Technology Insight

Why Solid State Batteries Are the Ideal Technology for Power Batteries

23.1.15

ADER-DES Consulting Team

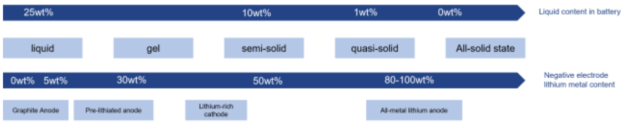
1

SOLID-STATE BATTERY: THE NEXT GENERATION OF BATTERY

1.1 Definition of Solid State Battery

Solid-state batteries refer to lithium batteries that use solid-state electrolytes instead of traditional electrolytes, and can be categorized into semi-solid-state batteries and full-solid- state batteries according to the amount of solid-state electrolytes used. Usually, we take 10% liquid content in the battery as the demarcation line between semi-solid and liquid batteries, while full-solid batteries will completely use solid electrolyte and the liquid content will be reduced to 0%.

Liquid lithium battery to solid lithium battery development process



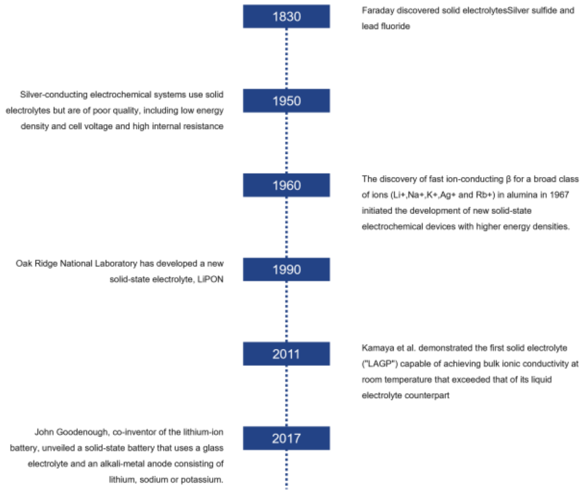
Liquid batteries use a liquid electrolyte to transfer ions and generate current. During the charging and discharging process, lithium ions are inserted or de-inserted and inserted or de-inserted back and forth between the positive and negative electrodes, and the diaphragm in the middle is used to isolate the positive and negative electrodes to avoid short-circuiting. Solid-state batteries, on the other hand, use solid electrodes and solid electrolytes, thus avoiding potential safety hazards such as short circuits caused by contact between positive and negative electrodes.

1.2 the beginning of industrialization

Fundamental research on solid-state batteries has a long history, with Michael Faraday's discovery of the solid electrolytes silver sulfide and lead fluoride in 1831-1834 laying the foundation for solid-state Ionics, and scientists discovering silver-conducting electrochemical systems using solid electrolytes in the late 1950's. The discovery of fast ionic conductor β in 1967, which can be used in alumina, initiated the development of new solid-state electrochemical devices with higher energy densities, such as the fused sodium/β- alumina/sulfur battery developed by

Ford Motor Company in the USA and NGK in Japan. In1967, the discovery of fast ion-conducting β, which could be used in alumina, initiated the development of new solid-state electrochemical devices with higher energy densities, such as the fused sodium/β-alumina/sulfur batteries developed by Ford Motor Company in the United States and by NGK in Japan. In system development, organic solid-state electrolytes (polyethylene oxide (PEO)) and inorganic solid-state electrolytes (NASICON) were discovered. In the 1990s, Oak Ridge National Laboratory (ORNL) developed a new type of solid-state electrolyte: lithium phosphine-oxygen nitride (LiPON), which could be used to make thin-film lithium-ion batteries. 2011 saw the demonstration of the first solid-state electrolyte (LAGP), capable of making thin-film lithium-ion batteries, by Kamaya et al. In 2011, Kamaya et al. demonstrated the first solid electrolyte ("LAGP") capable of achieving bulk ionic conductivity at room temperature that exceeded that of its liquid electrolyte counterpart, and in 2017, John Goodenough, co-inventor of the lithium-ion battery, unveiled a solid-state battery that uses a glass electrolyte and an alkali-metal anode consisting of lithium, sodium or potassium.

