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The Development of Lithium Solid-state Batteries and the Comparisons Between Lithium and Other Metal Elements

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Abstract. Due to the global trend of electric transportation and green energy storage, there has been an increase in research on battery materials. In particular, lithium-ion batteries are currently the most popular mobile electric energy source. Through the method of literature review, this paper discusses the advantages and operation principle of solid-state lithium-ion (Li-ion) batteries, and the comparisons between the Li-ion and other replaceable elements for batteries under different conditions. This paper gives conclusions that although large human forces researched lithium-ion batteries in the past and they became the most commonly applied metal ion battery, some other replaceable metal-ions also attracted much recent innovation attention due to some of their technical advances compared to Li-ion, but cannot replace lithium in the short run as a result of some other problems related to application in real situations.

Keywords: lithium-ion batteries, electric transportation, green energy

1. Introduction

The phenomenon that lithium-ion batteries are the most popular mobile electric energy source is due to the advantages of solid-state lithium batteries, which are outstanding compared to liquid-state batteries from many aspects. For example, the safety when conducting electricity has improved due to the removal of the flammable liquid and lower reactivity of the solid electrolyte, which also results in higher durability. In addition, the metal's lattice structure in the solid state strengthens the battery's ability to deal with extreme temperatures and the charge density due to the closer-packed ions. [1]

In particular, lithium batteries are still the most commonly used solid-state batteries worldwide, even though some other metals are also available. In 1991, the first time lithium battery technology was made known to the public was by the announcement of Sony. Subsequently, research on suitable electrodes and electrolytes was conducted by the various laboratories. [2]

As time passes, some new discoveries on alternative metal elements to substitute lithium are also worth researching due to some technical advances compared to Li. The sodium and magnesium batteries are typical examples that have currently discovered and further developed.

This paper emphasized the history of lithium solid-state batteries and their evolution. Also, the general advantages of solid-state batteries are suggested, as well as the comparison between particular elements. At last, this paper summarizes the future expectations and some common

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technical defects for solid-state batteries, followed by the essential improvements for sodium-ion batteries and magnesium-ion batteries. This paper aims to briefly introduce the current status of different metal-ion batteries, and compare them from various aspects with future expectations.

2. The development of components and application of Li battery

As mentioned, various components of lithium batteries have been integrated by many laboratories. The lithium batteries in use currently are far more complex and complicated than the original small ones. At the beginning, Armand raised the idea of a battery that allows lithium-ion to move forward and backward between two electrodes in the presence of certain intercalation materials. In the late 1970s, Lazzari and Scrosati have designed a lithiated tungsten dioxide electrode and a titanium disulfide electrode for the lithium batteries, and this discovery satisfied the need for a low potential range for lithium batteries. However, this design could only allow low voltages when charging and discharging, so there were many other scientists who kept integrating the efficiency and feasibility of lithium batteries. [2]

In the present day, lithium batteries are much more complicated in many aspects, which have been promoted by many new technologies and discoveries. For example, the ceramic coating technology on the positive electrode can help the electrode surface avoid a short circuit at the beginning. The small but conductive particles coated on the surface will improve the efficiency of operating the transactions of lithium ions between electrodes. For example, the motors in Tesla and Panasonic are using a Sumitomo separator, which involves ceramic and aromatic polyamide particles that boost the penetration strength of the coating [2].

Moreover, the integration of the electrodes of lithium batteries is also significant for its strong current status. Instead of the conventional graphite electrode, some silicon was added to the negative electrode of the lithium battery. Silicon is also added in the negative graphite electrode, which aims for the integration of stability and lifetime by improving the thermal specific capacity. The highly thermally stable giant covalent lattice of silicon can achieve an effective outcome when only a small amount of silicon is added to these anodes. Notably, the cost of production becomes slightly higher for these new negative electrodes [2]. Furthermore, discussing the positive electrodes, there are many types of alloys that are currently applied and some others are still in progress. The most commonly used cathode materials are $LiCoO_2$ and $LiMn_2O_4$ (LCO and LMO), while another alloy called NMC has a sound future potential. From the reliable survey from Pillot, the use of LCO as cathode material still occupied the largest proportion in early 2015 but in a decreasing trend. On the contrary, the use of NMC was improving due to its high flexibility, higher power applications and easier manufacturing process [2].

3. Some other elements that can be a raw material of a battery, their advantages and disadvantages compared to Li

3.1. Sodium ion batteries

Apart from the lithium-ion batteries that are mostly commonly used in various industries, there were some other metals and alloys that have also been developed to apply to the solid-state batteries. From the very beginning steps of electrode manufacturing, the natural abundance of Na is much greater than Li, which is estimated as 1180:1 parts per million. In addition, the overall extraction and purification cost for sodium is less than that of lithium when manufacturing batteries. Moreover, metal oxide and polyanion cathode materials that contain Na can be extracted from naturally

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abundant transition metals, which can avoid many expensive procedures that are essential for Li batteries. These advantages make Na-ion batteries more sustainable and affordable, especially for developing countries that do not have massive budgets. Based on the information that is currently available for research, the cost of Na-ion batteries is about 10−20% less than that of their Li-ion batteries, with most of the cost difference coming from the nature of the two metals [3].

The potential difference of sodium-ion batteries (SIBs) is lower than that of lithium-ion batteries (LIBs), as a common observation. A commonly acknowledged explanation is that the sodium's standard electrode potential is 340mV less negative than lithium's. However, this explanation is not entirely correct and only partly relates to the voltage difference between LIBs and SIBs.

