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Sodium Ion Battery from Sea Salt: A Review

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The electrical energy storage is important right now because it is influenced by increasing human energy needs, and the battery is a storage energy that is being developed simultaneously. Furthermore, it is planned to switch the lithium-ion batteries with the sodium-ion batteries and the abundance of the sodium element and its economical price compared to lithium is the main point. The main components anode and cathode have significant effect on the sodium battery performance. This review briefly describes the components of the sodium battery, including the anode, cathode, electrolyte, binder, and separator, and the sources of sodium raw material is the most important in material synthesis or installation. Sea salt or NaCl has potential ability as a raw material for sodium battery cathodes, and the usage of sea salt in the cathode synthesis process reduces production costs because the salt is very abundant and environmentally friendly as well. When a cathode using a source of Na_2CO_3 , which was synthesized independently from NaCl can save about 16.66% after being calculated and anode with sodium metal when synthesized independently with NaCl can save about 98% after being calculated because sodium metal is classified as expensive matter.

Keywords: energy storage, battery; sodium-ion; sea salt

Introduction

Researchers have established renewable resources usage as part of the Paris Agreement [1,2]. The agreement aims to reduce global greenhouse gas emissions to restrict the increment in global temperatures in 2°C above pre-industrial levels while pursuing ways to limit the increment in 1.5°C [3]. To achieve this goal, the obligation for transition from fossil energy to clean energy is conducted to get a better life. As a result, energy research and development has become a well-known topic and a major goal in world achievements.

The development of renewable power generation is inseparable from the importance of reliable and efficient energy storage technology [4]. Energy storage devices convert electrical energy into several forms that can be stored and released when they are used [5]. The energy storage system increases the reliability of the electricity

supply by storing electricity during off-peak hours and releasing during on-peak hours [6]. Several types of these devices include secondary batteries, ²⁵ compressed air energy storage (CAES), electrochemical double-layer capacitors (EDLC), flywheels, superconductive magnetic energy storage (SMES), fuel cells, and thermometric energy storage (TEES) [5]. Secondary batteries have a long-life cycle, flexible power, high round-trip efficiency, and easy maintenance among these energy storage devices. Secondary batteries will be good energy storage technology when integrated with renewable resources. Furthermore, the compact size of the battery is suitable to be used in distribution network locations [7]. The challenge is that some portable devices, i.e. mobile phones, laptops, digital cameras, and drones, turn out more expensive because of the batteries [8]. To get the desired specifications, selecting the type of battery is the main point. The type of battery chosen is undoubtedly related to the production cost, which is dominated by the material, about 70% of the total cost [9].

The Lithium-ion battery (LIB) contains the most expensive material but has many advantages [10]. High power density, high energy efficiency, and being environmentally friendly are the main advantages of this battery [11–13]. The research on LIB was conducted in 1970-1980s and Sony became a successful pioneer in the commercialization in 1991 [14]. The most important component of the LIB is the electrode (cathode and anode), the separator and the electrolyte. Commercial anodes in commercial LIB are generally made of graphite, which can easily diffuse Li ions over thousands of cycles. Since this battery is used widely, especially for electric vehicles and consumer use, its production increases every year [15]. As shown in Figure 1, the application of batteries has grown rapidly and is expected to increase simultaneously. The applications, which include portable devices such as video cameras, PCs, mobile phones, and a variety of

other electronic gadgets, are designated as "consumer use" and contain features and functionalities that were previously inaccessible.

Electric vehicles will progressively use lithium-ion batteries as an environmentally acceptable form of transportation, which is predicted to grow dramatically [16]. However, the main source of batteries, namely lithium, is a challenge for the future because it is a finite metal source. According to US geological surveys, it is estimated that worldwide lithium resources can meet market demand by 2100 [17]. Sodium is found in the form of brine and seawater, counted for 61.8% of the world's total (26.9 Mt), especially in the USA, Bolivia, Chile, Argentina and China. The remainder is in mineral form about 16.7 Mt [18]. However, actual demand may exceed this forecast demand coupled with hard-to-find lithium sources [17]. New sources of lithium are being explored, both primary sources from mining and secondary sources from recycled active materials. It is possible that the LIB will not be able to cross the growing demand [19].

The new battery source that is more readily available in nature and less expensive is the sodium-ion battery (SIB). Several studies have been carried out, therefore SIB can be an alternative to LIB for large-scale production [20]. From an economic point of view, SIB can compete with LIB in terms of price, as explained by Peters et al. [21]. In the same cell, such as the 18650-round cell, the SIB is cheaper than the LIB with an LFP / NMC cathode.

As the main source of SIB, sodium is the lightest metal and the second smallest after lithium [22]. Geographically, compared to the limited lithium, the availability of sodium is more abundant. Sodium can be resourced from both seawater and the earth's crust. In seawater, the sodium concentration is 10,800 ppm compared to the lithium concentration of only 0.1–0.2 ppm [23]. Similarly in the earth's crust, 2.8% sodium is provided [24], whereas lithium is only 0.002-0.006% [25]. The high gap in availability

further strengthens sodium as a raw material for new battery materials. Sodium sources can be reached from various compounds such as Na_2CO_3 , NaCH_3COO , NaCl and NaNO_3 . Most of the sodium salt can be produced using NaCl or saline salt. As the main SIB source, sea salt (NaCl) from seawater can be the main candidate [26,27] due to its abundant compounds and not geographically limited. NaCl can be activated into an electrode by inducing it electrochemically in a crystalline structure [26]. NaCl has been used in several components of sodium ion batteries, including electrolyte [28,29], as a raw material for electrodes and electrode doping [30]. Nowadays, the challenge in developing SIB is selecting the suitable electrode type.

This review examines SIB as an alternative to LIB for the future secondary battery using NaCl potential as a raw material especially from seawater. Seawater is processed in such a way into sea salt (NaCl) which is ready to use for production. NaCl can be used directly as raw material for SIB or processed into intermediate raw materials for SIB, such as Na_2CO_3 or NaNO_3 . Details on the seawater potential for the SIB component, its challenges, and future projections are discussed in the next section.

