Sodium-ion Batteries

From Fundamental Research To Engineering Exploration

24.08.01

ADER-DES Consulting Team

Lithium-ion batteries have become a ubiquitous feature of modern life and production, powering everything from consumer electronics to mobile energy storage devices such as electric vehicles, and semi-mobile or stationary energy storage devices such as emergency power supplies or energy storage power stations. The impact of these batteries on human life and work is profound. However, the rapid growth in demand for lithium-ion batteries has led to increasing tension in the supply of lithium resources, which is now a global focus of attention and competition. The European Union has listed lithium as one of 14 key raw materials, while the United States has identified it as one of 43 important mineral resources. China has also positioned lithium as one of 24 national strategic mineral resources. The ongoing expansion of lithium-ion battery use, including in the production of electric vehicles and energy storage power stations, will further exacerbate the current situation.

It is crucial to identify a suitable replacement or alternative energy storage technology for lithium-ion batteries. In this context, sodium-ion batteries, which have a similar working principle to lithium-ion batteries, have attracted increasing interest from researchers. The advantages of sodium-ion batteries can be summarised as follows: The abundance, uniform distribution and low cost of sodium resources are key advantages. Sodium-ion batteries have a similar working principle to lithium-ion batteries, and the majority of lithium-ion battery production equipment is compatible. Furthermore, aluminium and sodium do not undergo an alloying reaction at low potentials, meaning that inexpensive aluminium foil can be used as the collector for both positive and negative electrodes of sodium-ion batteries. In solid-state batteries, bipolar electrodes can be designed with positive and negative materials coated on both sides of the same aluminium foil. These electrodes can be stacked in cycles to achieve higher voltages in a single cell, and other inactive materials can be conserved to improve volumetric energy density.

The solvation energy of sodium ions is lower than that of lithium ions. It has a superior interfacial relationship with lithium-ion batteries, allowing for the achievement of higher voltages through the utilisation of a single aluminium foil for both the positive and negative electrodes. Its lower solvation energy than lithium ions facilitates enhanced interfacial ion diffusion. Additionally, the sodium ion Stokes diameter is smaller than that of lithium ions, resulting in a higher ionic conductivity at the same electrolyte concentration. A lithium salt electrolyte or a lower concentration of electrolyte can achieve the same ionic conductivity.

The preliminary results of the high and low temperature tests indicate that sodium-ion batteries perform better in high and low temperatures.

No fire was found in any of the safety project tests, which demonstrates that the batteries have an excellent safety performance. The internal resistance of sodium-ion batteries is slightly higher than that of lithium-ion batteries, which results in less instantaneous heat generation and a lower temperature rise in short-circuit and other safety tests. This is one of the reasons for the good safety performance. As the study progresses, further distinctive advantages of sodium-ion batteries will become apparent. Leveraging these advantages will enhance the differentiation of sodium-ion battery products, positioning them favourably in the future market. Consequently, sodium-ion batteries can serve as a crucial complementary technology to lithium-ion batteries in large-scale energy storage, offering significant economic value and strategic importance.

1

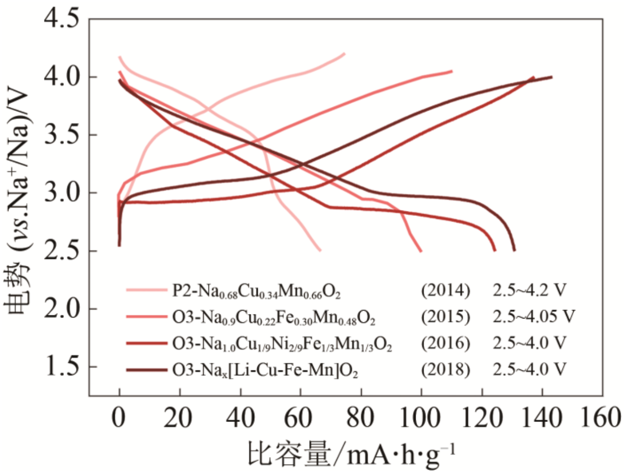
EXPLORATION OF LOW-COST ELECTRODE MATERIALS

1.1 Anode material

The use of layered oxides in sodium-ion batteries offers a cost advantage due to the ability to utilise the solid-phase or co-precipitation method, commonly employed in lithium-ion batteries, to achieve low-cost scale production. Additionally, the abundance of active elements available provides further cost savings. The transition metal elements most commonly used in layered oxide cathode materials for lithium-ion batteries are nickel, cobalt, and manganese. Elements such as titanium, vanadium, chromium, iron, and copper cannot be used as the main elements because they are not electrochemically active in lithium-ion layered oxides. Currently, there are numerous research reports on layered cathode materials for sodium-ion batteries, but the majority of them contain transition metal Ni or Co elements. Ni and Co are widely used in cathode materials for lithium-ion batteries. If they are also used in large quantities in sodium-ion batteries, the potential for cost reduction will be limited. Given the limited potential for cost reduction, it is unlikely that Ni and Co will be the preferred elements for cathode materials in sodium-ion batteries. Furthermore, the majority of currently reported layered oxides containing sodium are unstable in air, and most of these elements are not electrochemically active in lithium-ion layered oxides. Furthermore, the majority of currently reported sodium-containing layered oxides are unstable in air, which will inevitably increase production, transportation and storage costs, as well as affecting battery performance. Therefore, the development of new Ni and Co-free, air-stable electrode materials is of great practical significance.

