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Recent Progress in Presodiation Technique for High-Performance Na-Ion Batteries

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Na-ion batteries (NIBs) have been attracting growing interests in recent years with the increasing demand of energy storage owing to their dependence on more abundant Na than Li. The exploration of the industrialization of NIBs is also on the march, where some challenges are still limiting its step. For instance, the relatively low initial Coulombic efficiency (ICE) of anode can cause undesired energy density loss in the full cell. In addition to the strategies from the sight of materials design that to improve the capacity and ICE of electrodes, presodiation technique is another important method to efficiently offset the irreversible capacity and enhance the energy density. Meanwhile, the slow release of the extra Na during the cycling is able to improve the cycling stability. In this review, we would like to provide a general insight of presodiation technique for high-performance NIBs. The recent research progress including the principles and strategies of presodiation will be introduced, and some remaining challenges as well as our perspectives will be discussed. This review aims to exhibit the basic knowledge of presodiation to inspire the researchers for future studies.

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1. Introduction. With the rapid development of our society, the demand of energy has been significantly growing. Since China is rich in coal but lack of oil and gas, the current fossil-based energy system makes our energy highly dependent on import. Although the new energy technologies represented by Li-ion batteries (LIBs) have been well improving, the limited and non-uniformly distributed Li resources also bring the problems of high-ratio import as well as the increasing cost in the future, which is of disadvantage to our energy strategy security. As a result, developing other energy storage technology is emergent to supplement LIBs.

Na-ion batteries (NIBs) as one of the most promising alternatives to LIBs have been earning more and more attention in the past decades owing to the abundant and uniformly distributed Na resources over the world.[1] The replacement of some expensive elements (i.e., Co, Ni) by Cu in the cathode[2] as well as the Al current collector applied at anode can further decrease the cost of NIBs, which brings them great potential to share the market with LIBs, especially in large-grid energy storage.[3] Actually, NIBs were studied at almost the same period with LIBs in 1980s,[1,4,5] while the relatively poor electrochemical performance still requires more efforts. Except for the intrinsic limitation of the energy density due to the physical and chemical properties of Na compared to Li, the undesired capacity loss contributed from the irreversible decomposition of electrolytes to form solid electrolyte interphase (SEI) as well as some side reactions on the anode side is also a non-negligible part.[6] As cathode is the only Na source in the practical cells to provide not only the reversible Na^+ ions sodiated/desodiated into/from the anode, but also such irreversibility, the cells would suffer from the capacity decay and decrease of energy density in particular due to the anode side with lower initial Coulombic efficiency (ICE).

Similar to prelithiation in LIBs,[7,8] one efficient strategy to offset this energy density loss due to the limited Na source in cathode is presodiation. As shown in Fig. 1, without presodiation process, the Na loss is all from the active Na in cathode, while the presodiation is able to "dope" extra Na to cover this irreversibility so as to avoid the waste of active Na from cathode and the capacity decay. Presodiation technique is getting more and more attention in recent years and is regarded as an important research direction for both fundamental science and practical industrialization of NIB cells. There have been several presodiation strategies reported so far learned from prelithiation in LIBs by electrochemical or chemical

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ways. From the anode side, the anodes can be electrochemically pre-cycled in half cells[9,10] with Na metal as counter electrodes or direct contacted by the Na metal for activation.[11] Alternatively, chemical presodiation is also useful via the chemical presodiation agent.[12,13] Regarding the cathodes, mixing sacrificial additives[14–16] and using self-presodiation cathode materials are the most acceptable strategies.[17] Understanding the distinct properties and remaining challenges of each method is important to better design the presodiation process and applicable to future industrialization towards high-performance NIBs.

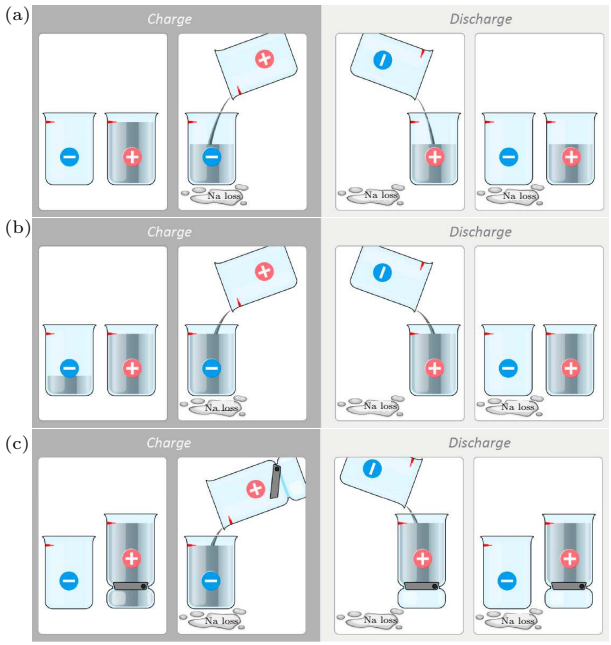

Fig. 1. Schematic illustration of (a) Na loss in the 1st cycle without any presodiation delivering unsatisfied capacity during discharge; (b) compensating the Na loss by the presodiation to the anode side so as to achieve more reversible capacity during discharge; (c) presodiation from the cathode side to compensate the Na loss and achieve more capacity during discharge.[18]

In this review, we would like to summarize the current state-of-the-art presodiation strategies and discuss the differences and challenges from our own perspectives. We hope that this article could provide a general insight for researchers to understand basically the presodiation technique and to facilitate the future study.