Sodium Ion-Battery

A Sodium-ion battery (SIB) is one of the options for LIB. Because of the comparatively high amount of sodium sources in the earth's encrustation and seawater, as well as its relatively inexpensive manufacturing costs, SIB has recently gained a lot of interest as a promising commercial choice for large-scale energy storage systems [20]. Furthermore, because sodium belongs to the same periodic table group as lithium and has similar physicochemical qualities, SIB's operating mechanism is extremely similar to LIB's [7].

Lithium and sodium are parts of the periodic table's elements in group 1. They are known as alkali metals because their valence shell has one loosely held electron. As a

result, alkali metals are extremely reactive, hardness, conductivity, melting point, and initial ionization energy fall as their progress through the group [31]. Table 1 summarizes some of the characteristics of sodium and lithium that interest in their development. The redox potential of the two alkali elements is one of the most important things to compare. The standard Na^+/Na reduction potential vs. SHE is -2.71 V, which is roughly 330 mV higher than Li^+/Li , which is -3.04 V. SIB's anodic electrode potential will always be greater than LIB's since this potentially specifies a thermodynamics minimum for the anode. However, because the ionic radius of Na (1.02) is much larger than that of Li (0.76), finding suitable crystalline host materials for Na^+ with sufficient capacity and cycling stability may be more difficult [19].

Similar as LIB, an SIB cell consists of a cathode, anode, and electrolyte. The cathode in SIB is made of a substance that can absorb Na cations reversibly at voltages significantly higher than 2 V positive for Na metal. The best anodes are those with low voltages (less than 2 V vs. Na). The active cathode material commonly used is NaFeO_2 and the negative electrode or anode is hard carbon. Throughout charging, the cathode (NaFeO_2) will donate electrons to the external circuit, which can cause oxidation for the transition metal. Some of the added sodium atoms dissolve as ions in the electrolyte to maintain charge neutrality. They travel to the anode (hard carbon) and are incorporated into the structure to restore charge neutrality to the site, which was disrupted by electrons transmitted and absorbed from the cathode side. During discharge, the procedure is iterated in the opposite direction. This complete cycle of reactions happens in a closed system. Each electron produced during oxidation is consumed in the reduction reaction at the opposite electrode [32]. Figure 2 shows the entire procedure diagrammatically.

The specific capacity, cyclic stability, and rate performance of the SIB need to be improved for commercialization. The electrochemical effect is influenced by the

electrode material used in cell manufacturing. The primary challenge is discovering an electrode material with a high and stable specific capacitance, minimal volume change during charge/discharge cycles, and adequate current performance [33]. Increasing the energy density of SIB can be achieved by enhancing the cathode's working voltage or decreasing the anode's working potential, increasing the capacity of specific electrodes, and generating solid-particle materials [19]. Another major challenge related to plated cathode materials is their hygroscopic properties after exposure to air, leading to poor cell performance and ultimately increasing transportation costs [34]. Due to some of these challenges, it is necessary to have a stable material towards the air exposure to produce good cell performance.

Na containing anode materials

Many types of anodes have been developed by researchers, including sodium metal, oxide-based, carbon-based, alloys, and convention anodes. They have a relatively low irreversible capacity, and most of their capacities are potentially close to that of sodium metal. The metal insertion mechanism of sodium is nearly identical to that of lithium [35].

Sodium metal has been studied by many researchers as the negative electrode in sodium-ion batteries [36] [37]. Due to its high density, it has a good anode for energy storage applications in the post lithium-ion battery era because of its large capacity (1166 mAhg^{-1}), availability on earth, and inexpensive cost. However, sodium metal anodes suffer from inconsistent plating, stripping and therefore, it cause a low Coulombic efficiency [37]. The large reactivity of sodium metal with organic electrolyte solvents and the production of dendrites during Na metal deposition are even more troublesome, and the low melting point of Na (98°C) poses a considerable safety hazard in devices intended for operation at room temperatures [19]. Tang et al. devised a method of "sodiophilic" coating an Au-Na alloy onto a Cu substrate that works as a current collector

to drastically minimize the propensity for nucleation over abundant to address this challenge. This coating significantly increases the coulombic efficiency of Na coating and stripping. NaCl allows to be used as a source of Na in this layer [37]. NaCl has been used in several components of sodium ion batteries, including anode component and sodium metal. Sodium metal is usually produced by electrolysis of sodium chloride (NaCl) in the liquid state at the cell, by sticking up a steel gauze diaphragm between the anode and cathode. The function of the diaphragm is for reducing the mixing of the anode and cathode products when traverse the electrolyte [38].

David S. Peterson in 1966, got sodium metal by electrolysis in a mixture of molten salt which consist of 28-36% sodium chloride (NaCl), 23-35% calcium chloride (CaCl₂), 10-25% strontium chloride (SrCl), and 13-30% barium chloride (BaCl₂) [26] takes pure NaCl as the SIB electrode. NaCl is a non-metallic compound, so when it is used as an electrode, it must be metalized, i.e. it must be electromagnetically active for a reversible cycle. The metallization process can be led at high temperatures, as described above, or by induction. During the induction process, an electrochemical before filling up to 4.2 V was brought out as an activation cycle. This process generates a partial transition from phase B1 to B2-NaCl. Furthermore, the release process of about 0.1 V was done, therefore Na⁺ was intercalated into the active compound. During the release process, the B2-NaCl phase can accommodate Na⁺ and form Na_xCl compounds, x > 1. The reactions that occur are as follows



The phase change from B1 to B2 is the key to the reversible process, therefore it can intensify the ionic and electrochemical conductivity. Na metal in NaCl can reversibly intercalate / deintercalate up to a discharge capacity of 267 mAhg⁻¹ [26]. The success of NaCl as an electrode is shown in Figure 3.

