Chapter 1 Introduction

1.1 Overview

Energy production and storage has been one of the hottest scientific topics in recent years. With the irreversible consumption of fossil fuel resources and increasingly severe environmental problems, renewable and clean energy source such as solar and wind energy are rapidly developing. However, some challenges are accompanied especially on how to smoothly and safely integrate the intermittent renewable energy into the grid. The application of a proper large-scale energy storage system will be extremely important and urgently needed. Among diverse potential energy storage technologies, electrochemical secondary batteries are competitive due to the advantages such as high energy conversion efficiency and simple maintenance. The major parameters for stationary batteries are low cost, high safety and long life span. Therefore, an earth-abundant, environmental friendly, stable and high-performance electrode material need to be researched to guarantee large-scale and long-term application, as well as to control the management cost[1-6].

To date, lithium-ion batteries (LIBs) are considered the most potential candidates. As witnessed in recent years, due to the highest energy density and long life span, LIBs has been widely applied in the field of portable electronics and electric vehicles, being a mature and commercialized product. Unfortunately, for large-scale applications, the demand for lithium resource is so huge that force us to reflect whether the rather limited lithium resource (Figure 1-1) is the best option. Besides, with the expansion of LIBs market, the utilization speed and price of lithium is increasing dramatically. Thus, rechargeable batteries based on

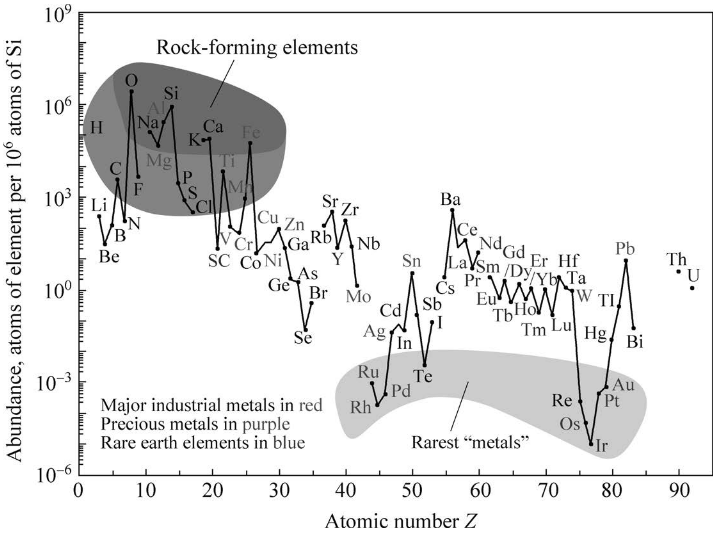

Figure 1-1 The abundance of chemical elements in Earth's crust[7] (see the color figure before)

more abundant element need further investigation. Sodium is the second smallest element of alkali metals and share similar physical and chemical properties with lithium, while sodium is much more abundant and inexpensive. Though there are some disadvantages of sodium such as relatively heavier mass, larger radius and higher operating potential, sodium is still promising for constructing a rocking-chair battery to be applied in large-scale field since gravimetric energy density is not the primary parameter for large-scale stationary batteries as discussed above (Table 1-1). Besides, it's interesting to note that for the anode current collector, lighter and cheaper aluminum foil can be used instead of copper, which will be another important advantage of sodium-ion batteries (SIBs). In summary, room-temperature SIBs are widely regarded as the most appropriate candidate for the grid-scale energy storage application and have made great research progress especially during last decades[8-10]. Encouragingly, commercialized products and start-ups related to SIBs are also flouring and developing rapidly, such as FARADION in UK, NAIADES in France and HiNa Battery in China. Apart from large-scale stationary application, low-speed electric vehicle has been developed as another important application field of commercialized SIBs.

Table 1-1 The comparison between Li and Na[7]

	Li	Na
Atomic mass/($g \cdot mol^{-1}$)	7	23
Ionic radius/nm	0.076	0.102
Redox potential/V	−3.04	−2.71
Content in earth crust/(wt. %)	0.0065	2.75
The price of carbonates/($\$ \cdot t^{-1}$)	13 900	152
Distribution	70% in South America	Globally
Anode current collector	Copper	Aluminum

As depicted in Figure 1-2, the most important part of SIBs is the electrode material, which will directly determine the sodium storage characteristic and performance. Among diverse electrode materials, carbon materials have attracted significant attention due to the following apparent advantages[12-15]: ① low cost and abundant resource; ②environmental benignity and facile production; ③high electrochemical activity; ④controllable microstructure and functionalization. In LIBs, graphite has been developed as the commercialized anode[15-17]. Besides, graphite can also be developed as a high-voltage intercalation-based cathode[18-21]. Moreover, some porous carbons or nano carbons can operate as capacitive cathodes with high power density[22-30]. Therefore, carbon materials are supposed to have a promising application perspective in SIBs as well.

