curve, while the percentage cost of the component was estimated from previous literature [19] [25] [26]. In particular, we point out the percentage of electrode active material (90%), the thickness of the electrodes (50 micrometers), and the thickness of the separator (25 micrometers). A conceptually easy way to increase the energy density is to increase the thickness of the electrodes. This reduces the weight contribution of the Inactive Material [24]. First, calculate the current energy density of a commercial LIB. Assuming Tesla is using the latest Panasonic battery in the vehicle, the model SP100D's 100kWh battery uses 8,256 cells in an 18650 form factor. This corresponds to a total cell volume of 136.5 l, which is volumetric energy. Density of 732 Wh / l. The weight of a single 18650 cell was not given in the decomposition [25], However, assuming that everyone weighs about 45 g, the weight energy density is about 270 Wh / kg. The performance limit of this chemical using the industry-wide cathode thickness was recently estimated to be 1200 Wh / l (400 Wh / kg) 2. Note that the basic chemical limit is approximately 470 Wh / kg when using zero inert ingredients. Using the same cathode, increasing the thickness of the electrodes by 60%, and replacing Lim with carbon as the anode, the output is estimated to be 1300 Wh / L (475 Wh / kg) 2. Note that increasing the thickness of the electrodes reduces the relative weight and volume contribution of the Inactive Material, thus increasing the energy density and reducing the cost³⁵. If Lim's increase in relative energy density (+ 8% Wh / L, + 19% Wh / kg) appears surprisingly small, as it is far from the simple 10-fold increase expected from a particular gravimetric analysis. there is. capacity. To understand why these numbers are lower than expected, consider defining the total weight capacity of the cell. The point of this equation is to show the non-linear relationship between the weight capacity of the anode and the weight energy density of the cell. In addition, Lim has a relatively low bulk density (g / cm³) compared to C, which adversely affects volumetric energy density. Using the same formula, you can change Q from mAh / g to mAh / mL and multiply the value by the material density (g / cm³) to calculate E (Wh / L). Coulomb efficiency (discharge capacity / charge capacity x 100) is also very important. The average Coulomb efficiency (CE) of the current LIB is over 99.99%. This is required to maintain 74 ° capacity after 10 years of use (assuming 300 full charge / discharge cycles per year). Instead, if the average CE is 99.98%, this looks very similar, but the capacity retention is only 55 per 10 years of use. Therefore, even the slightest difference in CE can make a huge difference in capacity retention after thousands of cycles. For these metrics (Wh / L, Wh / kg, CE), we will discuss the theoretical and actual SSB. Theoretical all-solid-state battery An ideal all-solid-state battery replaces the liquid electrolyte and separator with a solid electrolyte

that is opaque to Li metal dendrites. This allows Li metal as an anode. According to references. When low density SSEs (such as polymers and sulfides) are used with moderate amounts of active material (20 vol%), two SSBs using Li metal anodes can reach approximately 480 Wh / kg. Inactive component). Therefore, the SSB can have an energy density increase of about 20% compared to the current LIB, but it is unlikely to increase compared to the Lim Liquid LIB. In addition, when using a high density SSE such as Garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, the theoretical energy density can be 375 Wh / kg, which is no advantage over traditional liquid LIBs (Table 1). The main reason why the gain from the Lim anode is lower than expected was explained earlier. Further drawbacks of SSE are the high density of SSE compared to the liquid electrolyte, the assumption that the thickness of SSE is 20 microns, and to achieve reasonable cell conductivity in the working SSB . The proportion of active substances currently needed is low.[26].

Table 1. Comparison of present and future technology of solid and liquid LIB in terms of Volumetric and Gravimetric energy densities, cost, coulombic efficiencies and manufacturability.

Technology	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/L)	Cost (\$/kWh)	Coulombic efficiency	Manufacturability
Current liquid electrolyte LIBs	260	732	150	99.99%	Gigafactories operating
Future liquid electrolyte LIBs (no Li_m)	400	1200	100	99.998%	Multiple gigafactories planned
Future liquid electrolyte LIBs with Li_m	475	1300	?	?	?
Current SSBs (low density SSE)	155	?	?	~70%	?
Future SSBs (low density SSE)	480	?	?	?	?
Future SSBs (high density SSE)	375	?	?	?	?

Table 1 compares the numbers for current and future liquid electrolyte and solid electrolyte LIBs[23].

