

Review

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# An industrial pathway to emerging presodiation strategies for increasing the reversible ions in sodium-ion batteries and capacitors

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**How to cite this article:** Mu JJ, Liu ZM, Lai QS, Wang D, Gao XW, Yang DR, Chen H, Luo WB. An industrial pathway to emerging presodiation strategies for increasing the reversible ions in sodium-ion batteries and capacitors. *Energy Mater* 2022;2:200043. <https://dx.doi.org/10.20517/energymater.2022.57>

**Received:** 23 Sep 2022 **First Decision:** 28 Oct 2022 **Revised:** 25 Nov 2022 **Accepted:** 5 Dec 2022 **Published:** 23 Dec 2022

**Academic Editors:** Jiazhao Wang, Wei Tang **Copy Editor:** Fangling Lan **Production Editor:** Fangling Lan

## Abstract

Sodium-ion batteries (SIBs) and capacitors (SICs) have been drawing considerable interest in recent years and are considered two of the most promising candidates for next-generation battery technologies in the energy storage industry. Therefore, it is essential to explore feasible strategies to increase the energy density and cycling lifespan of these technologies for their future commercialization. However, relatively low Coulombic efficiency severely limits the energy density of sodium-ion full cells, particularly in the initial cycle, which gradually decreases the number of recyclable ions. Presodiation techniques are regarded as effective approaches to counteract the irreversible capacity in the initial cycle and boost the energy density of SIBs and SICs. Their cyclic stability can also be enhanced by the slow release of supplemental sodium and high-content recyclable ions during cycling. In this review, a general understanding of the sodium-ion loss pathways and presodiation process towards full cells with high Coulombic efficiency is summarized. From the perspectives of safety, operability and efficiency, the merits and drawbacks of various presodiation techniques are evaluated. This review attempts to provide a fundamental understanding of presodiation principles and strategies to promote the industrial development of SIBs and SICs.



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**Keywords:** Na-ion batteries, presodiation, recyclable ions, full cells, commercialization

## INTRODUCTION

In the upcoming decades, the widespread adoption of clean and efficient energy storage systems will be necessary to combat climate change<sup>[1-5]</sup>. Metal-ion batteries<sup>[6-9]</sup>, exemplified by lithium-ion batteries (LIBs), have received extensive attention due to their high energy density and low self-discharge and have been frequently applied in portable electronic devices, electric vehicles and grid-scale energy storage<sup>[6]</sup>. However, the limited and unevenly distributed lithium resources hinder the further development of LIBs<sup>[10,11]</sup>. It is therefore necessary to search for other energy storage technologies to substitute for LIBs. As a result of their significant abundance, high performance, low cost and similar physicochemical properties to LIBs, sodium-ion batteries (SIBs) and capacitors (SICs) are viable alternatives to LIBs<sup>[12-17]</sup>. Recently, remarkable research effort has been dedicated to the exploration of desirable electrode materials to meet the constantly expanding demand for next-generation applications<sup>[1,18-22]</sup>. However, there are still a series of potential problems that need to be further addressed. In addition to the inherent drawback of the energy density, there is also a non-negligible capacity loss caused by the loss of recyclable ions and the irreversible degradation of electrolytes to form the solid electrolyte interphase (SEI)<sup>[23]</sup>. Generally, the cathode, as the only sodium-ion source in the full cell, provides not only reversibly cyclic  $\text{Na}^+$  during charge and discharge but also irreversible  $\text{Na}^+$  during the first cycle. The cell will inevitably experience capacity and energy density decay due to the low initial Coulombic efficiency on the anode/cathode side and side reactions<sup>[24-30]</sup>. For example, prior to the regular battery operation of sodium-ion insertion and desorption, partial sodium ions are consumed and consolidated during the formation of the SEI layer on the active material surface, particularly in the initial formation process owing to the low initial Coulombic efficiency. Generally, presodiation technology is common for SIBs and SICs. For SICs, the reduction of Na ions in the electrolyte can be prevented by pre-embedding Na in the anode material.

It is without a doubt that increasing the cyclable sodium-ion content in a full-cell system can directly and efficiently improve its electrochemical performance by alleviating the sodium-ion loss in the initial cycle. Presodiation, known as the pre-doping of  $\text{Na}^+$ , is an efficient method to prevent the capacity loss introduced by constrained sodium sources in the cathode, which can also boost the operating voltage and elevate the concentration of recyclable ions in SIBs<sup>[14,31-35]</sup> and SICs<sup>[36-38]</sup>. As indicated in [Figure 1](#), under normal conditions, the active sodium ions in the cathode material are partly responsible for Na loss; however, the presodiated full cell can supply more active Na, which can compensate for the irreversibly recyclable Na, preventing Na loss in the cathode and the corresponding capacity decay. On this basis, the presodiation process is recognized as a practical method for bringing high-performance Na-ion full-cell manufacturing to fruition in the future. Based on the research on prelithiation in LIBs<sup>[33,39-42]</sup>, several presodiation strategies<sup>[33,35,43]</sup> have been reported containing physical, chemical and electrochemical approaches. Considering the cathode side, mixing the suitable Na-containing additives and coupling them with self-presodiation cathode materials are effective strategies to accomplish the presodiation process. For the anode side, physical, chemical and electrochemical approaches are acceptable. It is crucial to deeply consider and comprehend the various presodiation techniques for realizing the industrialization of SIBs and SICs. In this review, we summarize the reported achievements and explore the fundamentals and challenges of presodiation process from an industrial perspective, as well as state-of-the-art presodiation technologies. This review will help researchers to gain a broad grasp of the presodiation procedure and hasten the commercialization of SIBs and SICs.

