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Introduction

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1.1 Overview

Since humans have obtained energy by drilling wood for fire, every energy revolution has been accompanied by great progress in human civilization. However, the consumption of fossil energy has caused irreversible pollution and damage to the human environment, so it is urgent to replace fossil energy with renewable energy to get mankind out of the upcoming energy crisis and environmental disaster.

In recent years, the technology of converting wind, solar, hydraulic, tidal, and other renewable energies into electric energy has rapidly developed [1]. However, the power generation is limited by natural conditions, owing to randomness, intermittent and fluctuating characteristics, leading to a great impact on the state grid if the generated electric energy were to be fed directly into the grid. The new energy power generation industries are still facing serious energy wastage problems, such as wind and light wastage. Therefore, in order to greatly improve the utilization of renewable energy and establish a green, low-carbon, efficient, and sustainable development society, it is necessary to develop an efficient and convenient large-scale energy storage technology and form an “energy internet” of renewable energy–energy storage system–smart grid–users.

At present, the storage of electrical energy mainly includes physical energy storage, chemical energy storage, electrochemical energy storage, and other technologies [2]. Physical energy storage includes pumped hydro storage, compressed air energy storage, flywheel energy storage, and superconducting energy storage. Chemical energy storage includes various types of fossil fuels and hydrogen energy. Electrochemical energy storage includes secondary batteries and supercapacitors. Electrochemical energy storage, such as secondary batteries, has a wide range of application prospects in the energy field, owing to the advantages of high energy density, high energy conversion efficiency, and fast response speed. At present, there are four types of secondary batteries that have realized commercial applications: lead-acid batteries, high-temperature sodium batteries, vanadium flow batteries, and lithium-ion batteries. However, these batteries are limited by their

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disadvantages, such as lead-acid batteries with low energy density (30–50 W h kg^{-1}), high-temperature sodium batteries that need to operate at higher temperatures (300–350 °C), and the low energy conversion efficiency of vanadium flow batteries (75–82%).

The secondary battery represented by the lithium-ion battery has many advantages, such as high energy density, high energy storage efficiency and nonmemory effect, small self-discharge, long cycle life, and wide application range. Currently, lithium-ion batteries have been successfully used in small electronics, electric vehicles, and aerospace. At the same time, the research direction of lithium-ion batteries is gradually toward ultrahigh energy density and ultralong cycling life. However, lithium resources are relatively concentrated in a few countries, the overall reserves are limited, and the mining conditions are relatively harsh. So, it is difficult to support the development of electric vehicles and large-scale energy storage.

In recent years, sodium-ion batteries (SIBs) with the same working principle and similar battery components as lithium-ion batteries have received widespread attention, owing to the advantages of abundant sodium resources, cost-effectiveness, and outstanding comprehensive performance. SIBs can meet the requirements of low cost, long cycling, and high-safety performance, alleviating the limited development of energy storage batteries caused by the shortage of lithium resources, which is a promising supplement to lithium-ion batteries and can gradually replace lead-acid batteries. Therefore, SIBs are expected to play an important role in renewable energy storage [3].

In the early 1970s, the research on SIBs was almost simultaneously carried out with that on lithium-ion batteries, and lithium-ion batteries were successfully commercialized in 1991, while SIBs have not yet been commercialized. The research on SIBs can learn from the research experience of lithium-ion batteries because the working principle, materials, and battery components of the two batteries are similar. It is worth noting that it cannot be fully copied due to differences in charge carriers (Li^+ vs. Na^+). Therefore, finding suitable materials for SIBs and building suitable SIB systems are the key to its practical application. In recent years, a series of advances have been made at home and abroad on the core material systems (cathode material, negative electrode, electrolyte, and separator), main auxiliary materials (binders, conductive agents, and current collectors), key battery technologies (nonaqueous, aqueous, and solid-state batteries), and analytical characterization, material prediction, and failure mechanism, which have laid a solid foundation for the commercialization of SIBs [4, 5].