There are two different interface challenges. The first is to maintain contact with a strong interface, which generally applies to all SSEs. Sulfides are more malleable than oxides⁴⁹ (can be densified by cold pressing instead of high temperature sintering⁵⁰), but they still have high interfacial impedance and interfere with optimal cell operation. The second interface challenge, especially in the case of sulfides, is the reactivity with both the high voltage cathode and the Li_m anode. For example, the LGPS thermodynamic stability window is 1.7-2.14V. Li / Li^+ indicates instability at both the Li metal anode, which is 0V relative to Li / Li^+ , and the metal oxide cathode above 4V. [27][28][29][30][31]

III Results

Safer technology

Lithium batteries with commonly used electrolytes, made from a combination of liquids and polymers, can pose a fire hazard if the liquid is exposed to the air. Solid-state batteries are desirable because they replace the liquid polymer electrolytes commonly used in consumer lithium batteries with safer solid-state materials. Rupp explains. Other methods of producing lithium-rich ceramic materials on larger pellets or ribbons that are heated using a process called sintering can produce dense microstructures that maintain high concentrations of lithium. However, they require higher heat and result in bulkier materials. A new technology developed by Wrap and her students creates a thin film about 330 nanometers (less than one-1.5 millionth of an inch) thick. "Thin film structures instead of thick ceramics are generally attractive for battery electrolytes because of the large volume of electrodes that require active storage capacity, so the Holy Grail is thin and quick."

Faster ionic conduction

Instead, you need an electrolyte with faster conductivity. The unit of measurement for lithium ion conductivity is described in Siemens. The new multi-layer deposition technology creates the lithium garnet material (LLZO) with the fastest ionic conductivity ever for a lithium-based electrolyte compound. This is about 2.9×10 Siemens (0.0000029 Siemens) per centimeter. This ionic conductivity competes with LIPON (Lithium Phosphate Nitride Electrolyte) -based solid lithium battery thin film electrolytes, adding new membrane electrolyte materials to the landscape. This work is based on a lithium garnet electrolyte because low treatment temperatures open the door to the use of high voltage cathode materials that become unstable at high treatment temperatures and reduce the size of the electrolyte. It shows the way to the battery. Allows physically large cathode volume with the same battery size[31][32][33].

Preparation of the Thin Film Solid state Lithium Battery

Thin-film lithium batteries are manufactured by laminating a cathode thin film, a solid electrolyte thin film, and an anode thin film on a substrate. FIG. 3 shows a schematic cross-sectional view of the battery. The cathode is LiCoO_2 and the anode is lithium metal. An oxide buffer layer is inserted at the cathode interface to reduce interface resistance. A silicon layer is also inserted at the anode interface to prevent electrochemical reduction of the solid electrolyte. All films were deposited under vacuum. In particular, the cathode membrane was deposited by sputtering. The buffer layer, solid electrolyte, and Si layer were deposited by pulsed laser deposition (PLD). And the anode film by thin film deposition. All steps after deposition of the solid electrolyte membrane should be performed in a dry atmosphere [34][35][36][37][38]

Battery Performance at Low Temperature

Battery reactions are essentially chemical reactions, so they rarely react at low temperatures. In other words, the internal resistance of the battery increases, which reduces the output characteristics. In addition, an increase in the viscosity of the liquid electrolyte or freezing can cause the properties of the liquid battery to deteriorate rapidly. All-solid-state batteries assume that performance degradation is temperature dependent. Figure 8 shows the results of a charge / discharge test at a chamber temperature of 40°C .

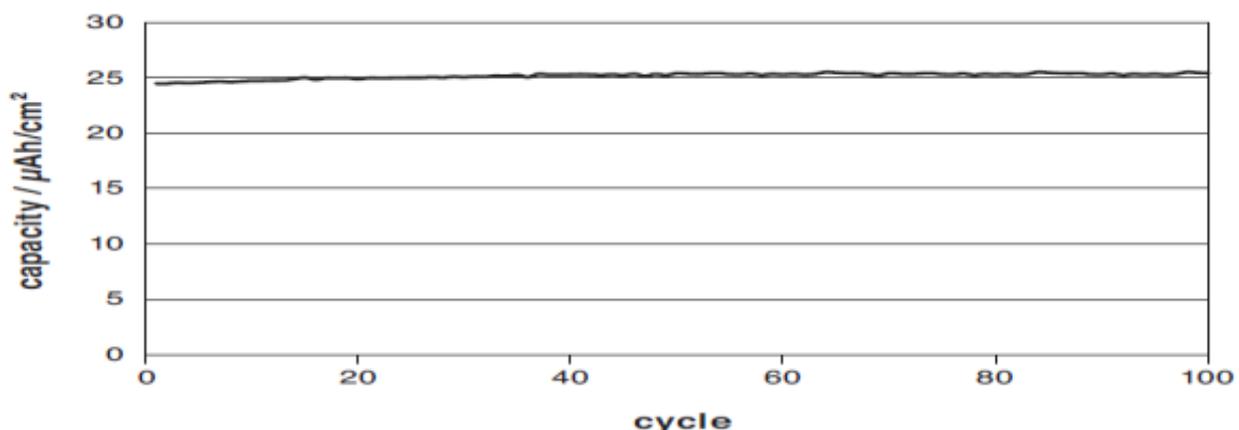


Fig. 8 Cycle performance of the thin film battery at low temperature (-40°C) (Mitsuyasu OGAWA*, Kentaro YOSHIDA and Keizo HARADA)