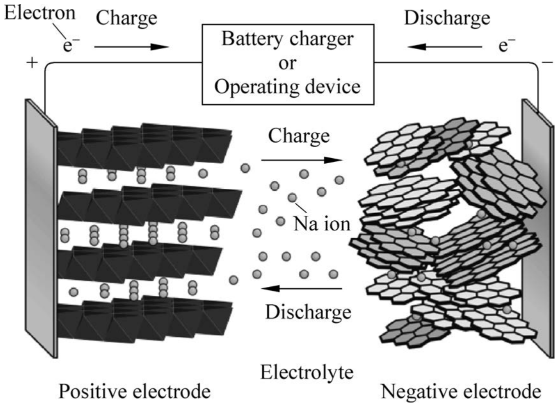

Figure 1-2 Schematic representation of a SIB system[11]

Unfortunately, graphite fails to be the optimum anode for SIBs[31], as shown in Figure 1-3. In LIBs, a high reversible capacity of 372 mA • h • g^{-1} can be delivered and there are long plateau regions in both discharge and charge profiles, resulting in a high energy density. In sharp contrast, rather limited capacity can be obtained in SIBs, almost impossible for practical application. Researchers turn to other kinds of carbon materials such as amorphous carbon or nano carbon materials[32-35]. As demonstrated in Figure 1-4, similar with graphite, soft carbon with partially disordered structure also deliver limited capacity (less than 100 mA • h • g^{-1}). For hard carbon with much more disordered structure, a much higher reversible capacity (around 300 mA • h • g^{-1}) and long plateaus can be obtained. Therefore, it has been widely regarded as the most promising anode material for high-energy application. Besides, some porous or nano carbons with high specific surface area present high reversible capacities but apparent hysteresis in discharge/charge profiles. Thus, they are promising for high-power application. On cathode side, graphite has been proved to be potential intercalation-based cathode with high average operating voltages over 4 V[36-38]. In addition, functionalized porous carbons or nano carbons are investigated as promising capacitive cathodes as well, with a high reversible capacity and excellent rate capability[24,39-41]. However, we have to confess that all above progress is not practical enough and there are some critical issues to be addressed before industrial application.

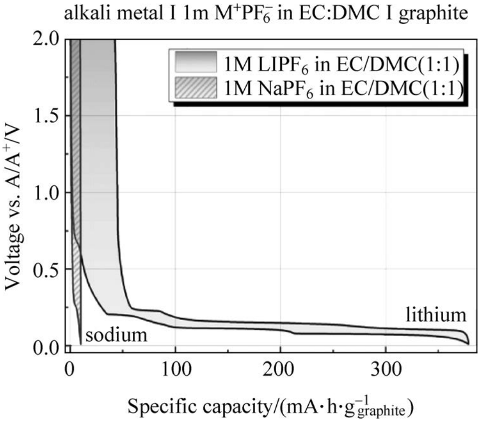

Figure 1-3　Charge/discharge profiles of graphite in LIB/SIB[31]

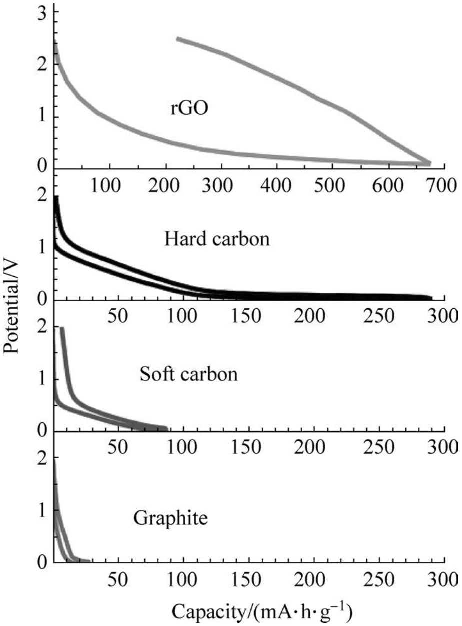

Figure 1-4　Typical charge/discharge profiles at second cycle in sodium half-cell consisting of graphite, soft carbon, hard carbon, and graphene[12]

For the development and investigation of carbon anodes, there are basically two critical parameters to be considered and optimized, namely reversible specific capacity and initial coulombic efficiency. Presently researchers are focusing on the preparation of novel hard carbons with optimized microstructure and modifying the interfacial electrochemistry of carbon anodes towards higher efficiency.

For the development and investigation of carbon cathodes, volumetric capacity is the most critical parameter to be improved, since carbon cathodes are mainly based on functionalized porous or nano carbons with relatively low density (typically lower than 0.6 $g \cdot cm^{-3}$). In contrast, commonly used inorganic cathode has inferior rate capability but much higher density (typically higher than 2.0 $g \cdot cm^{-3}$). From practical perspective, volumetric capacity is even more important than gravimetric capacity for carbon cathodes.

