Lithium All-Solid State Batteries Using on Electric Vehicles

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Abstract. For the past few years, as the society starting to realize the shortage of traditional resources like oil, coal and gas, which should be used in more irreplaceable places. The green house gases have also given a great disturbance to the whole society, which has been proved that most GHGs comes from coal-related events. Lithium-ion battery shows a great ability of storage energy that could be used on electric vehicles saving the usage of oil and reducing the emission of greenhouse gases. However, its limited energy density and safety issues need to be improved. This paper summarizes the pros and cons of liquid-state lithium-ion battery and the all-solid-state batteries (ASSBs) and the future roads of improvement of ASSBs. This upgrade of lithium-ion battery can improve its limited energy density, safety and low temperature performance with other drawbacks emerging. With the study of ceramic, polymer and hybrid electrolytes, the drawbacks of the ASSB, like expensive, point-contact, low ionic conductivity and the lack of supporting materials, could be solved in different extent. This paper hopes to help realize the promising of ASSB accelerating its application on the electric vehicles. Saving the energy and improving the efficiency of energy usage is greatly needed for our society. The ASSB could help realize these aspects.

Keywords: All-solid state battery, Lithium-ion batter, Electric Vehicle, Energy.

1. Introduction

As the demand of electric vehicles rises, the need of secondary batteries with high energy density rises as well. The lithium-ion battery is assumed as the most promising battery due to its principle and the structure giving great power to the electric vehicles comparing with other primary batteries and secondary batteries. However, the lithium-ion battery using these days is facing multiple challenges and questions from the public delaying the development of electric vehicles. The liquid electrolyte in the lithium-ion battery provides great energy density and non-memory effects with the risk of explosion and bad performance under low temperature. The all-solid-state batteries (ASSBs) which replaced the liquid electrolyte and the membrane with the solid-state electrolyte solves the safety problem by using non-flammable materials. Moreover, the ASSBs have many advantages giving the electric vehicles a more promising future in application. Its high energy density gives a longer range of driving when applying to electric vehicles, and reduces the frequency of charging saving the time when traveling on the road.

This paper comparing with other researches combines the pros and cons of liquid lithium-ion batteries and the ASSBs analysing these two kinds of batteries' future when applying on electric vehicles. On top of that, the all-solid-state batteries also face several problems tackling its application. Different types of solid-state electrolytes have their own benefits and drawbacks, which need to be upgraded to challenge the place of the lithium-ion battery. This paper summarizes those aspect as well pointing out the bright future application of the ASSB where could be keep improving.

This paper mainly focuses on the promising future of the all-solid-state batteries under this circumstances that the demand of the safety and the high energy density request of the battery. Firstly, the paper introduces the advantages of the using lithium-ion batteries and the limited energy density, safety and low temperature performance issues delaying its development. Secondly, the paper introduces the basic principle and its differences from liquid-state electrolyte batteries and the pros of the solid-state electrolyte batteries, which are their nonflammable, dendrites suppression, lighter, mechanical rigidity, and wide electrochemical window ability. Finally, this paper summarizes the recent researches about the improvement and measurement that could take to figure out the problems of various solid-state electrolytes, like expensive, point-contact, low ionic conductivity and the lack of supporting materials for ASSBs.

2. Liquid-state electrolyte lithium-ion battery

Lithium-ion battery containing liquid electrolytes are recently the best-performing and promising energy preserve way, especially about the application of phones and electric cars [1].

2.1. Principle of lithium-ion batteries

Like the basic secondary batteries, lithium-ion batteries generate electricity by the movement of electrons produced by the redox reaction. During the process, lithium-ions transfer from cathode material across the electrolyte and the membrane to anode material replacing and balancing the movement of electrons.

The high quality and number of lithium-ions movements lead to a high energy density of lithium-ion batteries. However, facing multiple disadvantages due to its principle as well.