Oxide-based materials have also been developed as well, as anodes ³³ in sodium-ion batteries, such as (NTP), $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_2\text{Ti}_3\text{O}_7$ and its composites with carbon, which have been studied by several researchers [39]; [29]. The three-dimensional structure of NTP, which creates an open framework of large interstitial spaces modified with NMNCO, with rate capability and cycle stability is increasing because a better structure can ensure stability between the phases [40]. A similar study was conducted by Hou using NTP / C composites with water-based electrolytes to achieve an energy density of 0.03 Wh / g and a coulombic efficiency close to 100%, due to the three-dimensional structure of NTP with an open framework and uniform nanoparticle shape [41]. NTP / C composites were also studied by Nakamoto using several types of electrolytes and $\text{Na}_2\text{FeP}_2\text{O}_7$ cathodes [42]. Chen et al. (2018) succeeded in manufacturing a desalination battery consisting of a ⁵ $\text{NaTi}_2(\text{PO}_4)_3$ anode and a silver cathode in an aqueous NaCl electrolyte ⁵ for the deionization of seawater as an aqueous energy storage system. ⁵ During the charging process, the sodium ions in the electrolyte are electrochemically caught into the $\text{NaTi}_2(\text{PO}_4)_3$ electrode while the chloride ions are captured and interacted with the silver electrode to generate AgCl. The discharge causes the release of sodium and chloride ions from the corresponding electrode. This will greatly contribute to more energy-efficient seawater desalination technology in the future [29].

SIB anodes have been reported to feature three different types of energy storage mechanisms such as intercalation reactions, conversion reactions, and alloying reactions. This mechanism occurs during sodiation and desodiation [31]. In SIB, carbon compounds are similarly subjected to the intercalation mechanism. Graphitic, hard carbon, and graphene are three types of carbon materials that are one of the most potential ² anodes for ³² SIBs due to their excellent charge/discharge voltage plateaus and low price [43]. Graphite is the most widely used anode material in LIB, with a capacity of 372 mAhg⁻¹. Graphite

² is not suitable for sodium-based systems because Na almost does not form gradual graphite intercalation compounds and the radius size of Na is larger than Li, which means Na ions cannot enter the graphite [44]. To overcome this limitation, Yang et al. created expanded graphite (EG) with a 4.3 interlayer lattice spacing by oxidizing and reducing some of the graphite. The long-range layer structure of EG is similar to that of graphite. They showed that Na⁺ may be absorbed into and removed from EG in a reversible manner [45].

Hard carbon has a lot of potential as SIB anodes because of its substantial ² intercalation capacity, low charge/discharge voltage plateaus, and low-cost methods of preparation [44]. The application of hard carbon as a sodium battery anode was investigated by Alcantara. ¹⁸ Sodium can be inserted reversibly in amorphous and non-porous hard carbon, ²⁹ resulting in a high irreversible capacity in the first cycle due to the carbon surface area [46]. Furthermore, due to its wide middle layer, adequate operating ³⁶ voltage, and inexpensive cost, hard carbon can be utilized as anode material for sodium-ion batteries. However, poor efficiency and initial coulombic performance remain a problem [47]. NaCl can also be combined as an additive on hard carbon to become the anode. The electrochemical properties of hard carbon can be improved by intercalating NaCl. Na⁺ and Cl⁻ can intercalate into the coating at high temperature and pressure, therefore the load transfer resistance can decrease sharply. With the addition of this NaCl, the capacity of the SIB can be increased to 100% [48].

² The capacity of Graphene-based carbon materials is ² higher than that of hard carbon. However, the density of tap graphene is often less than 1.0 g cm⁻³, far lower than that of hard carbon, lowering graphene's volumetric capacity. ² Due to the substantially higher outer surface area compared to hard carbon, these low ICEs are almost unsolvable. SIB anodes have been developed that combine graphene ² with conversion/alloy anodes to

generate bi-functional electrodes. Due to the synergistic effect, graphene can be combined with other electroactive materials, such as metals (or metal oxides), to supply much greater storage capacities and better cycle stability than metal samples (or metal oxides) [49].

Sodium can form alloys with elements such as Si, Ge, Pb, Sn, Sb, P, and Bi so that it can be used as a SIB anode. Single atoms of these elements can form an alloy with more than one Na^+ at an average working potential with less than 1 Volt for Na/Na^+ . Alloying anodes have large specific capacities, and advanced composite nanostructure alloying anodes offer good capacity and cycle stability [50]. During the sodiation phase, however, there is a significant volume growth. Furthermore, during long-term cycling, they are constantly pulverized, which creates a considerable obstacle to commercialization [44]. Their stability must also be increased by the development of advanced structures or interfacial electrode/electrolyte adjustment. Alloying anodes with advanced composite and nanostructures have been shown to have high capacity and cycling stability [51].

Conversion anodes are a typical way to make a high-capacity SIB anode. P, S, O, N, F, Se, and other conversion elements are examples. The components must be paired with metal or non-metal materials as a partial SIB anode, where the alloy metal's discharge product can give high conductivity while also shielding the alloying discharge product from agglomeration [40]. Conversion anodes have obstacles in its implementation such as volume expansion, poor cycle stability, and crushing during the charge-discharge process, all of which are significant impediments to practical implementation [44]. Fortunately, nano engineering of the alloying anode material can solve this volume change. Nano engineering approaches can help to increase the cycling performance of alloying anodes. Combining alloying and conversion elements is another key method for improving the capacity and stability of these materials. These anodes have good cycling

performance thanks to the synergism of conversion and alloying products. Combining alloying or conversion anodes with carbonaceous materials has been proven to be an excellent strategy for producing an extremely stable alloying or conversion anode [52].

Na containing cathode materials

One of the needful components in a sodium battery is the cathode. However, its development is relatively slow. Therefore, developing suitable cathode materials with high capacities and voltages is essential to develop the energy density of the SIB. Several cathode materials have been developed by many researchers such as layered transition metal oxide, sodium poly anion compound, prussian blue, sulfur and air, and other organic compounds. Nowadays, layered metal oxides (Na_xMO_2 , $0 < x < 1$, $M = \text{Fe, Mn, Co, Cu, Ni, etc.}$) and poly anion-type materials have been the most important thing for studying cathodes in SIB [31]. In the 1970s, Delmas et al. found the electrochemical characteristics and structural of Na insertion in NaCoO_2 as a viable cathode material for SIB, which prompted more research [53]. Other layered oxides of 3d transition metals such as Na_xCrO_2 [54], Na_xFeO_2 [55], and Na_xMnO_2 [56], were studied further in the early 1980s. These investigations were limited to 3.5 V versus Na^+/Na during that period and due to the electrolyte's instability in the beginning cycles [57]. Based on the nomenclature suggested by Delmas et al. in 1980., the layered TMOs prototype can be described in terms of $\text{Na}_{1-x}\text{MO}_2$ ($0 < x < 1$, M is a transition metal), and has two distinct types of structures which are presented in table II about types of cathode structures. The structural form of the layered TMO consists of P2-type or O3-type which is depicted in Figure 4. The letters “P” and “O” stand for prismatic and octahedral, respectively, denoting the lattice site inhabited by alkali ion, while the numbers “2” and “3” denote the number of layers or stacks in a repetition unit of the TMO crystal structure [58].