1.2 Recent progress of SIBs in academy and industry

For the cathode materials in SIBs[42-46] (Figure 1-5), 3d transition metal cations including Co, Mn, Fe or Ni as redox-active elements are preferred, similar with the situation in LIBs. Besides, aiming to further increase the energy density by increasing the redox potential or reversible capacity, other potential metal cations have also been investigated. In consideration of abundance and cost, Fe- and Mn-rich compounds are the best candidates. In summary, there are mainly two types of cathodes attracting most attention, namely layered transition metal oxides and poly-anionic compounds. Layered transition metal oxides are important due to their high theoretical capacity. For sodium-based layered oxides, they can be synthesized from a large variety of transition metals ranging from Ti to Cu, while synthesis is only limited to Mn, Ni and Co in case of LIBs. Therefore, mixing different transition metals is a popular and effective approach to tune the electrochemical characteristics of SIBs. Poly-anionic compounds are also important due to their structural diversity, high

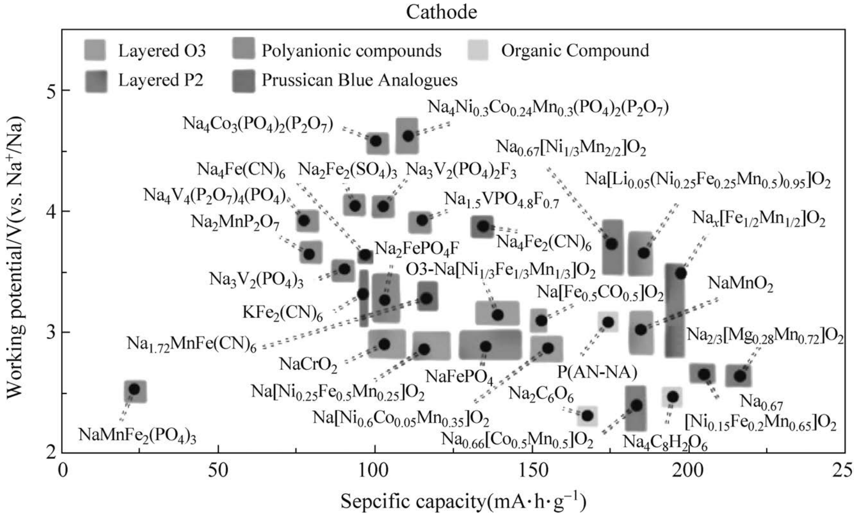

Figure 1-5 Recent research progress of cathode materials in SIBs[9] (see the color figure before)

working potential and high reversibility for intercalation/de-intercalation of sodium ions. NASICON-type framework demonstrates excellent cycling stability and rate capability despite relatively lower specific capacity.

For the anode materials in SIBs[12-13，32-33，47]（Figure 1-6），carbon materials and metals are most attracting options. Though graphite is nowadays applied exclusively in commercialized LIBs，its capacity is too low to be applied in SIBs when conventional carbonate-based electrolytes are used. An alternative to graphite is amorphous carbon which used to appear in the early-stage commercialized LIBs. Fortunately，a relatively higher reversible capacity can be delivered in amorphous carbons in conventional carbonate-based electrolytes. The microstructure and surface chemistry of amorphous carbons are highly dependent on the selection and preparation condition of precursors. Thus，different amorphous carbons can present considerably varying voltage profiles. The electrochemical properties of amorphous carbons are most promising among all anode candidates but the sodium storage mechanism needs further clarifying and initial coulombic efficiency needs further improving. Another potential anode category is metal alloy which can deliver extremely high reversible capacity. However，critical challenges can't be ignored such as large volume change（over two-fold increase），less protective SEI formation and

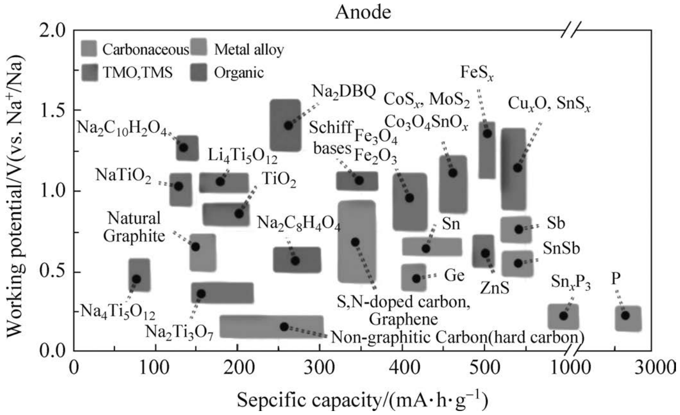

Figure 1-6 Recent research progress of anode materials in SIBs[9]（see the color figure before）

huge initial irreversible capacity loss.