With the deeper insight into this field, more and more potential advantages of SIBs have been found, which will give SIBs more characteristics and a favorable position in the future energy storage market [6]. Some advantages of SIBs are summarized (Figure 1.1):

(1) Sodium resources are abundant, widely distributed, economical, and there are no bottlenecks for the development of SIBs.
(2) The working principles of SIBs and lithium-ion batteries are similar, and they are compatible with the existing production equipment of lithium-ion batteries.

(3) Alloying reactions can be avoided between sodium and aluminum, and the current collectors of the positive and negative electrodes for SIBs can use cheap aluminum foil, which can further reduce costs with no overdischarge problems.

(4) Bipolar SIBs can be constructed; that is, the positive and negative electrode materials can be coated on both sides of the same aluminum foil. The electrodes are periodically stacked under the isolation of solid electrolytes, which can achieve higher voltage, save inactive materials, and improve the energy density.

(5) The Gibbs free energy of solvation of sodium ions is lower than that of lithium ions, which is beneficial for interface desolation.

(6) The Stokes diameter of the sodium ion is lesser than that of the lithium ion, and a high ionic conductivity can be achieved with a low concentration of sodium salt electrolyte, making the low salt concentration electrolyte suitable for use in SIBs.

(7) SIBs have excellent rate performance as well as outstanding cycling performance at high and low temperatures.

(8) The SIB does not catch fire or explode in the safety test, and the safety performance is good.

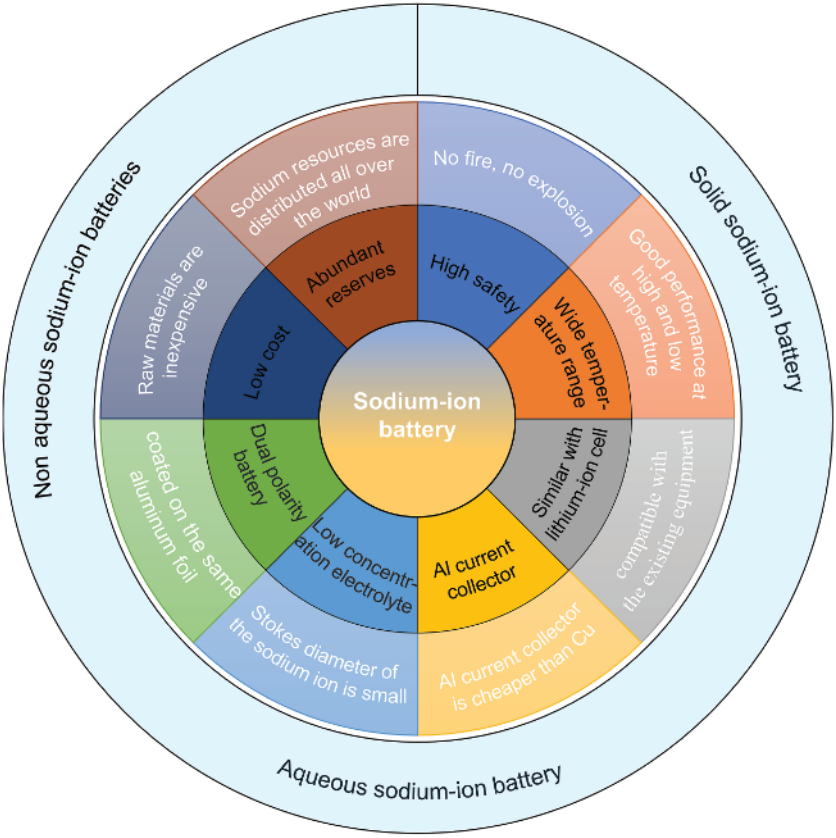

Figure 1.1 Characteristics of sodium-ion batteries.

1.2 The Birth and Development of Sodium-ion Batteries

Since the concept of sodium batteries was proposed in the science fiction novel “Twenty Thousand Leagues Under the Sea,” the real emergence of sodium batteries has taken nearly 100 years. In 1967, Yao and Kummer [7] found the conduction of Na^+ in Na-β''-Al_2O_3. In 1968, the Ford Company invented high-temperature sodium–sulfur battery (Na-Na-β''-Al_2O_3|S) (300–350 °C) with sodium and sulfur as the negative and positive electrodes, respectively, and Na-β''-Al_2O_3 as the solid electrolyte. In 1986, Coetzer [8] replaced sulfur with $NiCl_2$ and invented the ZEBRA battery (Na|Na-β''-Al_2O_3|$NiCl_2$). In 2003, NGK company realized the commercialization of high-temperature sodium–sulfur batteries. However, both sodium–sulfur batteries and ZEBRA batteries are sodium batteries that work at high temperatures. In order to reduce the working temperature of sodium batteries to improve their safety, a lot of research work began to develop sodium batteries that work at room temperature. Taking this into consideration, the development of room-temperature SIBs has undergone a long process (Figure 1.2).