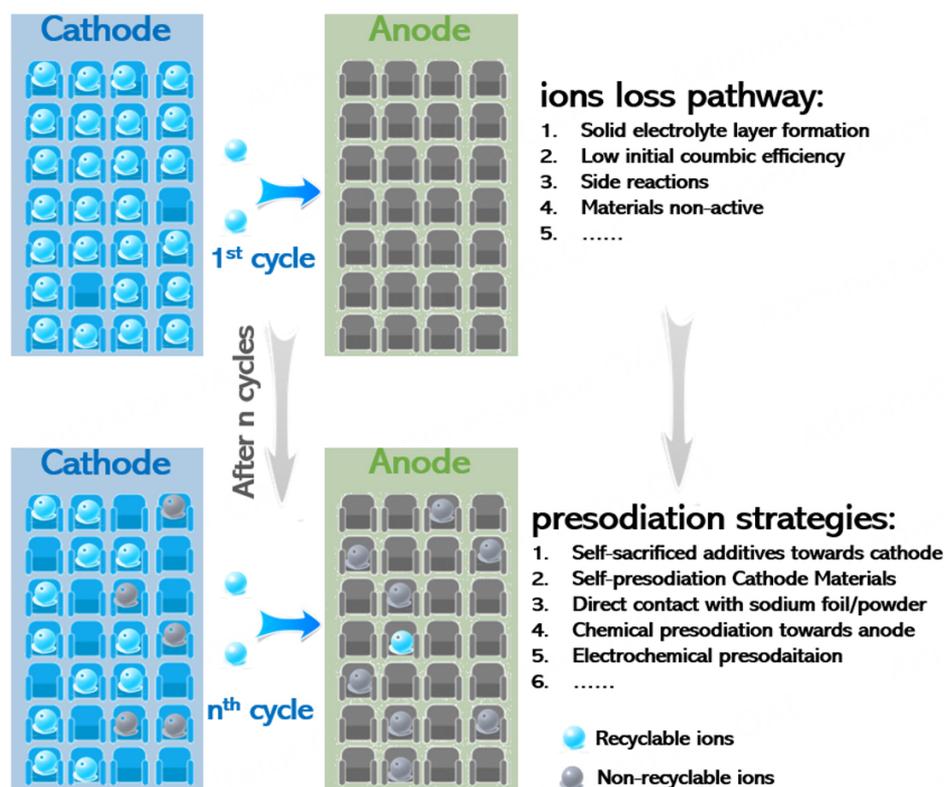


Figure 1. Schematic illustration of Na loss during initial cycle.

## FUNDAMENTALS AND STRATEGIES OF PRESODIATION

Similar to LIBs, the electrode materials from SIBs also suffer from Na loss during electrochemical cycles, as shown in Figure 1, leading to the deterioration of capacity and energy density. In SIBs, the following three factors are primarily responsible for the irreversible capacity loss:

(i) *Formation of SEI from electrolyte decomposition.* The electrolytes of SIBs mainly contain carbonate ester solvent and sodium salt, which are prone to irreversible decomposition reactions at low potential to form SEI film<sup>[44,45]</sup>, resulting in the reduction of Coulombic efficiency in the first cycle<sup>[44-47]</sup>. In particular, for an alloy anode that undergoes a significant volume change during Na storage<sup>[48-50]</sup>, the SEI film continuously splits and reconstructs during electrochemical cycling, leading to a further increase in Na consumption.

(ii) *Capture of Na<sup>+</sup> from structural defects.* Generally, the anode material has several structural flaws and sodiophilic functional groups that can permanently trap sodium ions and cause capacity deterioration<sup>[51,52]</sup>. In particular, for anode materials with a high surface area or porous structure, the Na<sup>+</sup> loss will be promoted.

(iii) *Na loss from side reactions.* For instance, coordinated water is present in cathode materials, such as Prussian blue, which is vulnerable to electrolyte side reactions at high potentials and results in Na consumption<sup>[53]</sup>. From the perspective of the Na-ion full cell, the SEI will develop on the surface of the anode during the first charge cycle, which consumes partial Na<sup>+</sup> from the energy storage system, causing a slight capacity loss and a drop in energy density.

If a second  $\text{Na}^+$  source can be provided in addition to the cathode compensating for the  $\text{Na}^+$  loss during charge and discharge, the capacity and energy density of SIBs can be further increased<sup>[33,43]</sup>. This process of providing an additional  $\text{Na}^+$  source is defined as presodiation. Additionally, the presodiation process can also increase the operating voltage and lower the electrolyte consumption during the formation of the SEI film in SICs. Among the strategies to enhance the initial Coulombic efficiency, such as surface engineering<sup>[54-56]</sup>, structural regulation<sup>[57]</sup> and new materials design<sup>[58]</sup>, the feasible presodiation technology appears more effective and enables the irreversible capacity to be activated, maximizing the energy density in SIBs. Presodiation methods vary in their benefits and drawbacks, and it is therefore crucial to comprehend the underlying mechanism.

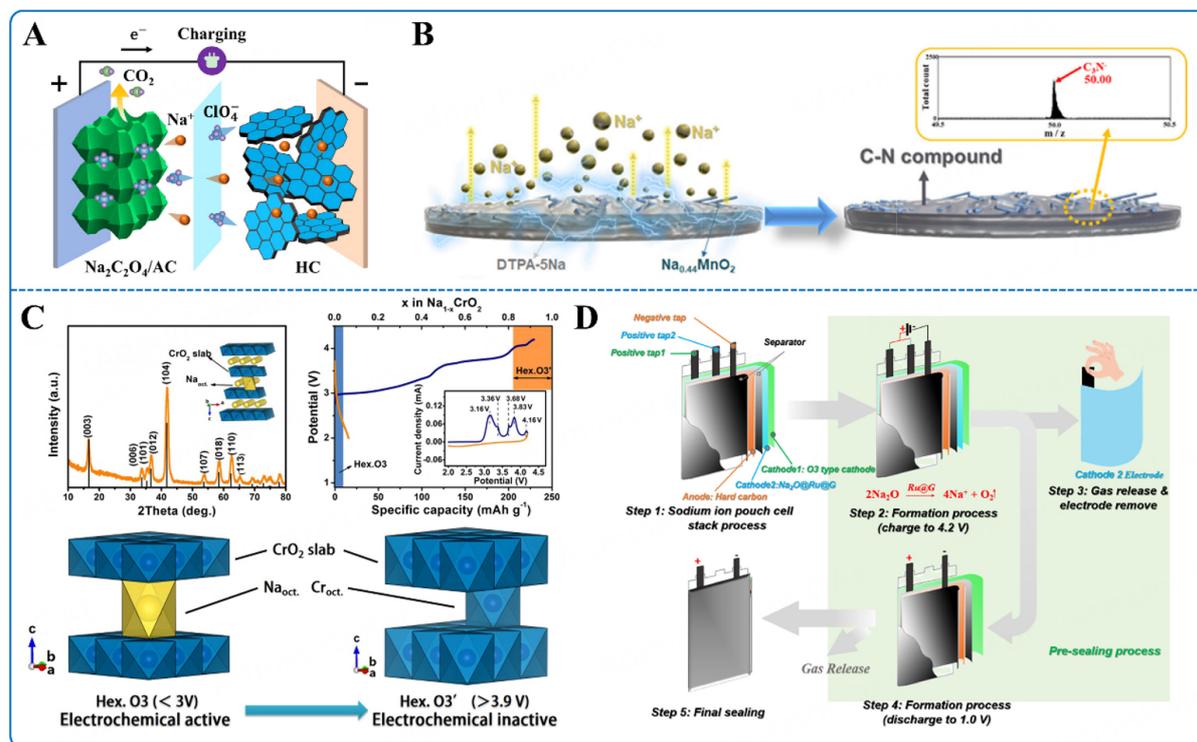
### Self-sacrificing Na-containing additives for cathodes

Recently, presodiation has been performed with the addition of supplementary Na-containing additives and a wide range of materials have been systematically investigated. Na-containing additives usually undergo electrochemical oxidation during the first charge-discharge operation, irreversibly releasing extra  $\text{Na}^+$  to compensate for the  $\text{Na}^+$  loss. For this, the decomposition potential of the additives should be lower than the working potential of the full cell to ensure that the Na-containing additives can be thoroughly electrochemically oxidized to release sufficient  $\text{Na}^+$  during the first charge<sup>[59]</sup>.