Electrolyte is not only an indispensable battery component but more importantly makes a big difference on the electrochemical characteristics and performance of electrodes[48-49]. Especially, electrolyte is not thermodynamically stable at lower potential in SIBs and decomposes to form a surface film on anode materials. To prevent continuous decomposition of electrolyte, the formed surface film must be electronically insulating but sodium ions conducting. Besides, this film should be compact and stable enough to protect the electrode during prolonged cycling. Therefore, a high-efficiency solid electrolyte interphase (SEI) is crucial for practical SIBs. More importantly, in typical laboratory half-cell tests, electrolyte and sodium metal are largely excess which are typically overlooked. EC-based carbonate electrolytes are most commonly used owing to their excellent passivation capability on anodes and oxidative stability on cathodes. However, less efficient and protective SEI is formed based on EC-based carbonate electrolytes on diverse anodes, unfortunately inducing huge electrochemical polarization. Interestingly, ether-based electrolytes are gradually accepted as a new electrolyte option in SIBs and more surprises are witnessed, such as triggering co-intercalation of both solvent molecules and sodium ions into graphite, and producing efficient and protective SEI on diverse anodes.

Another important component to improving the electrode performance is the binder used for powdery active materials[50-53]. Sodium storage performance will be dramatically influenced by specific binder and binder is also critical to stabilizing the electrode surface during cycling. PVDF (Poly-vinylidene Fluoride) is the most commonly used one with good chemical and electrochemical stability. However, there are still some problems during the preparation of the slurry such as the high production cost and accompanied utilization of a toxic organic solvent such as NMP. Recently, alternative water-soluble binders have been investigated including sodium carboxymethyl cellulose (Na-CMC), poly(acrylic acid) (PAA) and sodium alginate (Na-Alg). Generally, such binders are environmental friendly and inexpensive. Besides, they're capable of ensuring a good interfacial interaction between the binder and particles, and strong adhesion between the electrode layer and current collector. Better still, a more stable and efficient SEI could be constructed as well, enhancing the stability of electrode and reducing the electrochemical polarization.

As introduced and summarized above, SIB technologies are developing rapidly in recent years. Theoretically, the gravimetric energy density of SIBs has become competitive to the state-of-the-art LIBs (graphite as anode and $LiFePO_4$ as cathode). However, most current reports are based on half-cells employing sodium metal as the counter electrode. The development of SIBs full cells is quite nascent and challenging. Many research groups start focusing on the rational full cell design and have reported some updated results. Commercially, some representative battery companies strives to bring out novel full cell designs, already making remarkable progress in developing practical SIBs.

There are three representative SIBs companies at present in the world, as shown in Figure 1-7. The first one is HiNa Battery Technology Co., Ltd in China, which is located in the Science and Technology Industrial Park of Liyang City in Jiangsu Province. It is a new high-tech enterprise, focusing on the R&D and manufacture of the SIBs, and one of the few companies in the world that have core patents and technologies for SIBs. HiNa focuses on low-cost, long-life, high-safety and high-energy-density SIBs products. The potential applications cover low-speed electric vehicles, large-scale energy storage, electric vehicles, and national security. The company also supplies cathode and anode materials, and electrolytes for sodium ion batteries. The second one is Naiades in France, which aims to develop SIBs for sustainable stationary electric energy storage that would bring a radical decrease in cost with respect to the LIBs while ensuring sustainability and performance in terms of safety, cycle life, and energy density. The third one is Faradion in UK, which is in partnership with AGM Batteries Limited. The Faradion is part of Innovate UK's £38.2 m initiative to make the UK a global leader in emissions-cutting technology, and aim to see SIBs powering cars by as early as 2025.

Faradion and AGM will also develop and modify its SIBs technology to meet vehicle manufacturer specifications.

Figure 1-7 The most representative SIBs companies

(a) HiNa Battery; (b) Naiades; (c) Faradion

1.3 Potential application of carbon materials as cathode

Traditional cathodes are based on inorganic compound such as layered transition metal oxide or poly-anionic compounds, which can deliver relatively high reversible capacities and good cycling stability. However, the sluggish solid-state diffusion of sodium ions in these cathode materials leads to unsatisfactory rate performance. Interestingly, carbon materials can be potential cathode candidates by two totally different sodium storage mechanisms, aiming to further improve the energy density or power density compared with present cathode materials.

The first category is based on anion intercalation into graphite, whose advantages are high average operating voltage, safety and low cost. It has been vividly investigated in LIBs but is still immature in SIBs. The challenges are relatively low reversible capacity, instability during cycling and narrow voltage window. Tang et al. reported a novel tin-graphite dual-ion battery (DIB) using tin foil directly as both anode and current collector, and expanded graphite as cathode[54], as shown in Figure 1-8.