In 1976, Whittingham et al. [9] conducted a study of the behavior of Li^+ intercalating TiS_2, followed by the electrochemical reversible deintercalation of Na^+ in TiS_2 at room temperature [10]. France Armand [11] proposed the concept of “rocking chair batteries” at the NATO Conference on Materials for Advanced Batteries held in 1979, which opened up the research on lithium-ion and SIBs. In 1981, French Delmas et al. [12] firstly reported the electrochemical properties of Na_xCoO_2-layered oxide cathode materials and proposed a classification trend for layered oxide structures, according to the coordination environment of alkali metal ions. Layered oxides are divided into O type or P type (O refers to octahedron and P refers to triangular prisms), and numbers (such as 2 and 3.) represent the number of stacking layers of the least repeated oxygen units. During that period, a variety of sodium-containing transition metal-layered oxides, Na_xMO_2(M = Ni, Ti, Mn, Cr, Nb), were reported. When studying the behavior of Na^+ in the $NaTi_2(PO_4)_3$ electrode material, it was found that NASICON-structured solid electrolyte $Na_3M_2(PO_4)_3$ (M = Ti, V, Cr, Fe, etc.) [4] could also be used as electrode material. However, in the late 1980s, research reports on sodium-ion intercalating materials were very limited, and only a few papers and patents were published, mainly because [13]: (i) The research on lithium-ion intercalating materials was just beginning in this period, and a large number of researchers focused their research on lithium-ion batteries. (ii) Limited by the research conditions (such as the low purity of the electrolyte, the poor tightness of the glove box, and the low purity of argon.), it is difficult to use the active metal sodium as an electrode to accurately evaluate the performance of the electrode material in the half-batteries. (iii) The graphite successfully applied in lithium-ion batteries has almost no sodium storage capacity in carbonate electrolytes, resulting in the lack of suitable anode materials for the study of SIBs. In fact, before the successful commercialization of lithium-ion batteries, some companies in the United States and Japan carried out research on

Figure 1.2 The development of room-temperature sodium-ion batteries.

sodium-ion full batteries, such as P2-Na_xCoO_2, which was used as positive electrode and Na–Pb alloy as negative electrode. Although the SIB can reach 300 cycles, its average discharge voltage is below 3 V, which has no advantage over C||$LiCoO_2$ battery (3.7 V) and thus failed to attract the attention of researchers.

In 2000, the SIB got its first opportunity. Stevens and Dahn [14] prepared a hard carbon anode material for SIB via pyrolysis of glucose for the first time and demonstrated a specific capacity of 300 $mAh\,g^{-1}$. It is worth noting that, up to now, hard carbon materials are still the most promising anode materials for SIBs. The second important finding was the reversible variability of the Fe^{4+}/Fe^{3+} pair in $NaFeO_2$ reported by Okada et al. [13], which has no electrochemical activity in $LiFeO_2$. Except for the layered oxides, Na_2FePO_4F polyanionic material reported in 2007 by Nazar and coworkers [15] exhibits only 3.7% volumetric change