There are many Na-containing additives that have been carefully studied for the presodiation of Na-ion full cells, including  $\text{Na}_2\text{C}_2\text{O}_4$ <sup>[60]</sup>, DTPA-5Na<sup>[59]</sup>,  $\text{NaCrO}_2$ <sup>[61]</sup>,  $\text{Na}_2\text{O}$ <sup>[62]</sup>,  $\text{Na}_2\text{S}$ <sup>[63,64]</sup>,  $\text{NaN}_3$ <sup>[65]</sup>, and  $\text{NaNiO}_2$ <sup>[66]</sup>, which can be combined with the active cathode materials and provide sufficient extra  $\text{Na}^+$  sources during the first charge, as well as oxidizing the associated anions to release gases.  $\text{Na}_2\text{C}_2\text{O}_4$ , as a typical sacrificial additive, is environmentally friendly, low cost and can achieve no additional residues after  $\text{Na}^+$  extraction. As shown in [Figure 2A](#), Sun *et al.* systematically evaluated the role of  $\text{Na}_2\text{C}_2\text{O}_4$  in the presodiation of SICs<sup>[60]</sup>. They concluded that  $\text{Na}_2\text{C}_2\text{O}_4$  could be oxidized at  $\sim 3.7\text{-}4.0$  V (*vs.*  $\text{Na}^+/\text{Na}$ ) to yield a specific capacity of  $393.8$  mAh  $\text{g}^{-1}$ . Benefiting from the merit of “zero dead mass”, the boosted pouch-type SICs deliver remarkable energy and power densities of  $91.7$  Wh  $\text{kg}^{-1}$  and  $13.1$  kW  $\text{kg}^{-1}$ , respectively, when coupled with commercially available activated carbon as the cathode and commercially available hard carbon (HC) as the anode. Additionally, Zou *et al.* reported a labile organic sodium salt,  $\text{Na}_2\text{C}_6\text{O}_6$ , which could decompose to produce abundant  $\text{Na}^+$  at high voltage to make up for the irreversible capacity<sup>[31]</sup>.

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As shown in [Figure 2B](#), Jo *et al.* reported a new penta-sodium diethylenetriaminepentaacetic acid salt (DTPA-5Na), which could be irreversibly oxidized to achieve an excellent charge capacity of nearly  $363$  mAh  $\text{g}^{-1}$ <sup>[59]</sup>. By mixing 9 wt.% DTPA-5Na with a  $\text{Na}_{0.44}\text{MnO}_2$  cathode, the charge capacity delivers an



**Figure 2.** (A) Schematic illustration of presodiation mechanics by introduction of  $\text{Na}_2\text{C}_2\text{O}_4$  implemented by initial charge process<sup>[60]</sup>. (B) Schematic diagram showing multiple functions of  $\text{DTPA-5Na}$ <sup>[59]</sup>. (C) Crystal structure and electrochemical characteristics of  $\text{NaCrO}_2$ <sup>[61]</sup>. (D) Illustration of electrocatalytically-driven presodiation process based on pouch cell<sup>[62]</sup>.

obvious increase from 58 to 128  $\text{mAh g}^{-1}$ , indicating that  $\text{DTPA-5Na}$  could provide sufficient Na sources during the first charge. A comprehensive mechanism was also proposed.  $\text{Na}^+$  in  $\text{DTPA-5Na}$  can be electrochemically extracted after the first charge operation and the generation of poorly crystalline  $\text{C}_3\text{N}$  characteristics of electron conductivity on the surface of the cathode. Interestingly,  $\text{C}_3\text{N}$  could serve as a conductive network to accelerate the electron transfer in the composite cathode. In addition,  $\text{NaCrO}_2$  is usually employed as a self-sacrificing Na-containing additive for Na-ion full cells, which can offer an irreversible capacity of 230  $\text{mAh g}^{-1}$  from its irreversible phase transition at high voltage.

As shown in [Figure 2C](#), Shen *et al.* employed a  $\text{NaCrO}_2$  additive to achieve high capacity, low polarization, high energy density and excellent cycle stability in  $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}/\text{HC}$  full cells. During the first cycle, the full cell with  $\text{NaCrO}_2$  shows charge and discharge capacities of 308 and 118  $\text{mAh g}^{-1}$ <sup>[61]</sup>, respectively, which are higher than the capacities of the full cell without additives (charge capacity of 132  $\text{mAh g}^{-1}$  and discharge capacity of 50.7  $\text{mAh g}^{-1}$ ). In addition to traditional cathode additives, Zhang *et al.* developed an electrocatalytically driven decomposition of  $\text{Na}_2\text{O}$  with high  $\text{Na}^+$  content, which could provide a large number of recyclable  $\text{Na}^+$  without jeopardizing the integrity of the electrode materials, electrolytes and the overall battery [[Figure 2D](#)]<sup>[62]</sup>. High sodium content (88%) sodium oxide ( $\text{Na}_2\text{O}$ ) can provide sufficient cyclable sodium ions that are electrocatalytically-driven by a highly active ruthenium@graphene ( $\text{Ru@G}$ ) electrocatalyst to compensate the sodium loss during the initial SEI formation and following consumption. This additional electrocatalytically-driven cathode strategy not only provides numerous cyclable sodium but also has no adverse effects on the stability of the electrode materials, electrolyte or the whole battery system. All the steps were based on the current mature commercial battery fabrication process, which can efficiently ensure its potential practical application. Furthermore, this process does not induce unknown byproducts