2.2. Advantages of liquid electrolyte lithium-ion batteries

High capacity. Compared with other secondary batteries, lithium-ion battery is showing a better performance on its capacity and energy density [2]. No memory effect. For some batteries, they are facing a great limitation of memory effect, which reduces the battery's capacity if people charged the battery not until its fulling discharged. Since our habit do not prevent us from charging the battery all the time, the loss of battery capacity needs to be solved. Surprisingly, when it comes to the lithium-ion battery, it nearly has the memory effect, which gives it a more promising future development.

2.3. Disadvantages of liquid electrolyte lithium-ion batteries

2.3.1 Limited energy density.

Due to the battery's materials, the energy density and the power of a fully charged lithium-ion battery are still facing great limitations. Most electric vehicles with lithium-ion batteries hold an endurance mileage under 600km, while many car manufactories choose to produce hybrid electric vehicles giving a more promising endurance mileage for the customers. It's awkward having their vehicles' engines stop running in the middle of the street. Multiple materials are able to enlarge their energy density and raise their capacity. Those technologies including silicon nanowire anode, some special coating and decorating on the cathode material surface, and the replacement of liquid electrolyte still need time to be studied about how to reduce their cost and improve the quality.

2.3.2 Safety.

Many concerns from society are focusing on the explosion and safety issue of the lithium-ion battery. Electric vehicles on fire or blowing up are still happening in recent years. The main reason is that in the battery many electrolytes are explosive under a certain temperature. Also, as the battery produces its power, the internal structure will give out some dendritic crystal damaging the membrane, which causes internal short out leading to overheating and then the explosion. Moreover, the safety after interacting with an impact needs great notice. Most lithium-ion batteries applied to electric vehicles do not endure a huge impact, which will cause the same disaster [3].

2.3.3 Low temperature performance.

The power that generates from lithium-ion battery generates from the transmission of lithium ions and electrons through membrane and electrolyte, which becomes slower and much more difficult under low temperatures. The rising of the internal resistance can cause the energy hard to be used. When lithium-ion battery is used on electric vehicles, it happens to be difficult to start or have a sudden flame-out [4].

3. Solid-state lithium-ion batteries

In the meantime, the current study about new improvement of lithium-ion batteries including solid-state electrolytes has sparked intense interest about ASSBs [5]. The ASSB is a great replacement for traditional liquid electrolyte battery that uses nonflammable solid-state electrolyte (SE). Though its have more problem that needs to be solved, its believed to be the future trend of the battery.

3.1. Structure of ASSB

For the application of solid-state electrolytes of lithium-ion batteries, oxide electrolytes, sulfide electrolytes, and polymer electrolytes are the most important and promising material methods. The Polymer electrolytes, especially composite polymer electrolytes have risen attention of a deeply researches due to its great interface completely contact and the reduction of solid electrolyte causing great production possible. The basically using polymer container of the composite polymer electrolytes are PMMA, PEO, PAN, and PVDF, and the ceramic fillers can be classified into two kinds, which are passive ones and active ones [6]. Oxide electrolytes including LAGP, NASICON-type, LISICON-type, perovskite-type, LAGP, and garnet-type LLZO shows special heating stability, high electrochemical window, but the low ionic conductivity of lithium ions and interfacial point-contact with anode and cathode materials holds its back [7]. Sulfide electrolytes shows the highest ionic conductivity among all electrolytes even higher than the liquid state electrolytes, their good interface contact, and high deformability [8]. The improved rate capability, which is because of the great lithium ion transfer of most solid-state electrolytes and possibly not worth mentioning interfacial resistance with active anode materials such as graphite or lithium may lead to ASSB batteries outperforming Li-ion batteries.

3.2. Advantages of all-solid-state lithium-ion battery

3.2.1 Nonflammable.

The ASSB contains a solid-state electrolyte replacing combustible liquid-state electrolyte. The working temperature range rises to nearly four times than it used to be. Moreover, most solid electrolytes are incombustible, which prevents the battery from spontaneous ignition causing great disease. What is more important is that the ASSB is not facing the danger from sparking and shorting out after impact and puncture under testing. Applying ASSB to electric vehicles guarantees a safer driving experience for the driver and society [9].