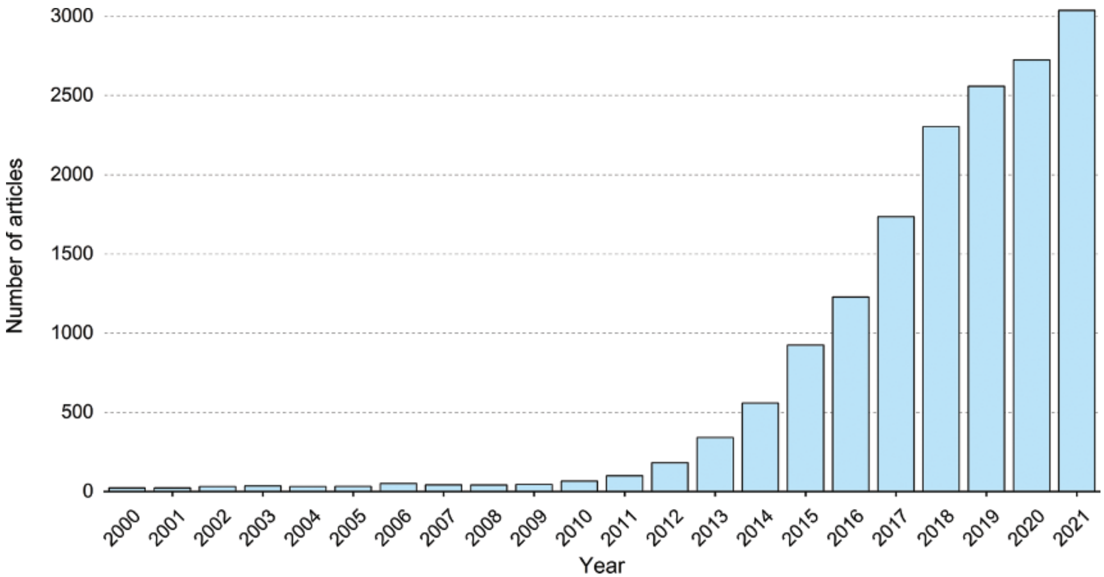

Figure 1.3 Research articles about sodium-ion batteries between 2000 and 2021.

during the deintercalating/intercalating of sodium ions, which is lower than that of olivine-type $NaFePO_4$ (15% volumetric change). So far, the papers published between 2000 and 2009 on SIB materials have shown a slow growth trend and are mainly concentrated in a few laboratories.

Since 2010, the research of SIBs has entered a period of revival, and the number of related articles has increased rapidly (Figure 1.3), mainly due to the following reasons [16]: (i) The research on lithium-ion battery materials at this time mainly focuses on the application improvement and the in-depth analysis of electrochemical processes, and the difficulty of developing new materials has significantly increased. So, many researchers turned to the exploration of SIB material systems. (ii) Concerns about lithium resources and the demand for new large-scale energy storage applications also make researchers to develop new battery systems. On this background, SIBs developed rapidly with the research experience of the lithium-ion battery. So far, researchers have reported a variety of SIB cathode materials, anode materials, and electrolyte systems [17]. Among them, cathode materials mainly include layered and tunneled transition metal oxides, polyanionic compounds, Prussian blue analogs, and organic materials. Anode materials mainly include carbon materials, alloys, phosphorus compounds, and organic carboxylates. Except for new material systems, the research and development of SIBs is also working in the direction of low cost and practicality. In 2011, Komaba et al. [18] firstly reported the electrochemical performances of hard carbon||$NaNi_{0.5}Mn_{0.5}O_2$full-cell. In the same year, the world's first SIB company, FARADION, was established in the United Kingdom. In 2013, Goodenough and coworkers [19] proposed a Prussian white cathode material with high voltage and excellent magnification performance. In 2017, China's first SIB company (HiNa Battery Technology Co., Ltd.) was founded, which built the first low-speed electric vehicle powered by SIB and the first 100 kW h SIB energy storage power station in 2018 and 2019, respectively [20]. As of 2020, more than 20 companies around the world are committed to the research and development of SIBs, indicating that SIBs are moving toward practical application. At the same time, in order to develop more secure SIBs for large-scale energy storage, the research and development of aqueous SIBs and solid-state SIBs that replace organic electrolytes with aqueous electrolytes and solid electrolytes, respectively, are also being carried out simultaneously.

Nowadays, the development of SIBs has attracted the attention of many countries around the world, and China is one of the strongest competitors in the research and development of SIB technology. HiNa Battery, Natrum Energy, and CATL have accelerated the commercialization of SIBs. In the near future, SIBs are expected to be applied in commercialization in China first, providing a strong guarantee for national energy security.

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