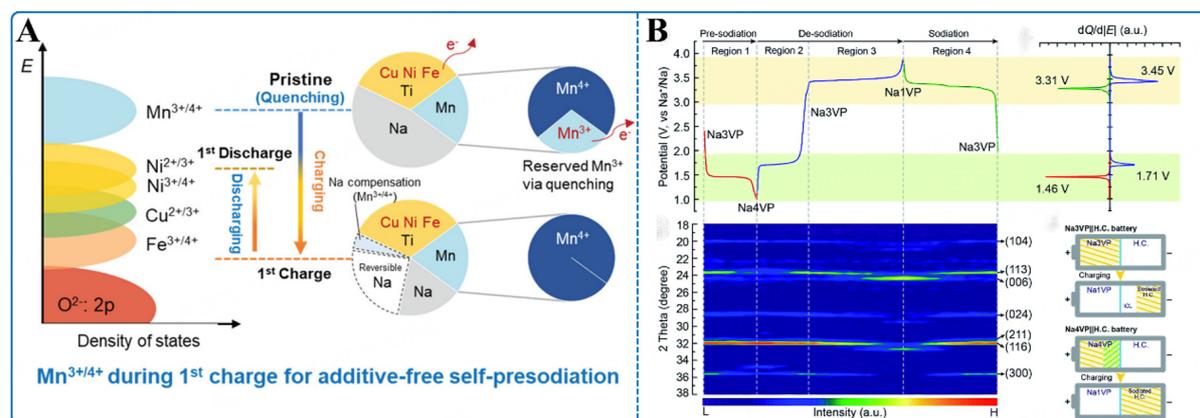
into sodium-ion full-cell systems. The catalytically-driven sodium-ion compensation was monitored by *in-situ* synchrotron X-ray diffraction (XRD). It was concluded that the Na<sub>2</sub>O@Ru@G electrode employed in a full-cell system not only provided extra cyclable sodium ions but also efficiently alleviated the continuous phase transformation of cathode materials. The extra cyclable sodium ions in the full-cell system can inhibit the surface phase transformation and alleviate the transition metal dissolution in the electrolyte. All of these can protect the hard carbon (HC) anode from increased resistance by suppressing the dissolution-migration-deposition process. After presodiation treatment for a Na[Li<sub>0.05</sub>Mn<sub>0.50</sub>Ni<sub>0.30</sub>Cu<sub>0.10</sub>Mg<sub>0.05</sub>]O<sub>2</sub>//HC pouch cell, the initial Coulombic efficiency and energy density can reach 90.0% and 295 Wh kg<sup>-1</sup>, respectively, and the cycle performance is also markedly improved. Moreover, this method also addresses the issues of the decomposition of cathode additives and the release of produced gas and residues.

In addition to experimental investigations, theoretical calculations are also useful tools for developing presodiation techniques. Zou *et al.* calculated the optimal binding energy of O-M (M = Li, Na or K) bonds in metal carboxylates<sup>[67-69]</sup>. After an in-depth analysis of the experimental results and density functional theory calculations, it was found that the cathode additive decomposition caused by irreversible decarboxylation is determined by the O-M (M = Li, Na or K) bond energy, which can be further affected by the electronic structure of the substituent and hardness/softness adjustment of metal elements. Furthermore, the bonding strength of O-M bonds can be regulated by the electron-donating effect of substituents and the low charge density of cations, resulting in a lower electrochemical oxidation potential.

The presodiation process by introducing Na-containing cathode additives has many advantages. First, it is straightforward and the total cost is determined by the cost of the additive substance, which is easy to commercialize and industrialize. Second, cathode additives have excellent environmental adaptability and high compatibility with current battery manufacturing technologies. However, there are still some remaining challenges facing cathode presodiation. For instance, the impact of cathode additive residues and emitted gases on the overall battery system is still not well understood at present. In particular, the released gases are likely to change the microstructure of cathode materials, which may have a significant influence on the long-time operation of the battery system.

### Self-presodiation cathode materials

The introduction of sacrificial additives results in an increase in cathode mass and the inevitable generation of gases and byproducts, which restrains their commercial and industrial application<sup>[60]</sup>. To overcome the above-mentioned problems, the researchers proposed a Na-rich cathode as an alternative approach towards presodiation. The Na-rich cathode is a solid solution including supersaturated Na, which can be irreversibly released to the electrolytes during cycling, compensating for active Na loss. As shown in [Figure 3A](#), the self-presodiation cathode compound O3-type Na<sub>0.9</sub>Cu<sub>0.11</sub>Ni<sub>0.11</sub>Fe<sub>0.30</sub>Mn<sub>0.48</sub>Ti<sub>0.10</sub>O<sub>2</sub> was prepared by the quenching treatment, which can retain a high sodium content (nearly 0.9) in the crystal structure by inhibiting the precipitation of carbonate. The quenched materials maintain high Mn<sup>3+</sup> and Na<sup>+</sup> contents, which can compensate for Na consumption during initial charging by releasing Na<sup>+</sup> activated by Mn<sup>3+</sup> oxidation. Other transition metals are employed to supply capacity for subsequent cycles. In contrast, the structural evolution of the naturally cooled cathode material was investigated by *in-situ* temperature-variable XRD, indicating that the Na<sub>2</sub>CO<sub>3</sub> layer formed on the surface of the cathode particles, accompanied by a large amount of Mn<sup>3+</sup> oxidation caused by the reaction between Na<sup>+</sup> precipitated from the layered oxide lattice and CO<sub>2</sub> molecules in the air. The quenching procedure could significantly suppress the emergence of surface carbonates and preserve the long-range structure of Na<sub>0.9</sub>Cu<sub>0.11</sub>Ni<sub>0.11</sub>Fe<sub>0.30</sub>Mn<sub>0.48</sub>Ti<sub>0.10</sub>O<sub>2</sub>, particularly the lattice oxygen array architecture. Paired with a commercially available HC anode in Na-ion full cell, the quenching cathode delivered a higher energy density of 256 Wh kg<sup>-1</sup>, representing a ~9.9% increase compared with that of the naturally cooled cathode<sup>[70]</sup>.