3.2.2 Dendrites suppression.

The basic internal character which makes the lithium-ion batteries failed to generate power is the growth of lithium dendrites. Lithium dendrite induces an internal short out and impedes large bigger production and application of Lithium-air battery and Lithium-sulfur battery. The lithium dendrites grow from anode and go through the membrane made of polymer materials which eventually leads to short-out when it gets to the cathode side. For the liquid-state electrolyte batteries formed by the Li^+ reduction chemical reaction, Li dendrites keep to consume the electrolytes, resulting in instability of their electrode/electrolyte interface, destroying the generated solid-state electrolyte interface film, and falling off the electrode, resulting in dead Li, resulting in low Li dendrites. The penetration of the coulombic efficiency into the crystal will lead to a series of hidden dangers such as explosion, thermal runaway and internal short out.

Comparing with liquid state electrolytes, solid electrolytes usually have a better mechanical modulus, which can prevent lithium dendrite from growing and diffusing to the certain extent. Solid electrolytes are proved to be efficient in decreasing the lithium dendrite growing from the beginning. The growth of dendrites in ASSB is due to defects and surface cracks along grain boundaries that generate current densities, leading to the localization of lithium-ion electrodes and penetration, like shows in figure 1.

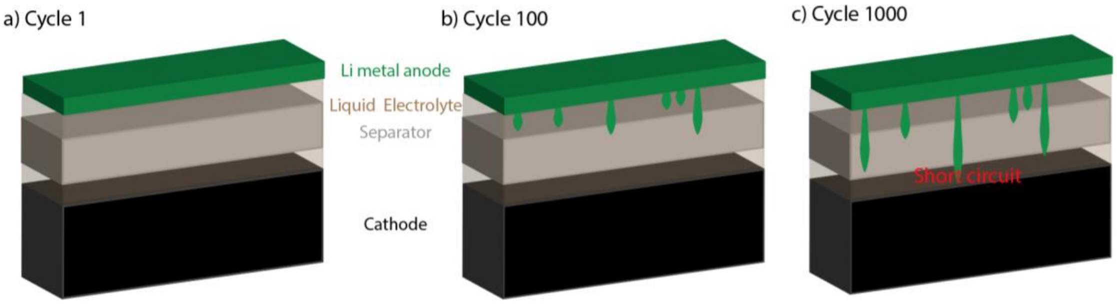

Figure 1. Illustration of repeated charging cycles leading to a lithium dendrites formation [10].

3.2.3 Mechanical rigidity.

Replacing the liquid-state electrolytes and membrane with the solid-state electrolytes could effectively reduce the thickness of the lithium-ion batteries. With a thin layer and not an easy-to-flow state of electrolyte, the ASSB has a better performance on mechanical rigidity. Much easier to bend or change sizes and will realize a bigger future applying market.

3.2.4 Lighter.

In a lithium-ion battery, liquid electrolyte takes nearly 30% of the whole weight. The solid-state electrolyte has a much higher energy density and specific energy, which can reduce the total usage to get the same power from the battery. Since the ASSB has no safety concerns, all the safety supervision devices and protections in the lithium-ion battery can be reduced or even abolished to make the battery lighter. Moreover, when the battery is used on electric vehicles, a lighter weight can improve its acceleration ability and the using efficiency of power. There is no denying that a heavy vehicle is more stable, so the designers can change the weight saving from a single battery to more batteries and other improvements to the batteries and vehicles.