NaCoO₂ is the oldest form of TMO cathode insertion material for SIB, having been investigated in the 1980s [53]. Research on NaCoO₂ was conducted by Ding et al showed a poor cycle life of around 100 cycles [59]. In their investigation of P2-Na_{0.7}CoO₂, Fang et al increased the electrochemical performance from 300 cycles and 86% initial capacity retention. [60]. In general, NaCoO₂ has a excellent voltage stability, high rate capability, and a large range of reversible sodium contents in its many polymorphs [60]. Despite this, it has a oblique voltage profile and has a inclination for reacting with electrolytes containing NaPF₆ [61]. The high cost of Co, on the other hand, is a major impediment to the widespread use of all Co-based electrode materials.

In the 1980s, Tekeda et al were prepared NaFeO₂ through solid-state method at 700 °C. In their examination of the effect of cutoff voltage on electrode performance, Yabuuchi et al. discovered that NaFeO₂ has capacity of 80-100 mAhg⁻¹. For a cutoff voltage of 3.4V, the electrode barely manages excellent capacity. When the cutoff voltage exceeds 3.5V, the material undergoes irreversible structural changes [58].

NaMnO₂ for cathode application was examined by Mendiboure et al on NaMnO₂ premise an impractical low reversible capacity of 54 mAhg⁻¹ [56]. Caballero et al synthesize P2-Na_{0.6}MnO₂ and gain a reversible capacity of 140 mAhg⁻¹ and incredible thermal stability [62]. NaNiO₂ and NaCrO₂ are also appointed as postulant electrode materials for SIB. The electrode NaCrO₂ was synthesized by Komaba et al by capacity of 120 mAhg⁻¹ in the first cycle. Vassilaras et al. defined the electrochemical characteristics of O'3-NaNiO₂ as a capacity of 120 mAhg⁻¹. Substitution part of Fe with either Mn [58], Co [63], or Ni [63]; [64] has attested to be a successful technique for dealing with structural changes and increasing storage capacity while keeping material costs down.

Other important type of cathode material is poly-anionic compounds. The most popular learning of poly-anionic groups contain phosphate (PO₄)³⁻, sulfate (SO₄)²⁻, and

pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) ions [65]. The most productive structures in the poly-anionic compounds family are the maricite, olivine, and NASICON [65]. In the case of SIB, maricite type NaFePO_4 is the thermodynamic stable. However, at temperatures above 450 °C, olivine-type NaFePO_4 change into maricite type NaFePO_4 . Analogous to carbonophosphates and $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_3\text{MePO}_4\text{CO}_3$ (where Me = Fe or Mn), has also been observed [66]. A promising poly-anionic carbonophosphate cathode material has been identified as the Mn compound. However, electrode tuning to reduce capacity loss by 50% in the initial cycles (from 200 to 100 mAhg^{-1}) is required to attain its full potential. Besides, the rate performance is unimpressive [67]. However, the observed reasonable capacity storage is adequate to generate optimization in this material [31].

NaCl can be utilized as an additional raw material in another compound cathode. In its pure form, NaCl is not considered to work properly. Yang et al [68] synthesizes $\text{Na}_4\text{Fe}(\text{CN})_6/\text{NaCl}$ as SIB cathode. NaCl has a part in increasing the Na^+ diffusion, therefore it improves the electrochemical performance of pure $\text{Na}_4\text{Fe}(\text{CN})_6$ [68]. Moreover, it [69] also synthesized the $\text{Na}_2\text{MnFe}(\text{CN})_6$ cathode with $\text{Na}_4\text{Fe}(\text{CN})_6$, NaCl and MnCl_2 raw materials using the co-precipitation method using deionized water as a solvent. By using water-based electrolyte, such as 32K₈Na (Acetate), electrochemical stability is gained and can use Al foil as a flux collector for the first time. Besides, the contact with NMHCF shows a clear dark yellow color shift from the production of iron hydroxide as a result of NMHCF decomposition, therefore it is necessary to develop a transition metal based on cathode to make it more stable.

Besides being an additional raw material, NaCl can be formed in other compounds, as shown in Table III, and therefore it can be used for SIB cathodes. The source of the raw material generally used is Na_2CO_3 , which requires a process to alter NaCl into

Na₂CO₃. Synthesis of Na₂CO₃ according to the solvay process with table salt, therefore it is more environmentally friendly in the equation below [70]:

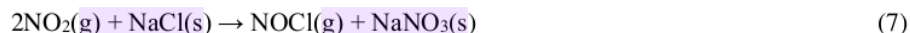
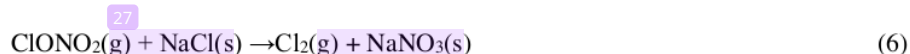
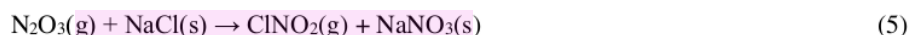
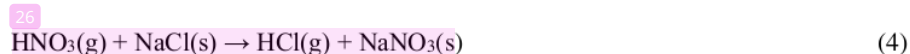


The recovered sodium bicarbonate can be altered to carbonate (soda-ash) by the arts skill method, through calcification (heating) at 170-190°C.



Na₂CO₃ is gained. After that, it ready to use as raw material for sodium ion battery cathode.

The sources of sodium can turn into NaNO₃ as well and some compounds can be reacted with NaCl to form NaNO₃ with heterogeneous reactions at atmospheric pressure such as [71]:



The formation of NaNO₃ from NaCl and HNO₃ begins with the recrystallization of NaCl using an ethanol-water mixture. The solid formed is filtered and dried to remove surface-bound H₂O. NaCl is formed from the precipitation process is not from porous. Dry HNO₃ steam was prepared by mixing HNO₃ and H₂SO₄. Furthermore, NaNO₃⁻ capping NaCl is produced by dry exposure and recrystallization of NaCl to dry HNO₃ in a closed container [72].