History of Solid State Battery Research



Faraday discovered solid electrolytesSilver sulfide and lead fluoride

Silver-conducting electrochemical systems use solid electrolytes but are of poor quality, including low energy density and cell voltage and high internal resistance

The discovery of fast ion-conducting β for a broad class of ions (Li+,Na+,K+,Ag+ and Rb+) in alumina in 1967 initiated the development of new solid-state electrochemical devices with higher energy densities.

Oak Ridge National Laboratory has developed a new solid-state electrolyte, LiPON

Kamaya et al. demonstrated the first solid electrolyte ("LAGP") capable of achieving bulk ionic conductivity at room temperature that exceeded that of its liquid electrolyte counterpart

John Goodenough, co-inventor of the lithium-ion battery, unveiled a solid-state battery that uses a glass electrolyte and an alkali-metal anode consisting of lithium, sodium or potassium.

1.3 high energy density, high safety and other performance advantages

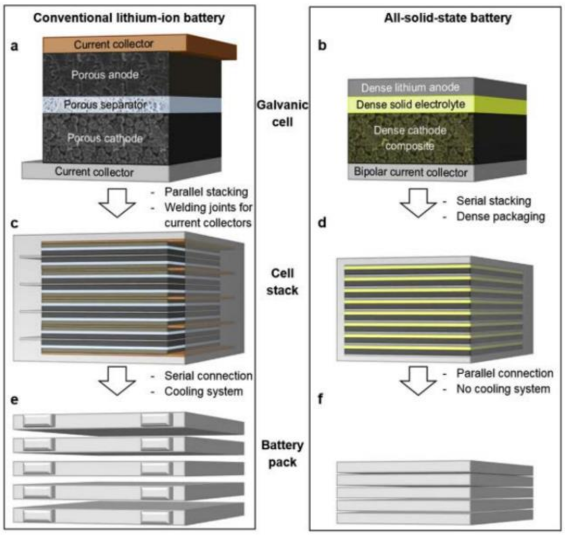
Strong demand for long range of new energy vehicles requires continuous improvement of energy density of lithium batteries. According to the formula: range = available power / energy consumption. In the same energy consumption remains unchanged, the battery pack size and weight are subject to severe limitations, the maximum driving range of EV mainly depends on the energy density of the battery. Therefore, in recent years, lithium battery materials have been developing in the direction of higher energy density.

The energy density of solid state battery is expected to exceed 400wh/kg, which is twice as much as that of current lithium iron battery. Currently, the energy density of lithium iron phosphate battery is around 200wh/kg, corresponding to a range of 300-500km, while the energy density of ternary battery is around 250wh/kg, corresponding to a range of 500-700km. If the solid state battery adopts the material system of high nickel ternary + lithium metal, the energy density is expected to be more than 400Wh/kg, and the range will be significantly improved.

Solid electrolyte compared to liquid electrolyte can solve the leakage of liquid Volatilization and other safety issues. Since the ignition point of solid electrolyte is very high, replacing liquid electrolyte with solid electrolyte material will effectively improve safety. The current state-of-the-art liquid lithium battery consists of porous electrodes and a spacer. The electrodes are coated with a fluid collector, which consists of conductive active materials, reagents and binders. Ion transfer takes place through a liquid electrolyte, which consists mainly of nonphotonic organic solvents and conductive salts. Many of the current safety concerns can be attributed to the flammability of the liquid electrolyte solvents. Replacing the traditional organic liquid electrolyte with a solid electrolyte would fundamentally solve the safety issues of leakage and evaporation of the electrolyte.

Solid-state batteries do not require electrolyte and diaphragm, and can realize the stacking of multi-layer positive electrode, solid electrolyte and negative electrode materials. Series connection and then package welding effectively simplify the package, so that the weight and volume of the overall battery pack can be reduced to enhance the range.

Liquid vs. Solid State Batteries at the Battery Pack Level



The solid electrolyte is a single ion conductor, so there are fewer side reactions and the cycle life is longer. Since the solid electrolyte does not have fluidity, the problem of repeated growth and dissolution of SEI film will not occur, which helps to realize stable cycle. In addition, transition metals are not easy to dissolve in all-solid-state batteries, thus avoiding the problems of capacity degradation at the positive electrode caused by the dissolution of transition metals, as well as the deposition of transition metals on the negative electrode side, which catalyzes the decomposition of SEI membranes.