3.2.5 Wide electrochemical window.

As people are charging the battery and using the battery, the internal voltage is changing during the process. The voltage is even higher than the public can expect when people pursue fast-speed charging. However, almost all the material components have their disintegrating voltage that can cause the material to have a red-ox reaction and lose its function. Especially in battery material, all the best cathode and anode materials have to enquire a wide and high electrochemical window to hold the material stable under high voltage to fulfill the request of fast-speed charging. For most liquid electrolyte lithium-ion batteries the maximum applied voltage is restricted by the liquid electrolyte's electrochemical window. The ASSBs using solid-state electrolyte can be applied under higher voltage rising the charging speed and higher capacity, which realize the biggest demand for electric vehicles [11].

3.3. Disadvantages of all-solid-state lithium-ion battery

3.3.1 Expensive.

The limited mental resources for synthesizing the solid-state electrolyte and the cathode accompanying it cause the price remaining higher than a liquid electrolyte lithium-ion battery. Moreover, the production line of ASSBs is yet mature enough to apply all the promising technology. The most promising technology is still in the first stage of development, which needs time and several times of upgrades to continually upgrade the behavior of ASSBs and reduce the huge cost of production.

3.3.2 Point-contact.

Since electrolyte state changing to solid state, the electrolyte and the electrode touching method of the lithium-ion battery has changed into the solid with solid touching ways. The surface contact between the cathode and solid-state electrolyte is different from liquid electrolyte. Battery cathode materials and solid electrolytes are usually on the micron scale. This same scale will lead to contact in the form of point contact. Compared with liquid electrolytes, the statement of solid and solid interfaces is no wettability, which lets it difficult to achieve complete contact. Low effective interfacial place between electrolyte and electrode can lead to a great possible barrier for charging transfer and form higher contact resistance.

Furthermore, the electrolyte and electrode interface where the chemical reactions happens during cycling have to be considered. Chemical reactions are respectively divided into chemical reactions between electrolytes and electrodes and redox electrolyte decomposition reactions. Decomposition reactions are depicted by only charge carriers and removal or insertion of electrons. These several chemical reactions can happen simultaneously or independently, which determine the electrochemical ability of LIBs. Point contact forms can lead to undesirable properties that affect chemical reactions.

The electrolyte and electrode interface modes make up a space charging layer, resulting in the dramatic rising in interior resistance. The best interfacial layer that can be imagined have to be an electronic insulator and an ionic conductor. If the interfacial layer is the ions and electrons mixed conductor or is in an unstable state, interfacial reactions are always taking place and the resulting reactants are deposited in the interfacial layer. When the interfacial layer’s thickness increases, the electrochemical performance deteriorates severely.

3.3.3 Low ionic conductivity.

Not only due to the form of contact in an ASSBs, but also in reasons of the interior character of the solid-state electrolyte. Most using solid-state electrolytes have a worse ionic conductivity compared with liquid electrolytes, which harms the electrochemical performance of the lithium-ion batteries, which is respectively cycle stability, rate capability, and low energy conversion efficiency.

3.3.4 Lack of supporting material.

The materials applied to the ASSB are still developing. The main part is the solid-state electrolyte, though the anode and cathode electrode supporting electrolytes need to be upgraded as well. The cathode, anode, and electrolyte should be matched up to realize the maximum of specific energy. Otherwise, using the same anode and cathode materials as the liquid-state lithium-ion battery is lead to even worse performance than an ASSB.

4. Current applying improvement

4.1. Hybrid electrolyte

Due to the drawbacks of ASSBs, scientists are studying new ways to increase the average specific energy and energy density of the lithium-ion battery. A small amount of solid electrolyte can be used in cathode coating, which realizes the improvement of the specific energy and the energy density of lithium-ion batteries at a low cost. The coatings prevent direct contact with the electrolyte, which improve structural stability, suppress phase transition, and decrease the disorder of cations in crystal sites. Eventually, heat generation and side reactions are decreased during charging cycles. The coating on the cathode of the battery is the same as a hybrid electrolyte, which adds some liquid electrolyte to a solid electrolyte [12]. Both ways help decrease the surface resistance and increase the ionic conductivity.