Na containing electrolytes

As explained in the previous point, the presence of electrolytes is very important in sodium batteries. The usage of electrolytes is also build upon the resistance of the electrode material used. Regarding of performance, electrolytes specify the properties of

ion transport and the solid electrolyte interface (SEI). The usage of electrolytes is also build upon the resistance of the electrode material used. Not only is ionic conductivity, electrochemical stability window, thermal and mechanical (for solid electrolytes) strength, safety, economics, and ecology important when choosing an electrolyte, as well as the mechanism of its interaction with electrode materials and the characteristics of the SEI produced [74]. For safety reasons, when it comes to thermal runaway or cell breakdown, the correct electrolyte can help reduce the chances of an explosion [73]. Highly modified intercalation compounds used as anodes likely need a customized SEI to allow stable for cycling in the cell, equal to the lithiated graphite electrodes in Li ion systems [19]. Organic electrolytes, ionic electrolytes, aqueous based electrolytes, inorganic solid electrolytes, and solid polymer electrolytes are among the electrolytes utilized in sodium batteries. Each of the electrolytes that are currently available is described below.

1. Organic electrolytes

Diluted sodium salt in organic solvent (ester based and ether based). First, linear carbonates (DMC, EMC, and DEC) and cyclic carbonates (EC and PC); second, ether-based organic solvents (diglyme and triglyme), which suppress dendritic formation, improve thermal stability, and lengthen the ESW [74]. Both sodium salt and solvent is important, the additive choice is important to improve the SIB performance (ester based). Organic solvents have several advantages, including a high dielectric constant (> 15) that promotes sodium salt dissociation, a low viscosity that promotes Na^+ migration, chemical and electrochemical stability to charged and discharged electrode materials within a particular voltage range, the formation of stable passivation films on electrode surfaces, and it is also cost effective for

commercial production [75]. However, organic electrolytes' flammability and instability at high temperatures are major challenges to practical usage [76]

Nowadays, the electrolytes used widely for sodium batteries are NaClO_4 , NaPF_6 , dissoluble in carbonate-based organic solvents, either made from a single solvent, such as polypropylene carbonate (PC), or a mixture of solvents.

2. Ionic Liquid electrolytes

Because some worse point of organic solvent, ionic liquid being used to solve. Cations and anions are the sole constituents of ionic liquids, often identified as room-temperature molten salts or ambient-temperature melts. Many studies on ionic liquid electrolytes have been led by their great thermal stability, no volatility, and broad Electrochemical Stability Windows (ESWs) (up to 6 V), which offer high-quality interfaces and good wetting qualities for separators. Furthermore, their uses have been limited to some extent because to their poor ionic conductivity and relatively high viscosity [65]. That is also because to the high costs of ingredients, manufacture, and purification, ionic liquid based battery are sometimes too expensive for large-scale energy storage system [76].

3. Inorganic solid electrolytes

Solid electrolyte may be divided into two main categories that is inorganic and organic solid electrolyte. Inorganic solid electrolytes shown a diverse group of crystalline ceramics and amorphous glasses. The primary goal of inorganic solid electrolyte development is to solve safety concerns while also increasing energy density and also the flammability case of previous electrolyte. This electrolyte began to be developed due to its non-flammability, strong thermal stability, mechanical qualities, and broad ESW. Sulfides, β -Alumina, NASICON, and Complex hydrides are examples of inorganic solid electrolytes that have been discovered. Sulfides are

known for their strong ionic conductivities, as well as their good mechanical characteristics and low grain-boundary resistances [74]. Because of its layered structure with open galleries separated by pillars through which Na^+ ions may easily move, β -Alumina has been employed as a rapid Na^+ ion conductor. NASICON for their compositional variety and exceptional performance. Complex hydrides have a wide ESW and excellent thermal stability, although they have a poor ionic conductivity.

Besides of their good thermal stability and mechanical strength, there are some point that being major concern on developing inorganic solid electrolyte. Which include poor interface contact, unfavourable chemical/electrochemical reaction with alkali metal, and solid state electrolytes with low thermodynamic and mechanical stability [77].

4. Solid Polymer Electrolyte

Organic solid electrolytes, which are mainly carbon-based polymers containing heteroatoms like oxygen or nitrogen capable of solvating embedded sodium ions, are another type of solid electrolyte. Solid polymer electrolytes are the subject of a lot of research because their mechanical strength and process ability efficiently increase ionic conductivity and expand ESW. Differ from liquid electrolyte that dissociated ions are easily move within the liquid, polymer electrolyte that contain no liquid, ions in polymer electrolytes migrate via the polymer network itself.

Some polymer that already developed is PEO, P(VDF-HFP), PMMA, PAN based gel electrolytes. Liquid plasticizers, organic solvents, and salt solutions immobilized inside polymer host matrices make up solid polymer electrolytes [78]. Because the loss of quick Na^+ ion transfer medium and interfacial compatibility during cycling has a detrimental impact on SPE performance, high-viscosity solvents must be used to

solve the problem. SPEs have low mechanical strength, which puts them at danger of dendritic penetration [76].

5. Aqueous Based Electrolyte

The development of aqueous electrolytes for SIBs is essential from the standpoints of sodium storage and interfacial stability. Diluted sodium salt in aqueous solution. The electrolyte concentration is regarded as an important index for improving aqueous electrolytes because of its direct effects on ionic conductivity and rate performance. The oxygen solubility decreases and becomes more stable as the electrolyte concentration rises. Because self-discharging is generated by oxygen that isn't soluble in the electrolyte, the higher the electrolyte concentration, the less self-discharging occurs.

Because of their low cost and great safety, aqueous electrolytes are widely studied. Because of the kinetic impact, the practical stability window of the aqueous electrolyte is greater than the thermodynamic limit, allowing for the use of a wider range of electrode materials in these systems. However, excessive salt concentrations cause corrosion. There is following aspect that can be considered to improve aqueous electrolytes: such as combination of adequate sodium salts with an appropriate anion to build a stable and low-resistance protective layer on the electrode surface; and inclusion of functional additives to increase interface stability and reduce side reactions in high-concentration electrolytes [76].