2

SOLID-STATE BATTERIES WILL CHANGE MATERIAL SYSTEM

2.1 Solid electrolyte:

the biggest difference between solid-state batteries and liquid batteries. Solid-state batteries are divided into three main routes: polymers, oxides, and sulfides, differentiated by the electrolytes used. Oxide and sulfide are inorganic solid-state electrolytes, and their architecture consists of a composite cathode made up of cathode active material, solid electrolyte particles, and conductive carbon, which is matched with an oxide or sulfide solid electrolyte layer and a lithium metal anode to form an all-solid-state battery. The polymer electrolyte consists of a solid polymer electrolyte (SPE) with lithium salt dissolved in it.

Ionic conductivity, interfacial compatibility, mechanical properties and electrochemical stability are the core measurements, the ideal solid state electrolyte should have high conductivity, wide electrochemical window and good electrochemical and mechanical properties. Currently, polymers are the earliest to be commercialized but have defects, oxide systems are in a faster pace of industrialization, and sulfides are in an early stage of development but have huge space for future development.

The polymer has good viscoelasticity and strong mechanical properties, but it has the disadvantages of high cost and low electrical conductivity due to high crystallization of the matrix.

Oxide oxidation potential is high and therefore the electrochemical window is wide, but the limiting factor for its development is the high impedance between electrolyte and electrolyte, and the interfacial reaction will cause the capacity of the battery to decay.

Although sulfide has poor interfacial stability, it has the highest conductivity and therefore has the greatest potential for development. However, the poor interfacial mechanical properties and low hardness of sulfide in its composite positive electrode, there is a certain degree of variability, need to enhance the interfacial physical contact by applying pressure.

The main difference between solid state battery and liquid battery preparation process is in the middle and back section, solid state battery preparation needs to be pressurized or sintered rather than injected into the liquid synthesis.

Sintering and tempering is required for the preparation of oxide batteries. The manufacturing process for oxide solid-state batteries involves preparing the cathode and solid-state electrolyte by ball milling, and then sputtering the solid-state battery onto the cathode. Because the cathode material reacts with the solid-state electrolyte, resulting in significant depletion of lithium ions and capacity degradation, the cathode- electrolyte material needs to be calcined at a high temperature to improve the solid- solid contact and thus increase the conductivity.

Sulfide battery preparation requires high pressure and is air sensitive, which makes it costly. The sulfide electrolyte layer is thick and requires high pressure for compaction. In addition, sulfide electrolytes are chemically unstable and susceptible to air oxidation.

Polymerbatteriesarerealizedbyroll-to-rollassemblyofelectrodesandelectrolytes. The roll-to-roll process is simple and suitable for mass production, but due to the limitation of ether polymer electrolyte material, it needs to work under high temperature, so it faces the problem of short circuit easily. In addition, the energy density is not high due to the difficulty of compatibility with high-voltage cathode materials.

The current development of solid state electrolytes still faces a number of technical pain points.

The main characteristic of solid-state battery is to inhibit the growth of lithium dendrites by its high strength, to match the lithium metal anode, so the strength of electrolyte material is very important. According to Newman and Monroe's prediction, when the shear modulus of the solid electrolyte is large enough (with a critical value of 9 GPa), the growth of lithium dendrites can be inhibited, avoiding safety issues such as short-circuits caused by lithium dendrite punctures. Polymer electrolytes are generally unable to inhibit the growth of lithium dendrites; sulfide electrolytes are expected to inhibit lithium dendrites; and oxide electrolytes have the best performance in inhibiting lithium dendrite growth.

Solid electrolyte/electrode solid-solid interface stability: In traditional lithium batteries, the electrode active material particles are completely immersed in the electrolyte, so good contact can be maintained between the electrode and the electrolyte. However, in solid- state lithium batteries, poor interfacial contact will lead to low utilization of active particles, high polarization, and even loss of contact during cycling. Polymer has elasticity and deformability, and the contact between electrolyte and positive electrode particles is better. Due to certain deformability, the contact between sulfide particles and cathode material is better. Due to their deformability, sulfide particles and cathode material particles can form a high compaction density and interfacial contact under pressure. Therefore, the contact between the active substance particles and the sulfide electrolyte can be significantly improved by applying pressure. Oxides are the hardest and most brittle, and the contact with the active material in composite electrodes obtained by cold pressing at room temperature is usually a point contact. Point contact leads to incomplete capacity utilization and causes uneven distribution of current and stress.