4.2. Ceramic electrolyte

Materials with lattice defect tunnel or glass network structure are the so-called fast ion ceramic electrolyte. Ions can travel through those tunnels in specific directions, which are closely related to crystal structure defects. Defects in the crystal structures can affect the transport ways for ion conduction. Crystal structure defect is easy to be affected by temperature. Generally, the concentration of ions or vacancies will rise, when the temperature rises. Therefore, solid-state electrolytes have a better ionic conductivity at high temperature. Moreover, Lithium-ions can show great ionic conductivity at around and even under 25℃ temperatures, because of their small radius and low valence [13].

4.3. Polymer-based electrolytes

First, for polymer electrolytes, it is critical to ensure that the polymer matrix is able to couple with lithium ions and dissolve lithium salts as well. When the temperature of the battery and electric vehicles using is lower than the glass transition temperature of these materials of polymer, increasing the decoupling resistance makes it more difficult for the lithium and polymer chains to dissociate. Additionally, in order to accelerate the dissociation of lithium elements in the polymer materials, the lithium materials selected need to have a polymer with low lattice energy and high dielectric constant. The number of free lithium-ion and chain mobility have an overwhelming influence on the lithium-ions mobility, where the number of lithium-ions depends on the extent of dissociation of lithium materials in the polymer electrolytes. Under the action of electrical applications, Lithium-ions can be transmitted. It was summarized in figure 2.

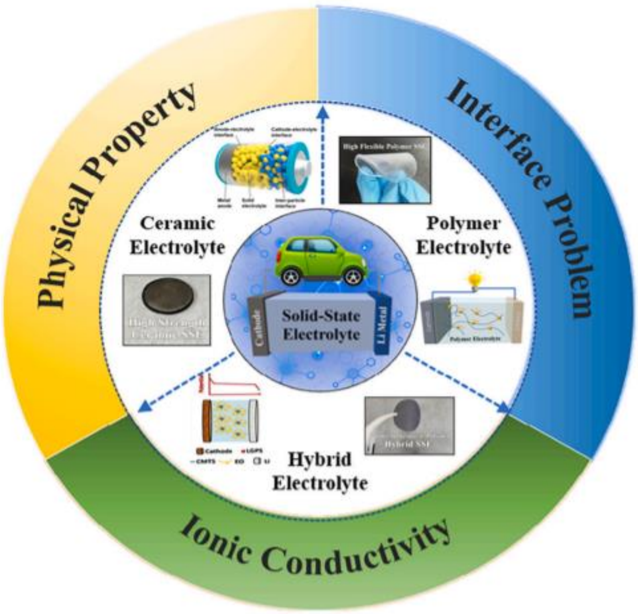

Figure 2. Illustration about the types and directions of improvement for solid-state electrolytes [14].

5. Conclusion

The ASSB is a great replacement for traditional liquid-state electrolyte battery that uses nonflammable solid-state electrolyte. Though its have more problem that needs to be solved, its believed to be the future trend of the battery. Hybrid electrolyte could be the first step of ASSB by reducing the usage of solid-state electrolyte in lithium-ion battery realizing a decrease of cost and a better contact surface with the cathode and anode. Ceramic and polymer electrolyte improves the ionic conductivity and the rigidity of the ASSB as well. In the future, more study should be focused on the improvements of these different electrolyte respectively. Moreover, sulfide electrolyte has also been given a promising future due to this ionic conductivity higher than liquid-state electrolyte. By pointing out the aspects need to be solved, the development of the all-solid-state batteries can be expedited reaching the demand of the lithium-ion battery and giving electric vehicles a more promising future. Replacing the traditional combustion engine vehicles is the future trend with multiple benefits to the driver and the environment relating to our personal health. The safety of the ASSB makes electric vehicles the most beneficiary among most battery applications. Eventually, the society will upgrade to a better level under the trend.

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