Aqueous based electrolyte or water used as a salt solvent has been studied deeply. The salt used are NaCl [29,79], Na₂SO₄ [80–82], and CH₃COONa [69,83,84]. Water electrolytes are promising candidates for an environmentally friendly SIB system due to long life and good performance, safe and low cost SIB system for grid scale applications [73]. Because of its high dielectric constant, low viscosity, strong ionic

conductivity, and low vapor pressure, water is an appealing choice as an ideal solvent for aqueous electrolytes, especially because of its inherent safety [79]. The majority of inorganic salts in aqueous electrolytes (such as Na₂SO₄, NaCl) have no influence on the electrochemical stability window [85]. Further development of NaCl as sodium salt electrolyte is really compromising because the abundance of NaCl in the form of sea salt in the world.

NaCl from sea salt has been one of promising point for sodium ion battery development. In fact, NaCl can be used separately as an electrolyte. As an electrolyte, NaCl is used as an additive in the NaPF₆ electrolyte. The concentration used is about 0.19% and was reported to improve cycling ability [86]. It can also be used as a raw material for the production of electrolytes by reacting with AlCl₃ at 300°C, and the electrolyte formed is NaAlCl₄ [87]. Furthermore, NaCl can be electrolyzed to become NaClO₄ and the electrolysis process occurs on the solid surface, in the case an electrode, and therefore the solid acts as a catalyst. The reaction mechanism in the formation of chlorides in perchlorates is through the formation of hypochlorite, chlorite, and chlorate compounds first. More specifically, the reaction mechanism is shown below [88]:

On the anode surface:



On the cathode surface:



In an electrolyte solution:



NaClO_4 have been widely used as sodium battery salt electrolyte. NaClO_4 can be used in organic solvent or aqueous solvent. The impact of extending the aqueous electrolyte's limited working potential window has also been examined using aqueous Na-ion batteries with highly concentrated electrolytes [89].

For Na^+ in aqueous solutions below 5M, which the water molecules surpass the salt level, the solvation shell consists of at least two layers a closely related primary and a relatively loose secondary solvation shell, with the first Na^+ solvation layer usually contains 6 oxygen. However, when the salt concentration is above 9M, there are hardly enough water molecules available to form the "classic" primary solvation sheath, and bring out "water-in-salt" solution then it can be visualized as molten salt [90].

Application of aqueous sodium ion batteries suffer from its poor cycling stability, lower voltage window and corrosion due to high salt concentration. One of the solution to widen the voltage window is focused on current collector. As a result, corrosion-resistant current collectors on the cathode and current collectors with a high hydrogen over potential on the anode should be used to build high-voltage and long-life sodium ion batteries [79].

Na containing other components

Separators, current collector, and binders are also important components for SIB. Fiber glass is used as a separator in cells with electrolyte dissolved in PC solvent. The usage of fiber glass can reduce the energy density lower build upon the weight or volume of SIB whole components [91]. Fiber glass that composed of nonmetallic fibers have a melting point more than 500°C and excellent fire-resistance performance. But it also has disadvantages such as bad flexibility, mechanical strength and high cost. It makes the difficulty in the assembly process and also bring great safety hidden danger in large scale application [92]. Here is the requirement of separator for SIBs [93] (1) Minimal cost to fulfill the requirements of large-scale energy storage; (2) Due to the high viscosity of SIB electrolyte, better chemical stability and wettability of separators are required; (3) Na dendrites have a higher reaction rate and risk than Li dendrites, and SIB separators should be more resistant to dendrites; (4) Other safety indexes of SIB separators, such as thermal stability and mechanical strength, are also strongly. Several separator modifications have also been unfolded, including the Electrospun Hybrid PVDF-HFP / SiO₂ fibers-based separator, which is applied to sodium-ion batteries and the electrolyte absorption shows no swelling, and stable interface [93]. The present research on SIB separators is mostly focused on the modification of polyolefin separators and the manufacture of nonwoven separators in order to ensure that the separator can retain chemical stability in the electrolyte while also having a high affinity for the electrolyte.

Another major component for the development of practical SIB is the binder used for powdered electrode materials. A binder's key functions may be described as follows: functioning as a dispersant or thickening agent to bind the active material together and provide consistent mixing of electrode components; maintaining the electrode structure's integrity by functioning as a conductive agent and fluid collector; allowing the electrode

to conduct the requisite amount of electrons; increasing the electrolyte's wettability and encouraging ion transport between the electrode and the electrolyte contact [94]. The most used binders are PVDF and CMC. Furthermore, PVDF is used with NMP (N-methyl-2-pyrrolidone) solvent which is pestilent and volatile, while CMC is water-soluble, consequently, it is become easier and safer. Due to its great mechanical properties, high electrochemical stability, thermal stability, good interaction with electrolyte solutions, and the proven ability to make this feasible, PVDF has been the dominant binder in the battery industry for the transport of Li^+ . The main damage of using PVDF are the usage of toxic solvents during its processing and the poor adhesion/consistency of power collectors [95].

Another important external component in the operation of a battery is the binder that holds the electrode material to the current collector. The electrochemically active mass must be fastened to the current collector unless the electrode material is naturally self-standing and may be used as a monolith anode. As briefly mentioned in the previous point, corrosion-resistant current collectors on the cathode and current collectors with a high hydrogen over potential on the anode should be used to develop sodium ion batteries with high voltage and longer life [79]. As a result, strong electronic conductivity and long-term viability in a certain electrochemical environment are key parameters for the current collector. It also doesn't have to be overly thick or heavy to avoid lowering the system's gravimetric and volumetric energy densities [96]. There have been proposed for sodium batteries current collector such as prepatterned current collectors, porous Al and Cu current collectors, carbon felt, and conducting polymer paper-derived mesoporous 3D N-doped carbon [97].

Sodium Source

Sodium can be found from sea salt and the earth's crust. There is 2.8% sodium available in the earth's crust [24]. Figure 5 demonstrated the relative abundance of the eight most abundant elements.