Figure 1 illustrates how electrode potentials and following cell voltages differ between LIBs and SIBs. Sodium batteries usually have lower voltages because the positive electrode materials experience a bigger drop in redox potential compared to most negative electrode materials. Also, graphite is a common anode in LIBs, but it cannot operate well in SIBs under most situations. However, some materials can actually produce a higher voltage in sodium batteries, such as $ACoO_2$ and $A_2Ti_3O_7$, which means they can help to avoid the defect of SIBs from the infeasible graphite electrode. This happens because the shift in redox potential for sodium is smaller in $ACoO_2$ (0.57 V) than in $A_2Ti_3O_7$ (1.09 V).

The high-voltage sodium-ion batteries are indeed possible from a theoretical perspective. Sodium's properties suggest it could even provide 0.53 V higher voltage than lithium due to its lower cohesive energy. However, in practice, sodium ions don't fit as well into most electrode materials as lithium ions, making the energy storage process less efficient. As a result, SIBs usually end up with lower overall voltages [4].

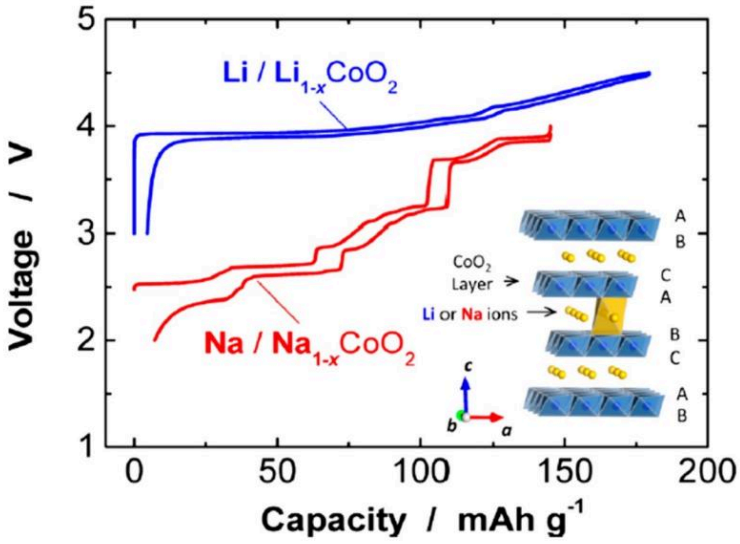


Figure 1: The difference between LIBs and SIBs [4]

In addition, some additional electrode materials, such as $Na_4Co_3(PO_4)_2P_2O_7$ (redox activity between 4.1 and 4.7 V compared with Na/Na^+ half cell), are also available in theories. Although many practical challenges remain, this shows that the sodium-ion batteries can also lead to very high redox potentials. [4]

It is said that the main advantage of Na-ion batteries is their sustainability. The Na-ion batteries can deliver better performance for applications such as electric vehicles and large energy storage.

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But this technology is not mature enough today, which needs further research to make it become more practical in the future.

3.2. Magnesium ion batteries

Apart from sodium, magnesium ion batteries are also currently being developed. Magnesium has many features that make it useful for many applications, including as a potential negative electrode in batteries, as being common in the Earth's crust, lightweight, cheap, and electrochemically active. It is also environmentally friendly and biodegradable, and its by-products are safely removed through urine, as most magnesium compounds are non-toxic. Mg can donate two electrons per reaction, giving it a high theoretical capacity of 2205 Ah/kg, which makes it a promising material for large-scale battery systems. It is also more chemically stable than lithium (Li) and sodium (Na), meaning it reacts less with the environment and the container. This stability makes magnesium-based energy storage systems easier to design and safer compared to Li and Na technologies. With the right design, magnesium batteries could achieve energy densities of 150-200 Wh/kg and operate at 2–3 V, making them a strong option for storing energy from wind and solar power [5].

However, the techniques related to magnesium-ion batteries are not mature enough to be applied on a wide scale. One of the main concerns is that the nature of magnesium-ion electrodes cannot support a large number of charging and discharging cycles. Although Mg has high reversibility when it acts as anode, it is also highly reactive during the transfer of electrons. The surface of metallic magnesium will be covered by magnesium compounds such as MgO and $Mg(OH)_2$ in the electrolyte, which means the efficiency of the batteries will be readily reduced because of the isolation of the active metal anode by the ionic compound film. As a result, the inconvenience will be much greater than with lithium-ion batteries because extra efforts are needed to deal with the routine reduction of charging and discharging power, which will be less available to be applied for continuous manufacturing processes [5].

Aurbach was the first one to state the two main problems holding back the development of rechargeable magnesium batteries. Firstly, create non-water-based liquid electrolytes that contain Mg^{2+} ions, which need to have high conductivity and a strong ability to dissolve magnesium for it to be deposited and removed effectively. Secondly, search for a way to prevent or reduce the formation of a blocking layer on the magnesium electrode, which could weaken the battery's performance [5].

4. Conclusion

Having an efficient, environment-friendly and sustainable energy resource has been a popular and vital topic ever since the industrial revolution, and it will also continue to develop in the future. However, among the solid-state metal ion batteries, there are only relative advantages and drawbacks in the current situation. For example, magnesium-ion batteries impose fewer side effects on the environment than lithium-ion batteries, but more practical defects exist in magnesium-ion technologies. The current status of energy sources can reflect the importance of this topic, which suggests that the reliance on non-renewable and non-sustainable sources needs to be eliminated for a more sustainable human future.

Some limitations are indeed presented in this paper, including some common side effects and common technical defects, such as the lack of experimental data and analysis in different usage environments. Different industrial processes have different requirements and limitations for the components and outcomes of different metal-ion batteries. In the future, the author will further

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explore the possibilities of situations where the metal-ion batteries can be applied with more efficient abilities than other batteries.

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