Electrochemical Stability: When a solid electrolyte is in contact with an electrode, electrochemical reactions occur at the interface, primarily redox decomposition of the electrolyte itself, including the embedding or de-embedding of electrons or carriers. These two reactions can occur separately or simultaneously and together determine the electrochemical window of the electrolyte. The electrochemical window of an electrolyte is the voltage range in which there are no redox decomposition reactions. Oxides have the best reduction resistance on the negative side and are therefore more electrochemically stable. Sulfides have a narrower electrochemical stability range and are subject to redox decomposition, which means that sulfides are electrochemically unstable on both the positive and negative sides due to side reactions. The polymer electrolyte is less stable on the positive side at high voltage, and is prone to oxidative decomposition, which causes a sharp decline in battery performance.

2.2 Anode: Developing towards high energy density such as high nickel, cobalt-free, lithium-rich

Solid-state batteries require high energy density, and anode is developing in the direction of high nickel, cobalt-free and lithium-rich. Currently, mainstream anode materials in the market include lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP) and ternary anode materials (NCM and NCA). Ternary materials are characterized by high energy density, of which, the upper limits of specific capacity of medium-high nickel (5- series and 6-series) and high-nickel ternary materials (8-series and 9-series) can reach 205mAh/g and 220mAh/g, respectively, and the trend of high-nickelization of solid-state batteries is strengthened due to the requirement of high energy density. 8-series ternary materials' market share will grow from 36% in 2021 to 43% in 2022, while the 5-series ternary materials' market share will increase from 36% to 43% in 2022. The market share of 8-series ternary will increase from 36% in 2021 to 43% in 2022, and the market share of 5-series ternary will decrease from 48% in 2021 to 35% in 2022, mainly due to the fact that the high nickel route is adopted by many medium- and high-end models at home and abroad, leading to the significant growth of high nickel batteries installed in the international market of China, Japan and South Korea's leading battery enterprises, including CATL, Panasonic, LG Energy, Samsung SDI and SKI. In the long run, as the industrialization of semi-solid/solid-state batteries accelerates, the advantages of high energy density and good cycle life of ternary materials can still ensure their superiority in the competition of high-end battery market, therefore, it is expected that high nickel will continue to develop in depth.

As an emerging cathode material with higher energy density limit, Li-rich manganese-based cathode material is expected to be the optimal choice of cathode material for solid-state batteries in the future. Li-rich Mn-based cathode materials are layered oxides composed of Li_2MnO_3 and $LiMO_2$, and their high capacity is due to the combined effect of two mechanisms: redox reaction of transition metals and redox reaction of oxygen ions.

2.3 Negative electrode: silicon negative electrode, lithium metal is expected to become the future choice

Silicon-based materials with high capacity and low voltage platforms have great application potential if they can meet the needs of high energy density solid-state batteries:

- Silicon is alloyed with lithium at room temperature, with a theoretical specific capacity of up to 4000mAh/g, more than ten times that of current graphite-based anode materials.
- Compared with graphite, silicon is abundant and widely distributed in the earth's crust, accounting for 25.8% of the crust's mass, making it the second most abundant element in the earth's crust.
- silicon has a voltage platform of 0.3-0.5 V, eliminating lithium precipitation and significantly improving safety.

- Silicon-based anode materials have excellent low-temperature performance compared to graphite;

Lithium metal anode is expected to be the best choice of anode for solid-state batteries in the future. According to QuantumScape, a leading manufacturer of solid-state batteries, the energy density of lithium anode can be close to 600mAh/g, while that of silicon anode is 300mAh/g. Although the theoretical specific capacity of lithium anode (3860mAh/g) is still lower than that of silicon-based material (4200mAh/g), there are some defects in silicone material, which has a volume expansion coefficient of 300% (compared with 5-10% for commercialized graphite anode) in the process of charging and discharging. However, silicon material has some defects, its volume expansion coefficient during charging and discharging reaches 300% (the expansion coefficient of commercial graphite anode is 5-10%). Therefore, it is expected that lithium metal anode will be the choice of solid state battery anode in the future.