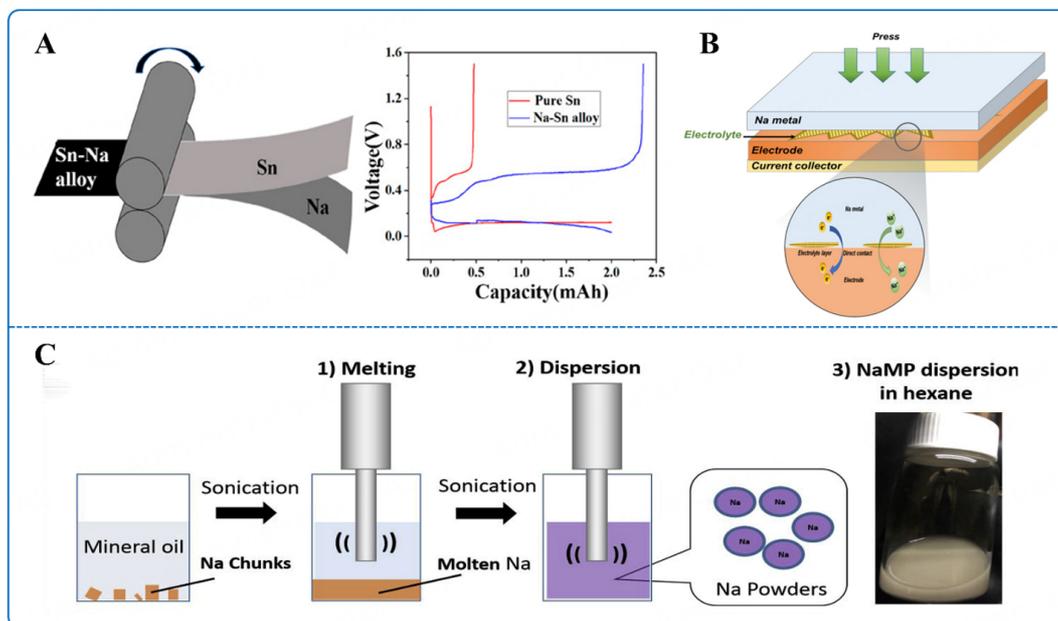
**Figure 3.** (A) Schematic illustrations of redox behavior of TM cations and oxygen anions of O3-type Na<sub>x</sub>TMO<sub>2</sub> cathode (left) and quenching process for self-presodiation cathode (right)<sup>[70]</sup>. (B) Schematic diagram of reaction mechanism of desodiation procedure for cathode<sup>[71]</sup>.

In addition, another Na-rich cathode, Na<sub>4</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, was systematically investigated by Mirza *et al.*<sup>[71]</sup>. As shown in Figure 3B, the electrochemical presodiation strategy was applied, in which Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Na<sub>3</sub>VP) was first converted to Na<sub>4</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Na<sub>4</sub>VP) by a sodium foil and then the desodiation process of Na<sub>4</sub>VP was performed below 2.2 V vs. Na<sup>+</sup>/Na. The whole reaction process was characterized by operando XRD. During this process, the additional Na per formula unit of Na<sub>4</sub>VP is extracted into the electrolyte to compensate for the irreversible Na depletion and the corresponding Na<sub>3</sub>VP generated after desodiation from Na<sub>4</sub>VP is directly regarded as the cathode. As a result, the Na<sub>4</sub>VP//HC full cell achieves an excellent energy density of 265 Wh kg<sup>-1</sup>, which is 76% higher than that of the Na<sub>3</sub>VP//HC full cell. The reversible capacities of the Na<sub>4</sub>VP//HC and Na<sub>3</sub>VP//HC full cells are 103.76 and 51.02 mAh g<sup>-1</sup>, respectively, while the initial Coulombic efficiency of the Na<sub>4</sub>VP//HC full cell is ~95%, which is nearly double that of the Na<sub>3</sub>VP//HC full cell.

### Direct contact with sodium foil/powder

Learning from the prelithiation process of LIBs employing metallic Li or Li powder<sup>[72]</sup>, metallic Na has also been widely explored in direct contact with anode materials for presodiation. As shown in Figure 4A, Liu *et al.* reported a presodiation method by spontaneous alloying between Na and Sn, where the Na and Sn foils are in direct contact under pressure using a roller<sup>[73]</sup>. After presodiation, the initial Coulombic efficiency increases from 24.96% to 75.0% in the Na<sub>3</sub>V<sub>2</sub>PO<sub>4</sub>F<sub>3</sub>//NaSn full cell, which is attributed to the release of extra Na from the NaSn alloy to compensate for the irreversible Na loss during the initial stage. In addition to alloying presodiation, a potential-driven presodiation has also been reported, similar to prelithiation in LIBs<sup>[74]</sup>, in which Na metal was directly attached<sup>[74]</sup> to an electrode separated with a small amount of electrolyte and the potential gap between Na and the active materials, such as Na<sub>0.67</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (NFMO) or commercial HC, could act as a driving force for the migration of Na ions and electrons. By directly contacting Na metal with electrodes, Na<sup>+</sup> will be introduced into the active electrode materials, which can compensate for the Na loss during the initial cycle. Therefore, the PS-HC//NFMO full cell exhibits a discharge capacity of 102 mAh g<sup>-1</sup>, representing a 60.0% increase over the HC//NFMO full cell [Figure 4B].

Similar to Li metal, metallic Na is extremely active and difficult to store stably and safely in air, so the presodiation with Na metal or powder can only be performed in an oxygen- and water-free glove box. Simultaneously, the manufacture of metallic Na powder is laborious and the risk of thermal runaway exists when the anode and metallic Na powder are pressure coated. Additionally, excessive Na powder input will



**Figure 4.** (A) Schematic illustration of synthesis process of Na-Sn alloy anode and corresponding electrochemical performance during first cycle<sup>[73]</sup>. (B) Schematic of direct contact with Na metal<sup>[74]</sup>. (C) Schematic illustration of ultrasonic dispersion of sodium metal powder and electrode preparation<sup>[75]</sup>.

promote the growth of Na dendrites and cause safety problems, so accurate calculations of the amount of Na metal or powder are required. Given these drawbacks, several researchers have experimented with a variety of solutions. For instance, an ultrasound-assisted synthesis of Na powder was reported by Tang *et al.*, in which solid Na chunks were heated, melted and then broken up in an organic solvent (hexane) with the assistance of an ultrasonic process, as shown in Figure 4C<sup>[75]</sup>. The Na powder suspended in hexane is added dropwise to the electrode as an additive, followed by vacuum drying to remove the solvent. After rolling the electrode and Na powder in good contact, the purpose of presodiation can be achieved. This method is feasible for creating a well-dispersed Na powder in hexane and makes the presodiation process practical to sprinkle the Na powder directly onto the electrode surface. In a half cell, the glucose-derived HC anode (GC1100) after presodiation can lower the open-circuit potential by ~1 V and the irreversible Coulombic efficiency of the initial cycle to 8.0% from 19.3%. Paired with NaCrO<sub>2</sub> in the full cell, the presodiated GC1100 causes a ~10.0% enhancement in cycling capacity and a 5% improvement in energy density. In general, the application of Na metal or powder as a presodiation agent can optimize the overall performance of batteries by providing extra Na sources but how to enhance the stability of metallic Na powder is a critical issue that needs to be solved in the future.