According to the 2013 Geospatial Information Agency, Indonesia has a coastline of 99,093 km, which is the second longest in the world after Canada. It shows that the country has a great potential for salt development.

The quality of saltwater, the procedure, and the technology which are have an impact on the salt production. The production of salt in Indonesia is in the middle class. Based on Ministry of Industry, Indonesia 2018 the average national salt production is 1,281,522tons and the average national salt consumption is 3,185,194tons that means the national salt production cannot meet national salt consumption [98]. It contains 85-90 percents sodium chloride. The sodium chloride level of those salts is still beneath the Indonesian National Standard (SNI) for human salt consumption (dry base) [99] and for salt industry is 98.5 % [100].

A method is needed for the salt production to fulfill the needs based on the quality of the generated salt and the salt requirements for human salt consumption and salt industry. There are plenty methods for increasing salt quality, including physical and chemical approaches. A physical method is one method that improves salt quality without using chemicals, such as hydro-extraction and evaporation (re-crystallization) [101] and chemicals such as sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), barium chloride (BaCl_2), calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium chloride (CaCl_2), and others are used in the chemical procedure [102]. The hydro-extraction procedure is an extraction or separation of a solid-phase component using a liquid phase as a solvent. The salt is the solid phase, while the salt solution is the solvent in this context. The size of salt, the

²⁰ concentration of the salt solution as a solvent, and the extraction period all work on ⁴ the performance of the hydro-extraction process.

The high abundance and an urge to develop Indonesian salt industries made sodium ion batteries from sea salt is an interesting research field to develop. Sodium can be extracted from sea salt ³⁹ to be used for sodium ion batteries. As explained before, desalination batteries also have been developed and use seawater in the case of NaCl. Besides of using seawater directly to the battery system, a lot of sodium salt have been used. Some of the sodium salts used by researchers to gain sodium batteries are Na_2CO_3 [81,84,103–107], NaCH_3COO [29,69,108–110], NaCl [30,69,87,111–113], NaNO_3 [57,59,114,115], Na_2O [64,116], NaOH [83], NaI [82] as shown in Table III below. Na_2CO_3 is the dominant salt in the manufacturing of sodium ion battery cathodes.

For example, of the using of Na_2CO_3 , Sauvage, 2007, synthesized single-phase $\text{Na}_{0.44}\text{MnO}_2$ powder via ²⁸ a classic solid-state reaction using MnCO_3 and Na_2CO_3 (with excess stoichiometry of 10 wt %). Billaud also performed a solid-state method with combining Na_2CO_3 and Mn_2O_3 ; then 15% excess sodium weight was used to obtain $\beta\text{-NaMnO}_2$ [117]. Another study conducted by Jo, 2014, synthesized $\alpha\text{-NaMnO}_2$ ³⁷ by a conventional solid-state method using a mixture of Mn_2O_3 and Na_2CO_3 at a molar ratio of 2:1. This selection is due to the fact that nano-sized Na_2CO_3 as a source of Na has a good size distribution, and Mn_2O_3 as a source of Mn has polygon pieces with micro sizes. The synthesized $\alpha\text{-NaMnO}_2$ shows an agglomerate stick shape with an average particle size of more than 10-50 nm, but due to the high surface activity, the small powder stick form having a 4-5 nm size can be agglomerated easily [105]. The $\beta\text{-NaMnO}_2$ sample was synthesized by the ¹³ solid-state method. The solid-state route implicate mixing Na_2CO_3 and Mn_2O_3 ; then 15% excess sodium weight was used. The significant proportion of Na atoms at this intermediate site indicates that $\alpha\text{-NaMnO}_2$ has a strong probability to produce

planar breakdown. The compound shows a high discharge capacity of 190 mAhg⁻¹ at a low C/20 level when it examined as a cathode in a sodium-ion battery [107].

The source of the raw material generally used is Na₂CO₃, which requires a process to alter NaCl into Na₂CO₃. Synthesis of Na₂CO₃ according to the solvay process with table salt, therefore it is more environmentally friendly in the equation below [70]:



The recovered sodium bicarbonate can be altered to carbonate (soda-ash) by the arts skill method, through calcification (heating) at 170-190°C.



Na₂CO₃ is gained. After that, it ready to use as raw material for sodium ion battery cathode.

Potential of NaCl for Sodium Ion Batteries

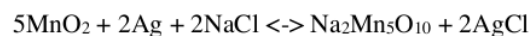
The various sources of sodium, sodium chloride (NaCl) or commonly considered as salt, mentioning above that they have been known for a long time and used widely in various industrial fields. Salt is easy to obtain from evaporation of seawater. This dominates mineral deposits as well, especially in the form of halite [118]. The physical and chemical properties of NaCl can be seen in Table IV below.

NaCl is predicted to be thermodynamically stable by preserving its electronic properties and bond structure. The chemical properties of NaCl under ambient conditions can be understandable, but under a very high-pressure conditions, they can turn the NaCl bond properties. The turning can make differences in mechanical and electronic properties. NaCl runs into a phase transformation from F-centered B1 to primitive B2 phase in the NaCl to CsCl structure at pressures between 20-30 GPa, depending on the temperature [119].

NaCl has been used in several components of sodium ion batteries, including electrolyte [28,29], as a raw material for electrodes and electrode doping [30]. NaCl as an electrolyte was examined by Liu and compared to NaNO₃, it has a lower ionic strength with the same conductivity [28]. Chen utilizes NaCl as a template for the carbon airgel, with NaCl and flux, a carbon air-gel having a wave-like morphology with overflow micro-pores, large accessible surface area and strong structural stability. Furthermore, it can provide an increasing specific capacity and a better capability for sodium storage [66].

Future projection of SIBs obtained from cheap Na sources

There is something more interesting about the use of sea salt in batteries, namely the desalination batteries. Desalination batteries recover sodium and chloride ions from seawater and create fresh water using an electrical energy input, firstly developed by Pasta, 2012 [120]. They used Na_{2-x}Mn₅O₁₀ as cathode for capture Na⁺ ions and Ag electrode was used to capture Cl⁻ ions with this following reaction.



