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Review

A review of lithium and non-lithium based solid state batteries

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HIGHLIGHTS

- A comprehensive review of all aspects of solid state batteries: design, materials.
- Tabular representations to underscore the characteristics of solid state batteries.
- Solid state electrolytes to overcome the safety issues of liquid electrolytes.

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ABSTRACT

Conventional lithium-ion liquid-electrolyte batteries are widely used in portable electronic equipment such as laptop computers, cell phones, and electric vehicles; however, they have several drawbacks, including expensive sealing agents and inherent hazards of fire and leakages. All solid state batteries utilize solid state electrolytes to overcome the safety issues of liquid electrolytes. Drawbacks for all-solid state lithium-ion batteries include high resistance at ambient temperatures and design intricacies. This paper is a comprehensive review of all aspects of solid state batteries: their design, the materials used, and a detailed literature review of various important advances made in research. The paper exhaustively studies lithium based solid state batteries, as they are the most prevalent, but also considers non-lithium based systems. Non-lithium based solid state batteries are attaining widespread commercial applications, as are also lithium based polymeric solid state electrolytes. Tabular representations and schematic diagrams are provided to underscore the unique characteristics of solid state batteries and their capacity to occupy a niche in the alternative energy sector.

1. Introduction and background

The advent of solid state batteries must be understood in the context of the challenges faced by modern storage systems, especially Li-ion batteries. Existing Li-ion batteries, apart from the storage and active components, contain considerable quantities of auxiliary materials and cooling equipment [1]. Loss of battery quality due to continuous charging and discharging cycles, flammability, dissolution of the electrolyte, and from vehicle to grid utilization has been another important concern. Solid state batteries are being extensively studied and researched with a view to solving these problems [1,2]. Conventional batteries, e.g., the Li-ion battery, usually consist of a liquid electrolyte, which helps transport Li ions to and from the cathode and anode [3–5]. However, this increases the chance of leakage of the electrolyte if any holes are present; this is one of the main drawbacks of the conventional Li-ion battery. Another problem inherent in the liquid electrolyte battery is the formation of dendrites of Li, which make it prone to explosion [5,6]. In order to surmount these problems, a solid electrolyte can be positioned between the electrodes. This is the principle underlying the solid state battery [3,4]. The advantage of this type of battery is a reduction in the net weight and volume of the battery, greater energy output, and easy transfer of Li ions, which affords better efficiency [3,5]. Solid state batteries also exhibit some advantages over the other commonly known energy

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storage devices, capacitors [7,8]. The advantages lie in the very small self-discharge of the solid state batteries, minimal wear and tear, and yield of a more uniform output voltage [7,8]. In recent decades, solid state batteries, especially solid state lithium ion batteries, have been widely used [9–13]. Ideally, a solid state electrolyte should have high cation conductivity, with good mechanical properties and good chemical stability that cannot be easily reduced by the metal itself [9,14]. Moreover, owing to rapidly growing microelectronics and integrated optoelectronics circuits, there is an increasing demand for new, lightweight batteries with high-cycle life and high energy density. In a commercial lithium ion battery, the liquid electrolyte carries the risk of explosion and fire; moreover, the separators and packaging limit the size of the batteries. All these factors have contributed to the development of all-solid state batteries [14–16]. However, solid state batteries also present challenges, such as their relatively lower power density, high ionic resistance at room temperatures, and manufacturing cost [3,15]. The atomic layer deposition (ALD) technique is an important method applied in the manufacture of solid state thin film electrolytes [17–20], but it is rather costly and indeed forms the bulk of the cost of the battery [3,21].

2. Solid state batteries

A solid state battery is similar to a liquid electrolyte battery except in that it primarily employs a solid electrolyte. The parts of the solid state Li ion battery include the anode, cathode and the solid electrolyte [22,23]. The anode is attached to copper foil, which helps improve the electrical conductivity of the battery. [22]. During the charging cycle, there is movement of the Li ions of the $LiCoO_2$ crystal toward the electrolyte interface [22,24]. As a result, the Li ions cross over to the carbon layers in the anode through the electrolyte. During the discharging cycle, the reverse process takes place, and the Li ions travel via the electrolyte toward the $LiCoO_2$ particles [22,23,25]. Solid state batteries can overcome some of the inherent problems of liquid electrolyte batteries, being less hazardous and having a less flammable electrolyte-electrode system and better storage capacity. In the field of power supply for cardiac pacemakers with low-power requirements, all solid state batteries are well established because of safety, lifetime, and achievable energy density [26,27]. As mentioned in a book, all solid state battery is one of new type of batteries with excellent safety and high energy density [28]. Substitution of liquid electrolyte by a solid allows simplification of the cell structure, and many restrictions in terms of architecture and safety are eliminated [29,30]. Solid state electrolytes are being intensively researched as the key which present safety advantages over present liquid Li-ion technology [31–33]. The non-flammability of their solid electrolytes offers a fundamental solution to safety concerns and remarkable environmental compatibility [34–38].