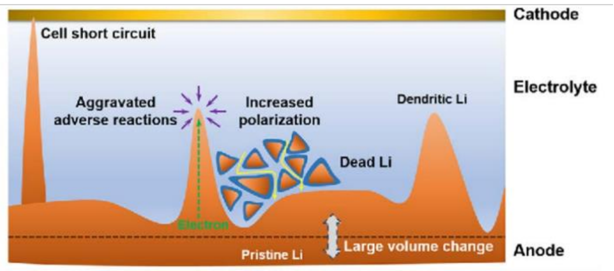
Lithium metal is expected to play a huge role in solid-state battery cost reduction. According to the comparison of four types of lithium batteries, the total cost of solid-state batteries using lithium anode materials is the lowest. The price of lithium is significantly lower than the price of silicon, and the simplified manufacturing process significantly reduces the manufacturing cost, making lithium metal anode has obvious cost advantages.

Norm	**Liquid Lithium Battery**		**solid state battery**	
	Graphite Anode	Silicon Carbon Negative Electrode	Graphite Anode	Lithium Anode
Material Costs ($/KWh)	93.2	83.2	137.9	86.5
Production costs ($/KWh)	25.5	24	20.9	15.5
Total Battery Cost ($/KWh)	118.7	107.2	158.8	102

Data sources： Energy Technologies

Lithium metal anodes for semisolid/solid state battery applications are still threatened by lithium dendrites. Technically there is still dendritic growth of lithium metal, which will likely result in short circuits (leading to thermal runaway) and low coulombic efficiency with poor cycle life.

Lithium metal still needs to address lithium dendrites



2.4 Diaphragms: as a transition stage option for semi-solid batteries

All-solid-state batteries may replace diaphragm applications, while semi-solid-state batteries, as a transitional option, still require high diaphragm safety. Solid-state batteries utilize a solid electrolyte, which ensures the free movement of lithium ions between the positive and negative electrodes, thus replacing the electrolyte and diaphragm. Semi-solid batteries, on the other hand, still require an electrolyte for ionic conduction, and therefore require a diaphragm to insulate and prevent direct contact between the positive and negative electrodes. The high nickelization associated with semisolid/solid-state batteries can lead to active cathode materials that can make the battery unsafe, so the diaphragm needs to be combined with a coating process for semisolid-state batteries.

On the one hand, coating effectively improves diaphragm performance. Due to the tensile strength and low puncture strength of wet and dry process, the stability of diaphragm is poor. The coated diaphragm greatly improves the thermal stability and puncture strength of the diaphragm, preventing large contact between positive and negative electrodes due to diaphragm shrinkage, and effectively improving product yield and safety. Taking ceramic coating as an example, the coated diaphragm's resistance to shrinkage is greatly improved due to the presence of ceramic layer, which results in better mechanical properties and safety. On the other hand, the coating process has an impact on the high energy density requirements and still needs to be combined with the wet process for semi solid-state batteries. The thickness of the coating material diaphragm is higher than that of the dry and wet processes, and the energy density is affected by the low ion passage rate. Therefore, wet process + diaphragm coating will be the main choice for semi solid-state battery in the future. Coating materials are divided into two categories: inorganic and organic. Inorganic coating materials are mainly divided into boehmite and alumina, which are the main coating materials used in the current market.

2.5 Cells: series connection can effectively increase the voltage of solid-state batteries

Improvement of cell energy density has a great impact on the performance of solid-state battery. Traditional lithium batteries can only realize external series connection but not internal series connection due to the use of liquid electrolyte inside the single cell and the possibility of easy decomposition or even explosion after the carrying voltage exceeds 5V. However, solid-state batteries can be realized in series connection within the battery, so that the voltage of the single battery is much higher than the traditional power battery. Take 4 cells with rated voltage of 3.6V as an example, 13.6V can be realized by series connection, while only 3.6V can be realized by parallel connection.

In semi solid-state batteries, a sealant is used to encapsulate both sides of a single cell. When the electrolyte cannot flow in all directions and the cells are connected in series, the use of non-essential structural components can be reduced, dramatically increasing the storage efficiency of solid-state batteries, and thus increasing the energy density of the cells.