The desalination battery is simple to build, employs commonly accessible materials, has a promising energy efficiency, runs at room temperature with less corrosion issues than conventional desalination technologies, and it has the potential to be Na⁺ and Cl⁻ selective, obviating the need for resalination [120].

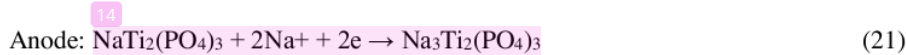
Other desalination method also developed by Lee, 2014. They created a novel way of desalting water by merging CDI and battery systems to improve the desalination performance of capacitive approaches, dubbed "hybrid capacitive deionization (HCDI)". A sodium manganese oxide (NMO) electrode, an anion exchange membrane, and a porous carbon electrode make up the HCDI asymmetric system [121]. The result is the

¹⁰ HCDI system has successfully desalted high capacity sodium chloride solution, faster ⁴⁵ ion removal rate, excellent stability and gotten higher specific capacity of the batteries.

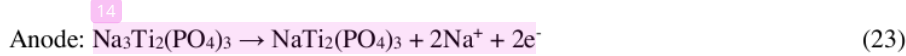
Lately, Cao, 2019 also developed HCDI system for desalination using $\text{Na}_3\text{V}_2(\text{PO}_4)_3@\text{C}$ as sodium ions trapper ³¹ while chloride ions are physically trapped or released by the AC electrode. From the result, conclude that the removal ion rates increased as the water concentrations increased [122].

NaCl as an electrolyte also examined by Liu and compared to NaNO_3 , it has a lower ionic strength with the same conductivity [28]. Another by Chen, Na^+ during charging is captured by the $\text{NaTi}_2(\text{PO}_4)_3$ cathode, while Cl^- is captured by the silver electrode to form AgCl , and vice versa [29]. The function of the NaCl is to provide better ion conduction. This research use ⁵ 0.6M NaCl that is equivalent to seawater and increase into 1M NaCl to ⁵ make sure that ion conduction is enough during charge process.

The charge process is described in the following reaction:



In contrast, the discharge process occurs as follows:



Therefore, the overall reaction occurs ⁴² as follows:



The charge-discharge process shows good stability [29]. Besides conducted new battery system. This alternative also contributed to renewable energy storage from desalination process because it's used natural seawater and collect the salt.

From an economic point of view, SIB can compete with LIB in terms of price, as explained by [21] in Figure 6. In the same cell, such as the 18650-round cell, the SIB is

cheaper than LIB with an LFP / NMC cathode. The changing of lithium salt into sodium salt, changing copper foil to aluminium foil for anodes and some additive can help decrease the material cost production [123]. Furthermore, the use of NaCl as an electrode, additive and electrolyte is also a factor that gives contribution in reducing production costs, especially in raw materials. When a cathode using a source of Na_2CO_3 , which was synthesized independently from NaCl can save about 16.66% after being calculated and anode with sodium metal when synthesized independently with NaCl can save about 98% after being calculated because sodium metal is classified as expensive matter. Because of the congested areas of Na, developing aqueous Na-ion batteries is both valuable and possible (NaCl, Na_2SO_4 , NaNO_3 , etc.).

As an alternative to LIB, SIB looks forward to have a low environmental impact. Peters [124] quantify the impact of SIB on the environment and compare it with LIB. Consequently, SIB has less impact due to the following reasons:

1. It is possible to use aluminium for both cathode and anode
2. When the anode uses hard-carbon, it may be possible to use hard-carbon from organic waste.
3. It can reduce the use of nickel, which is commonly used for LIB cathodes, therefore the impact of nickel mining on the environment can also be reduced. However, more in-depth research is needed.
4. The binder commonly used in LIB, such as PVDF, in its production, causes a high greenhouse gas effect, therefore an alternative water-based binder is needed.

Bossche et al [125] classify battery types with adverse environmental impacts, including lithium-ion, nickel-cadmium, lead-acid, sodium-nickel chloride, and nickel-metal hydride. The sodium-based battery type has the lowest environmental impact than others.

Some of researchers also have been conducted life cycle assessment (LCA) for sodium ion batteries. LCA is a defined approach for calculating the environmental effects of commodities, products, and activities. It considers the entire life cycle, from resource extraction to production, usage, and end-of-life management, as well as waste recycling and disposal [126]. Except for LFP–LTO type LIBs, the examined SIB would already beat existing LIBs in terms of environmental performance with lifetimes of roughly 3000 cycles.

Sodium-ion batteries are still one of the most promising alternatives for next-generation stationary batteries, where the lack of volumetric limits and a focus on economy, safety, and extended life are well linked with SIB features.

Conclusion

Lithium-ion batteries (LIB) have long dominant energy storage technology in electric vehicles and hand-held electronics. The cost and limited quantities of lithium in the earth's encrustation may prevent LIBs from being used in future large-scale renewable energy storage. Lithium metal, if used simultaneously, is depleted easily. The searching for new sources of lithium batteries and recycling is not expected to meet the high demand. The increasing demand for LIB has led researchers to look for alternative batteries.

Because of their abundant sodium supplies and similar electrochemical principles, sodium-ion batteries (SIB) are being explored as a viable alternative to lithium-ion batteries in large-scale renewable energy storage applications. Na raw material base is much greater. The sources are more abundant in nature and cheaper than lithium Na thought that it has similar characteristics in batteries to Li. Many potential raw materials for Na. The sources of sodium in the form of NaCl (table salt) can be the primary source

of SIB both as electrodes, doping, and electrolytes. NaCl can also be used in the form of other compounds such as Na_2CO_3 which is the most commonly applied to SIB right now.

The use of NaCl as an electrode, additive, and electrolyte contributes to make production costs lower, particularly in terms of raw materials. Because sodium metal is classified as expensive matter, a cathode using a source of Na_2CO_3 that was synthesized independently from NaCl can save about 16.66 percent after being calculated, and an anode with sodium metal that was synthesized independently from NaCl can save about 98 percent after being calculated.

The generation of solid-particle material cannot be separated from the selection of raw materials. Sodium sources from seawater can be chosen as raw materials because they can be processed into other forms of sodium salt or used directly. The source of this materials can meet the possible high demand for SIB in the future. As will be explained in the next section, NaCl from seawater can contribute to all SIB components, both cathode, anode, and electrolyte.

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