### Chemical presodiation for anodes

Chemical presodiation, similar to chemical prelithiation<sup>[76-79]</sup>, is rapidly gaining popularity as a reliable and efficient presodiation technique that can substitute for the conventional operation of directly employing active Na metal. Generally, this process involves soaking sodium metal into an organic ether solvent containing naphthalene(Naph)/biphenyl (Bp), followed by electron transfer between sodium metal and Naph/Bp resulting in the production of highly active polycyclic aromatic sodium and the generation of a complex with ether solvent (Na-Naph or Na-Bp). Because of the potential difference, the Na-Naph or Na-Bp complex containing large amounts of sodium free radicals can react rapidly with anode materials for presodiation.

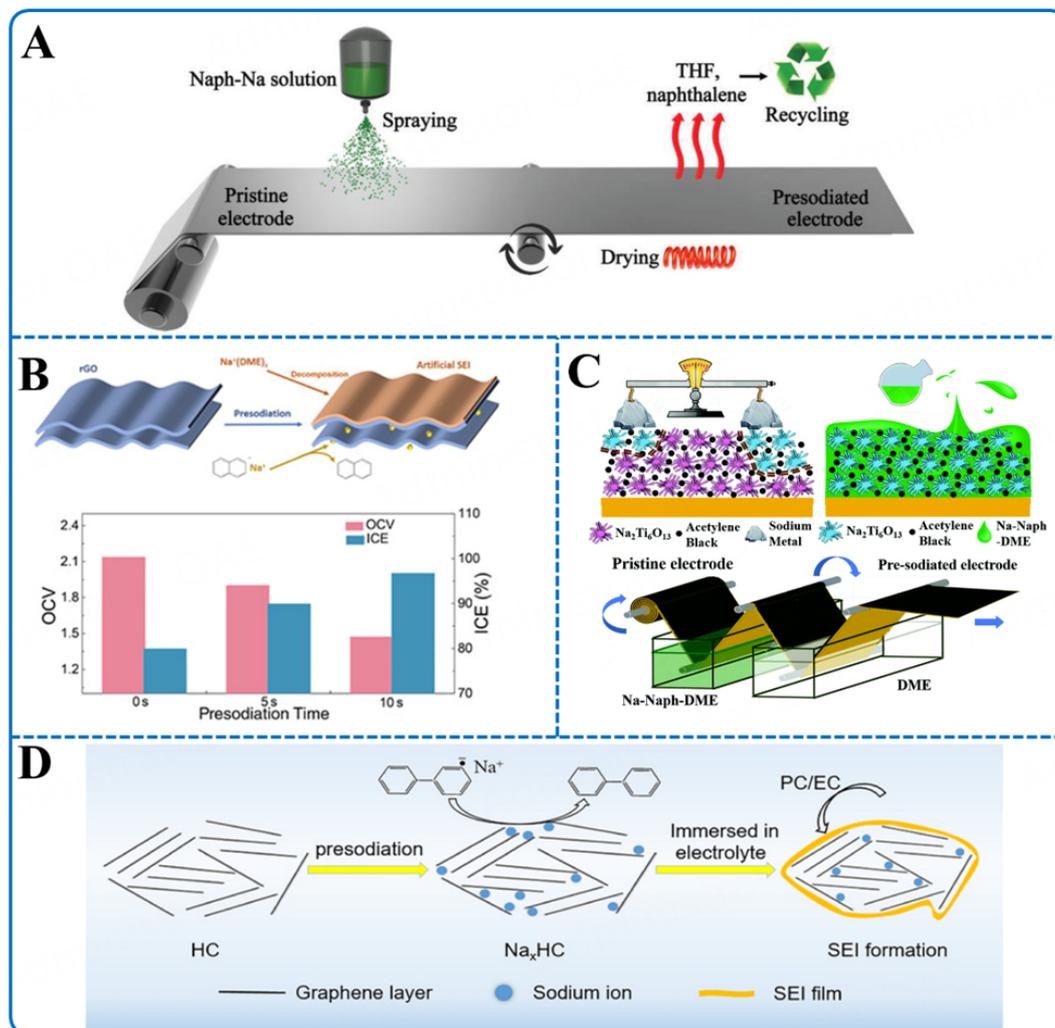
In contrast to conventional wet chemical presodiation, Liu *et al.* proposed a continuous presodiation process by solution spraying, where 0.1 M Na-Naph in tetrahydrofuran (THF) solvent was sprayed with a precise dosage of Na-Naph ( $38 \mu\text{L cm}^{-2}$ ) onto commercially available HC anodes, followed by drying to eliminate any remaining Naph and THF [Figure 5A]<sup>[32]</sup>. The results indicate that the presodiation treatment boosts the reversible capacity by  $60 \text{ mAh g}^{-1}$ , the initial Coulombic efficiency by 20.0% and the energy density from 141 to  $240 \text{ Wh kg}^{-1}$  for the  $\text{Na}_{0.9}[\text{Cu}_{0.22}\text{Fe}_{0.30}\text{Mn}_{0.48}]\text{O}_2//\text{HC}$  full cell. Interestingly, after chemical presodiation, a stable SEI film is generated on the surface of the HC anodes, which effectively reduces the irreversible loss of Na during the initial stage. To suppress the decomposition of electrolytes during battery assembly, Zheng *et al.* used Na-Naph in a DME solvent as the presodiation reagent to perform an ultrafast chemical pretreatment, as shown in Figure 5B<sup>[30]</sup>. Presodiation treatment successfully raises the initial Coulombic efficiency of rGO to 96.8% and results in the decomposition of the Na-containing complex to generate an artificial SEI layer on the anode surface. As a result of the suppressed decomposition of the excessive electrolyte by the artificial SEI, a homogenous and inorganic-rich SEI film generated on the surface of rGO, facilitated rapid interfacial ion transfer. Therefore, an outstanding capacity of  $198.5 \text{ mAh g}^{-1}$  at  $5 \text{ A g}^{-1}$  is displayed by the presodiated rGO anode.