Also the solid state electrolytes tend to last longer, as they undergo less wear and tear during operation, are more proof against shocks and vibrations, and can operate within a larger temperature range, up to about 200 °C. However, they have several disadvantages as well [6]. Solid state electrolytes, and consequently batteries, are not suitable for use in low and ambient temperature conditions, and the power and current output is generally less [39,40]. This is because of the large resistance of the solid oxide at room temperature to ionic conductivity, whereas this does not occur at elevated temperatures. In addition, at ambient or room temperature, the stress created at the electrode-electrolyte interface due to continuous contact with the solid electrolyte tends to reduce the longevity of the battery [6,41]. Fig. 1 is a schematic diagram of a lithium based solid state battery. The curved arrows indicate the movement of the Li ions during the charging and the discharging process, respectively. The electrons produced due to the reaction are used to drive a load in the external circuit. The set of cathode and anode materials and their corresponding suitable electrolytes are also given in Fig. 1, marked with matching colors (in the web version).

2.1. Structure of solid state batteries

2.1.1. Cathode

The cathode in the solid state battery is important, as it supplies the battery with the necessary ions during the charging process and vice versa during the discharging process. The cathode must be structurally stable during this process. It is important that the ionic conductivity of the cathode be good, as the charging and discharging process involves the transference of ions across it [6,24,42]. Commonly used cathode materials for lithium based solid state batteries are lithium metal oxides, as they exhibit most of the above necessary properties. Lithium cobalt oxide (LCO), which has the stoichiometric structure $LiCoO_2$, is a widely used lithium metal based oxide. LCO exhibits a layered structure that is suitable for the lithiation/delithiation process, and it has a relatively high specific energy of about 150 mAh g^{-1}, which makes it a preferred cathode material [6,24,43]. LCO exhibits an octahedral arrangement with a layer of lithium atoms between oxygen and cobalt [44,45]. However, it is relatively costly to manufacture, especially with the use of cobalt [45]. Lithium manganese oxide ($LiMn_2O_4$) is another material used in the cathode of solid state batteries [46,47]. This compound produces very little resistance to the passage of lithium ions during the lithiation and delithiation process, thanks to its spinel based structure, which makes it suitable for use [6]. $LiMn_2O_4$ has its drawbacks too, notably phase change during the ion transfer process, which hinders stability, and a lower capacity than LCO. $LiFePO_4$, another lithium based phosphate, has the advantage of being less hazardous and less expensive to produce than the other lithium based oxide materials [6,48]. Moreover, $LiFePO_4$ has an olivine based structure (a one-dimensional chain of lithium ions), which greatly assists the transfer of ions and provides less resistance to the path of ion transfer [6,24]. On the other hand, phosphorus has a high self-discharge rate, which reduces the longevity of this material.

Apart from these lithium based oxides, vanadium based oxides have also been tested, as they exhibit similar layered structures that help during the lithiation/delithiation process. However, they produce low output voltages and sometimes they lack longevity, which has limited their use as cathode materials in solid state batteries [6,49,50]. In fact, the overall performance of a solid state battery is still limited by the performance of cathode materials, as its specific capacity is generally lower [14]. The application of nanoparticles to the typical cathode, such as $LiCoO_2$, can produce better properties, but they will react more strongly with the electrolyte at high temperature and lead to more safety issues than using such materials in the micrometer range [14,51]. Coating the nanoparticles with a stabilizing layer can reduce this problem, but it also reduces the lithiation/delithiation rate of the cathode.

2.1.2. Anode

Materials that can store Li/Li^+ to great capacity are usually potentially good anode materials. This is because the anode is where the lithiation takes place during the charging process. Pure lithium metal has been tried as an anode material. Unemoto et al. have used lithium anodes in lithium sulfur battery systems with room temperature ionic lithium (RTIL) liquid fused with silica nanoparticle solid state electrolyte and they were able to achieve a discharge capacity of 690 mAh g^{-1} after 45 cycles of operation [52]. Cai et al. have used lithium metal anode with a $LiMn_2O_4$ cathode