2.6 Encapsulation:

the use of soft package encapsulation form, is expected to increase the amount of aluminum-plastic film solid-state batteries are expected to use soft package encapsulation system, will increase the demand for aluminum-plastic film. According to the different shell, lithium battery cell packaging is mainly divided into two categories: hard shell and soft pack. Hard shell encapsulation materials are mainly steel and aluminum shell, according to its internal arrangement of positive and negative poles are different, and is divided into cylindrical and square, while the soft package encapsulation mainly uses aluminum-plastic film. When solid-state batteries use solid-state electrolytes, the battery cells do not need the protection of hard shell packaging. Therefore, soft pack may be the most suitable packaging form for solid-state batteries in the future, and will benefit from the industrialization of solid-state batteries and develop significantly.

3

THE STATE OF INDUSTRIALIZATION

Solid-state batteries are currently in the initial stage. It is expected that China's solid state battery shipments will reach 251.1GWh in 2030, and the market space in 2030 is expected to reach 3 Billion USD.
A number of new energy vehicle enterprises at home and abroad have announced the semi- solid state battery installation planning. BMW, Mercedes-Benz, Volkswagen and Toyota and other overseas giants are planning to launch electric vehicles equipped with solid-state batteries around 2025.

Representative enterprises in Europe, the United States, Japan, South Korea and China are actively promoting the layout of solid-state batteries. Among them, there are many startups in the United States, and QuantumScape, Solid Power and other enterprises have become the main force in the industry. European enterprises are mainly car companies investing in startups, and Volkswagen invested $100 million to form a new joint venture with QuantumScape. BMW has joined hands with Solid Power to develop new solid-state batteries. Japanese and South Korean companies have been working together in groups, with Japanese companies such as Mitsubishi, Nissan, and Panasonic setting up joint R&D centers based on their independent R&D teams. The three leading battery companies in South Korea - LG Chem, Samsung, and Sankyo - are working together to develop new solid-state batteries.
Star SDI and SKI have also formed an alliance to collaborate on solid-state batteries. Chinese companies are late to the game, but they are participating actively in the development of solid-state batteries. There are a lot of people with them, while car companies work closely with battery companies.

United States:

Founded by Jagdeep Singh, Fritz Prinz and Tim Holme, the company has over 200 patents on solid state battery technology. With investments from Bill Gates, Volkswagen Group, Continental AG and SAIC. The company has a market capitalization of more than $40 billion and is now the leading developer of solid state battery technology.

Europe:

Bolloré is the first company to commercialize solid-state batteries on a large scale, but the energy density of these batteries is only 100 Wh/kg; its self-developed electric car Bluecar is equipped with a 30kWh lithium metal-polymer battery produced by its subsidiary Batscap, with a range of 120km. 2,900 units of the Bluecar have been placed in Autolib, a car- sharing service in Paris, which is the first international case of using solid-state lithium battery. About 2,900 Bluecars were placed in the Paris car-sharing program Autolib, the first international case of an electriccar using solid-state lithium batteries. BatScap chose the polymer technology route, using LFP for the cathode, lithium metal for the anode, and polyethylene oxide (PEO) for the electrolyte.

Japan and South Korea:

Nissan, the representative company, has put forward the "Nissan Motor Vision 2030", and plans to build a pilot plant for solid-state batteries by 2024. By 2026, it will invest a total of RMB 112.8 billion to accelerate the transformation of electric technology. Meanwhile, Nissan plans to realize large-scale mass production of solid-state batteries in 2028, and launch the first electric vehicle equipped with the company's all-solid-state batteries in the same year. In addition, on April 9, 2022, the company announced that it has partnered with NASA to develop a new all-solid-state battery that will be used for the 2028 product launch and the 2024 pilot plant.

China:

At present, domestic solid-state & semi-solid-state battery manufacturers mainly include Qingtao Energy, Welion New Energy, Ganfeng Lithium, Farasis Energy and Gotion HT, etc., which have all realized the industrialization of semi-solid-state battery.

Web：www.ader-des.com

Contacts：Luna

E-mail：luna@ader-des.com