Referring to the traditional prelithiation process, Cao *et al.* reported a liquid-phase immersion presodiation method, as shown in Figure 5C<sup>[31]</sup>. To finish the presodiation process, a  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  cathode was submerged into the stable liquid Na-Naph-DME for 10 min, followed by rinsing with a DME solution. As a result, the initial Coulombic efficiency of  $\text{Na}_2\text{Ti}_6\text{O}_{13}$  in the half cell is significantly boosted to 100% from 65%. The presodiation treatment could raise the initial efficiency from 40% to 80% in a  $\text{Na}_3\text{V}_2(\text{PO}_4)_3//\text{Na}_2\text{Ti}_6\text{O}_{13}$  full cell and the electrode after presodiation still exhibited high rate capability and cycle performance. To raise the initial Coulombic efficiency of commercial HC, Liu *et al.* developed a feasible and efficient chemical presodiation method, in which the HC anode was submerged into a DME solution containing Na-Bp and the presodiation level could be carefully regulated by varying the immersion time [Figure 5D]<sup>[30]</sup>. The presodiated HC anode shows a dramatically increased initial Coulombic efficiency by 30%, originating from the provided extra Na sources by presodiation treatment. The  $\text{Na}_3\text{V}_2(\text{PO}_4)_3//\text{Na}_x\text{HC}$  full cell demonstrates a significantly improved energy density and capacity retention using this presodiated HC anode.

The chemical presodiation strategy can easily regulate the presodiation degree by changing the soaking time and  $\text{Na}^+$  concentration in the solution. Compared with Na metal, the safety of liquid sodium sources is significantly improved, which can remain safe even in harsh conditions with water.

### Electrochemical presodiation

The electrochemical presodiation involves two steps of assembling and disassembling the half cell<sup>[43]</sup>. Firstly, the anode is assembled with Na metal in a half cell and then pre-cycled to generate the stable SEI film on the anode surface before disassembling. During electrochemical presodiation, the current density should be sufficiently low to ensure the integrity and uniformity of the SEI film. The detailed electrochemical presodiation process is given in Figure 6A<sup>[82]</sup>. By assembling a Na//PH5 (or Na//HC) half cell, the PH5 and HC are both successfully presodiated during the first discharge process. Consequently, the full cell (Na-PH5//NVP) assembled with presodiated anode exhibits an excellent reversible capacity of nearly  $107 \text{ mAh g}^{-1}$  and an energy density of  $150 \text{ Wh kg}^{-1}$ . In addition to HC anodes, other anode materials can also be presodiated by the electrochemical procedure. Recently, Liu *et al.* proposed a novel Na-Sb@ZMF/C anode with excellent cycle stability and attractive Coulombic efficiency<sup>[83]</sup>. In the course of *in-situ* presodiation, Na-Sb and Na-Sn intermediates were introduced and dispersed in the  $\text{Na}_2\text{O}$  matrix, which not only induced directed  $\text{Na}^+$  flux and electron transfer but also facilitated  $\text{Na}^+$  absorption through the uniform alloying process, as shown in Figure 6B. When paired with a  $\text{NaVPO}_4\text{F}$  cathode, the Na-Sb@ZMF/C anode reduced the polarization voltage of the full cell to 31 mV and exhibited an outstanding rate performance

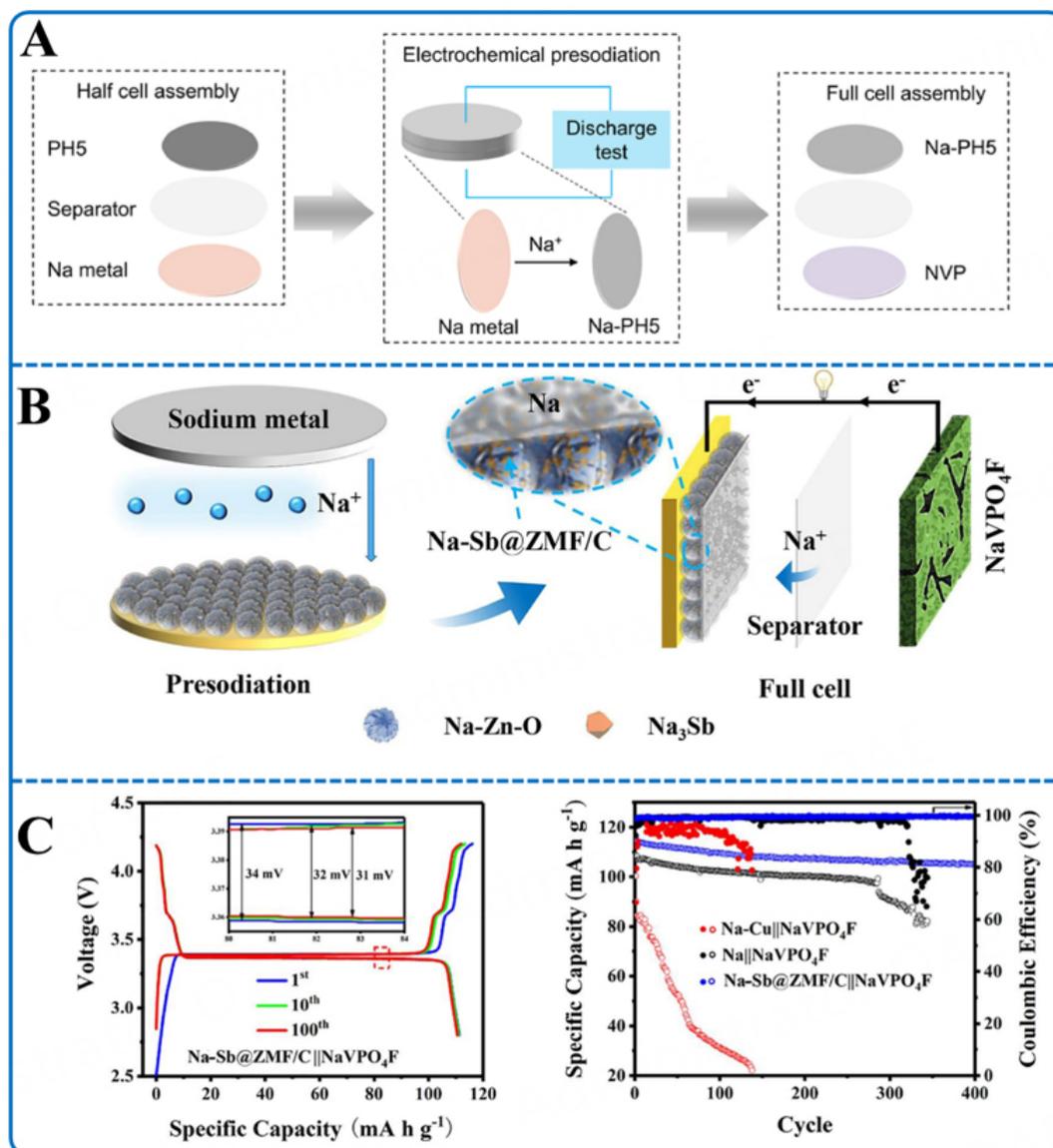


**Figure 5.** (A) Schematic illustration of chemical presodiation of commercial HC anode with a Naph-Na solution<sup>[32]</sup>. (B) Schematic diagram of ultrafast presodiation of reduced graphene oxide (rGO) anode in using Na-Naph dissolved in DME (top) and the open-circuit voltage and initial Coulombic efficiency of rGO anode with various presodiation times (bottom)<sup>[80]</sup>. (C) Scheme of presodiation process with different Na sources (left: Na metal, right: Na-Naph-DME) and a suggested scalable roll-to-roll technique for industrial manufacturing<sup>[81]</sup>. (D) Schematic illustration of chemical presodiation and the following SEI film generation process on available HC anodes<sup>[30]</sup>.