Battery Performance at High Temperature

As mentioned above, lithium-ion secondary batteries have the problem of boiling and evaporation of organic liquid electrolytes that exist at temperatures below about 60°C . Also, at high temperatures, electrolyte deterioration and side reactions are accelerated, so battery life generally tends to be shorter than at room temperature. Figure 9 shows the results of a charge / discharge test of a thin film battery at a high temperature of 170°C . [38].

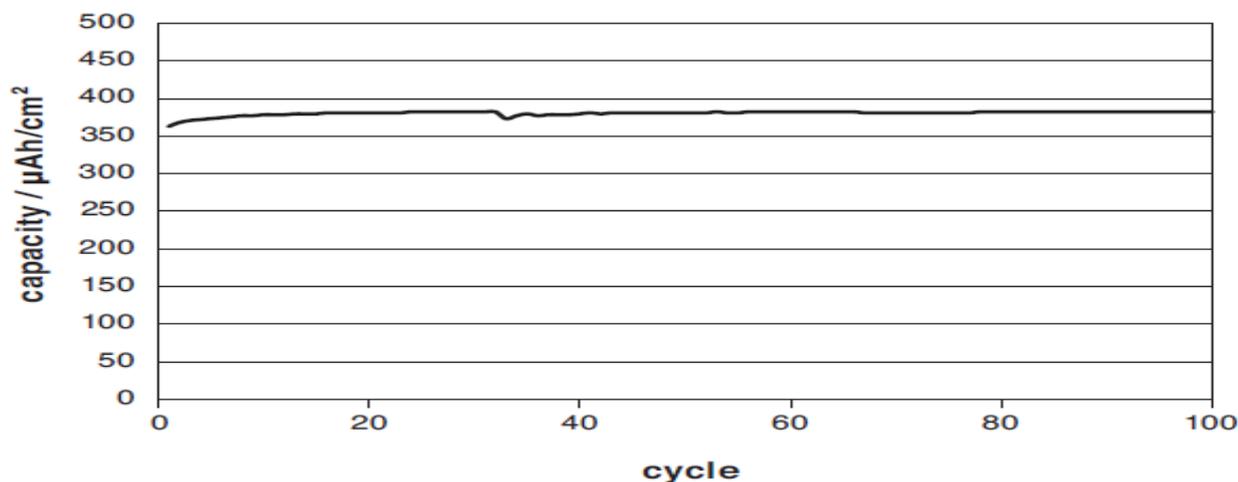


Fig. 9 Cycle performance of the thin film battery at high temperature (170°C)

Different companies working with different technologies is shown in figure. 10

SOLID STATE BATTERY COMPANIES & TECHNOLOGIES
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Company	ANODE	ELECTROLYTE
QuantumScape	Anode-free Lithium	Oxidic & Sulfidic Ceramic
solid energy	Lithium	Semi-solid Solvent-in-Salt
ionic MATERIALS	Lithium or Graphite	Doped Pi-conjugated Polymer
Sion Power	Lithium	Hybrid Ceramic-Polymer
Solid Power	Lithium	Sulfidic Glass-Ceramic
Bolloré	Lithium	PEO-based Polymer
ProLogium	Lithium or Graphite/Si	Oxidic Ceramic
Hydro Québec	Lithium	e.g. PEO-based Polymer
Panasonic	Lithium	Oxidic & Sulfidic Ceramic
SAMSUNG	Lithium Ag-C coated	Sulfidic Glass-Ceramic

Fig. 10 Different Solid -state battery companies with their technologies [23]

IV Conclusions

SSE provides a way to improve the weight and volumetric energy density of LIB by enabling the use of Lim. However, many challenges remain, and potential performance improvements are often over-promised and over-sold. Researchers report the weight of the active material, specifically the amount of Lim used, and the weight of the Inactive material, specifically the density and thickness of the SSE, so that it can be compared correctly with the current LIB. need to do it. There are applications where SSE offers the following important benefits: B. Fast charge / discharge (speed above 10 ° C), extreme heat resistance (greater than 80 ° C or less than 10 ° C), and improved safety. These applications are important, but not much more extensive than automotive, consumer electronics, and fixed storage applications. The performance of all-solid-state batteries at high and low temperatures has been investigated, and it has been confirmed that they operate stably at high and low temperatures, and the current LIB paradigm may continue for the time being.

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