A Chinese research team has developed a new generation of Li-doped high-specific-capacity Cu-Fe-Mn-based cathode materials. This has been achieved by combining elemental doping, increasing the sodium content, and adjusting the ratio of the elements. The specific capacity of these materials is approximately 130 mA-h/g, and this has been demonstrated in the voltage range of 2.5-4.0 V. The elements of Cu, Fe, and Mn are cost-effective, widely available, and can demonstrate comprehensive performance that is on par with that of Ni, Co, and other oxide materials, making them highly promising for applications. Oxide cathode materials are a particularly promising avenue for further development. The initial charge/discharge curves for the aforementioned materials are presented in Fig.

Typical first charge/discharge profiles of several Cu-based oxide cathode materials



1.2 Cathode material

Carbon materials, including coal, graphite and bitumen, are used extensively in a wide range of applications across various sectors. Graphite is currently the most widely used anode material in lithium-ion batteries, offering a cost-effective solution with high specific capacity (up to 360 mA-h/g, theoretical 372 mA-h/g). However, the reversible specific capacity of graphite in sodium-ion batteries containing carbonate electrolyte is less than 50 mA-h/g, which limits its potential applications. In comparison, amorphous carbon-based anodes (including hard and soft carbon) exhibit higher reversible specific capacity and better cycling performance in sodium-ion batteries. Since their discovery, researchers have conducted extensive explorations and studies on such materials.

The Chinese research team used phenolic resin as a precursor and ethanol as a pore-forming agent to precisely regulate the microstructure of hard carbon through the formation of closed pores. This resulted in a hard carbon anode with a reversible specific capacity of approximately 410 mA-h/g, which surpassed the lithium storage capacity of graphite.

2

COMPARISON WITH OTHER SECONDARY BATTERIES

Lithium-ion and lead-acid batteries represent the two most prominent secondary battery technologies currently available on the market. The following table provides a summary of the technical specifications for lithium-ion, lead-acid, and sodium-ion batteries, with values based on a single cell. Lead-acid batteries were first developed in the 19th century and have since become a mature secondary battery technology. They are widely used in a range of applications, including electric bicycles, automotive, communications, and military. Following over a century of technological advancement, the energy density, service life, cost and other key performance indicators of lead-acid batteries have reached a plateau. Despite the clear disadvantages of lead-acid batteries in comparison to lithium-ion in terms of energy density, cycle life, and environmental impact, their lower selling price and recycling value contribute to their continued market presence. Lithium-ion batteries are available in a variety of configurations, with different anode options including lithium cobalt, ternary, lithium iron phosphate, lithium manganate, and others. Additionally, the anode can be paired with graphite or lithium titanate, among other options. The lithium iron phosphate/graphite system offers a lower cost, higher energy density, better safety profile and long cycle life. In terms of cost-effectiveness, safety and other factors, the sodium-ion battery is positioned similarly, making it a suitable comparison.

Norm	Lead-acid battery	Lithium ion battery (Li-FePO4/Graphite system)	Sodium-ion battery (Copper Oxide/Coal-based carbon systems)
Mass-energy density (MED)①	30~50 W·h/kg	120~180 W·h /kg	100~150 W·h /kg
Volumetric energy density (VED)①	60~100 W·h /L	200~350 W·h /L	180~280 W·h /L
Raw material cost per unit of energy②③	$0.06/ W·h	$0.06/W·h	$0.04/(W·h)
Cycle life①	300~500 cycles	More than 3000 cycles	More than 2000 cycles
Average Working Voltage①	2.0 V	3.2 V	3.2 V
Capacity retention at -20°C	< 60%	< 70%	> 88%
Over-discharge resistance	Inferior	Inferior	Dischargeable to 0 V
Safety	Excellent	Excellent	Excellent
Environmentally Friendly Properties	Inferior	Excellent	Excellent
Mass-energy density (MED)①	30~51 W·h/kg	120~181 W·h /kg	100~151 W·h /kg

Note: ① Corresponding value of single cell; ② Considering only the cost of raw materials, the raw materials include positive electrode, negative electrode, electrolyte, diaphragm and other assembly objects; ③ If recycling is taken into account, the cost of raw materials for lead-acid batteries is about $0.03/W-h.

The above table demonstrates that, while there is still a gap in terms of energy density and other aspects between the current copper-based sodium-ion batteries and lithium iron phosphate batteries, lithium iron phosphate batteries perform better in low-temperature conditions, are safer, and are more environmentally friendly. In terms of raw material costs, copper-based sodium-ion batteries have a clear advantage over lithium iron phosphate batteries, with a price of 0.29 yuan/Wh compared to 0.43 yuan/Wh. Lead-acid batteries are cheaper, but without considering recycling, their price per unit of energy is similar to lithium iron phosphate batteries, which is mainly due to their low energy density. This is largely attributable to its relatively low energy density. The working principles and production processes of sodium-ion and lithium-ion batteries are similar. The main factor influencing cost differences is the use of different raw materials. Sodium-ion batteries have lower raw material costs, primarily due to: The raw material costs for lithium iron phosphate are approximately half those of copper, iron and manganese oxide; the raw material costs for coal-based carbon anode are less than one-tenth of those of graphite; and the electrolyte costs for sodium-ion batteries can be reduced by using a low concentration, which is another cost saving. Sodium-ion batteries offer significant advantages over lead-acid batteries. They are smaller, lighter, and have a specific energy more than two times higher. They also have a longer cycle life. These features make them well-positioned to replace lead-acid batteries in a variety of applications, including low-speed electric vehicles, energy storage, and other fields. The potential exists for lead-acid batteries to be replaced in the future with lead-free alternatives in low-speed electric vehicles and energy storage.

Web：www.ader-des.com

Contacts：Luna

E-mail：luna@ader-des.com