and Coulombic efficiency of 95.7% during the initial cycle [Figure 6C]. Generally, the electrochemical presodiation treatment can generate a homogenous and stable SEI film on the surface of the anode, which can effectively suppress electrolyte decomposition and active Na loss during the initial cycle, boosting the initial Coulombic efficiency. However, in contrast, the complex process of assembling and disassembling the half cell reduces the feasibility of scalable production. To address the above problems, an additional Na metal electrode was introduced between the electrolyte and anode of the full cell, which could accomplish the presodiation process by a specific charging step<sup>[35]</sup>.

## CONCLUSIONS AND OUTLOOK

Sodium-based energy storage devices provide a highly economic, efficient and sustainable alternative for large-scale electrochemical energy storage systems. However, many challenges are remaining towards further commercialization and industrialization, such as the low initial Coulombic efficiency and



**Figure 6.** (A) Schematic illustration of electrochemical presodiation of PH5<sup>[82]</sup>. (B) Scheme of voltage-driven presodiation process of Sb@ZMF/C anode and full cell configuration<sup>[83]</sup>. (C) Charge-discharge voltage profiles of Na-Sb@ZMF/C||NaVPO<sub>4</sub>F model after presodiation (left) and specific capacity and Coulombic efficiencies of Na-Sb@ZMF/C||NaVPO<sub>4</sub>F, Na-Cu||NaVPO<sub>4</sub>F and Na||NaVPO<sub>4</sub>F full cells at 0.5 C (right)<sup>[83]</sup>.

unsatisfactory energy density. The presodiation technique is considered as an effective method to alleviate the above issue, not only compensating for irreversible Na<sup>+</sup> depletion but also facilitating the energy density, rate performance and cycle lifespan. The presodiation by introducing self-sacrificing Na-containing additives for the cathode is seen to be a simple process without any complex operation. However, the introduction of Na-containing additives increases the weight of SIBs, causing the reduction of energy density and additional reactions. Unavoidably, the electrochemical oxidation of sacrificial reagents will generate gases or solid byproducts, which will reduce the battery system security or affect the electrochemical performance. How to alleviate the adverse consequences induced by the above issues will be the focus of future research.

**Table 1. Comparison of different presodiation strategies and possible research directions**

Side	Method	Disadvantage	Research direction
Cathode	Self-sacrificed materials	Residual materials, gas release	Presodiation mechanism
	Self-presodiation	Limited materials	<i>In-situ</i> characterization Theoretical calculation
Anode	Direct contact	Dangerous	New self-presodiation cathode design
	Chemical presodiation	Air-sensitive, complex	
	Electrochemical presodiation	Dangerous, disassembly	

In comparison, self-presodiation cathode materials are regarded as superior materials due to their “zero dead mass” and lack of gas release during the electrochemical process. Notably, the self-presodiation method is strongly associated with the development of high-performance Na-rich cathodes. In addition to presodiation for cathodes, presodiation for anodes has also attracted significant attention. Physical presodiation based on direct contact with Na foil/powder is the most direct method but the handling of high-risk Na foil/powder limits the industrialization of this method. In contrast, chemical presodiation technique offers greater potential for application in the manufacture of commercial electrodes because of the high feasibility. The presodiation reagent involves a THF or DME solution containing Na-Naph/Na-Bp, which can maintain its stability in dry air. The Na storage mechanism during the chemical presodiation is different from that during the electrochemical cycle, which may result in an additional side reaction during the following electrochemical cycles in the full cell. Furthermore, the anion type in the presodiation solution may also influence the formation of SEI film, which is necessary for further study. Different from chemical presodiation, electrochemical presodiation by precycling in a half cell can make the anode presodiated in real cell conditions. The Na storage mechanism and SEI film are in accordance with those in the normal electrochemical process. It is easy to regulate the presodiation degree by controlling the cut-off voltage during discharge. The greatest challenge is the complex procedure, including assembling the half cells, disassembling the half cells and reconstructing the full cells, which is unfeasible for industrialization.

Although presodiation technology has been extensively investigated, there remain significant issues that need to be resolved urgently, as shown in Table 1. In particular, the underlying mechanics of various presodiation methods are still mysterious and need further investigation. *In-situ* characterization methods, including *in-situ* XRD, spectroscopy, and TEM, need to be applied during the first charge and discharge to understand the aforementioned mechanism. In addition, whether there is a difference between the conventional SEI film and the SEI film formed after presodiation needs to be systematically evaluated, especially considering the morphology and composition of the SEI film. As powerful tools, theoretical calculations should be used to analyze the presodiation process, which can reveal the presodiation mechanism from the electronic and atomic scales. To comprehend and grasp such crucial factors, in-depth research should be conducted to promote the further development of Na-based energy storage devices.

Overall, the current presodiation technique for SIBs is still in its infancy due to it being quite different from that of LIBs and therefore requires further exploration to pave the route from basic scientific research to industrialization. The fundamental issues, such as the Na storage mechanism and SEI formation process during chemical presodiation, should be intrinsically addressed, which benefits the development of presodiation technique. This review provides feasible principles and strategies of presodiation to help researchers to gain a comprehensive understanding of the presodiation process.

## DECLARATIONS

### Authors' contributions

Conceived the idea, designed the manuscript: Gao XW

Prepared most figures: Liu ZM, Lai QS, Chen H

Wrote the paper: Mu JJ, Gao XW, Wang D, Yang DR

All authors participated in the writing and revision and commented on the manuscript.

### Availability of data and materials

Not applicable.

### Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China (Grant No.52272194 and 52204308), Liaoning Revitalization Talents Program (No. XLYC2007155), the Fundamental Research Funds for the Central Universities (N2025018, N2025009), China Postdoctoral Science Foundation (2022M710639).

### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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