2. The Significance of Presodiation. As mentioned above, there would be unavoidable capacity loss during the first cycle especially at the anode side, leading to a low ICE. This is generally derived from the electrolyte decomposition, SEI formation, irreversible Na^+ ions trap (at defects, functional groups or between the graphene planes for carbon anodes), irreversible conversion reactions for the conversion-type anodes and some unexpected side reactions.[19–24] This situation is much less serious for cathode so that the ICE of anode is usually much smaller than cathode, making anode the major limitation of the improvement of energy density.

It is known that for the "rocking-chair" secondary batteries including NIBs, the cathode is the only Na source to provide the active Na^+ ions to transport between cathode and anode. Herein, in an NIB full cell, the anode with much smaller ICE requires heavier cathode to provide more active Na^+ ions to cover this unavoidable irreversibility at anode, which causes the waste of the active Na^+ ions and energy density decay. Improving the ICE of anode materials is also one of the biggest challenges and one of the most important research directions in the future.[25]

Taking the most promising anode candidate, disordered carbons, as an example, strategies such as the surface engineering[26–29] and structures modification (defects, heteroatoms and functional groups, etc.)[22,23,30–32] have been widely investigated to effectively enhance the ICE. These methods from the view of materials design usually depend on more complicated synthesis, and some strategies may only suitable for specific anode materials. On the other hand, the improvement of ICE is usually up to slightly above 90%,[23,33,34] implying that the effects of materials optimization is relatively limited and difficult.

Comparatively, the presodiation technique seems more effectively, and the irreversible capacity is able to be fully implemented by controlling the presodiation degree, which enables the energy density to be maximum released in practical NIBs. The presodiation process could be performed at either the anode or cathode side, and different strategies have their own advantages and challenges. The recent progress in presodiation techniques and the specific strategies will be discussed in the following sections.

3. Presodiation from the Anode Side.—3.1 Electrochemical Pre-cycling in Half Cell Towards Na Metal. The easiest method for presodiation is to pre-cycle the anode in a half cell against the Na metal counter electrode to form the SEI and release the irreversible capacity in advance the "formal" full cell assembly. In the work of Zhang *et al.*,[9] a 30-min presodiation of the hard carbon anode in half cell could reduce the open circuit voltage (OCV) to 0.6 V (vs Na^+/Na) and increase the ICE from 61.4% for the untreated pristine sample to 99.1% for the presodiated sample, while the reversible capacity, rate capability and cycling stability were not influenced. De Llave *et al.*[35] also reported that the use of pre-cycled hard carbon anode can deliver a high discharge capacity of 115 mAh/g in full cell when paired with $NaNi_{0.5}Mn_{0.5}O_2$ cathode, which is much higher than 65 mAh/g for the untreated anode.

The electrochemical presodiation process by pre-cycling the anode in a half cell is simple and direct

to improve the ICE of anode, and therefore enhancing the performance in the subsequent full cell. In addition, this pre-cycling strategy can maximum maintain the real situation of sodiation in the first cycle without introducing other undesired reactions compared to other presodiation methods, which has the least negative effects of the general electrochemical performance. Nevertheless, this is only suitable at the academic level in the lab because the disassembly of the half cell, reconstruction of the subsequent "formal" full cell as well as the handling of metallic Na strongly limit the application in the practical industrialization.[36]

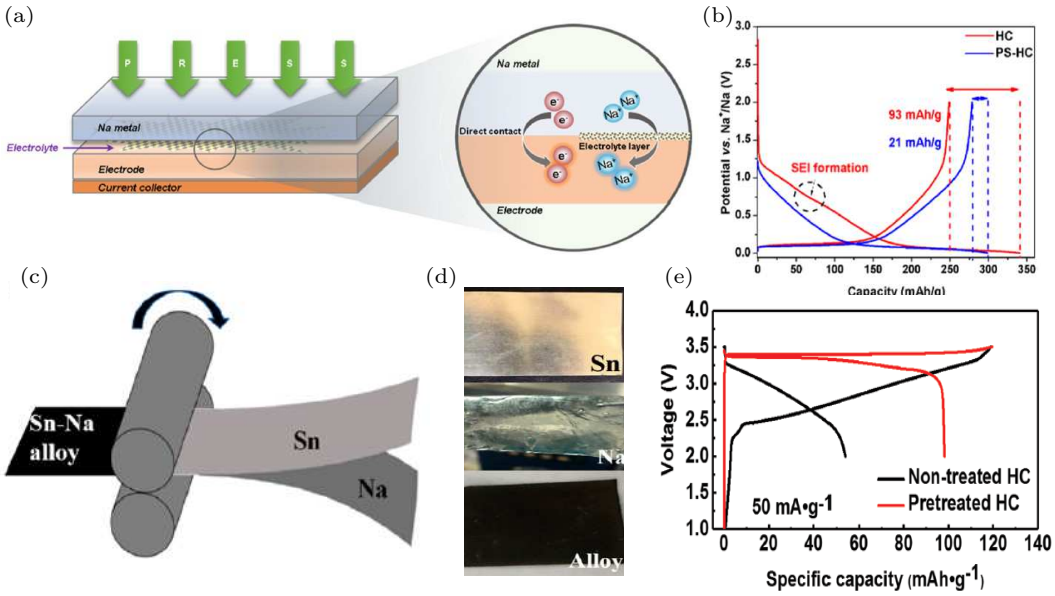

Fig. 2. (a) Scheme of Na metal contact method for presodiation; (b) initial discharge/charge curves of the hard carbon and presodiated hard carbon anodes.[11] (c) Scheme of the Sn–Na alloy presodiation process; (d) photographs of pure Sn, Na anode and the alloy.[37] (e) Charge/discharge curves of the full cells with NVP cathode and non-treated/pretreated HC anodes.[38]

3.2 Direct Activation by Na Metal. Similar to the prelithiation technique for LIBs that use Li metal to direct contact with the anode,[39,40] Na metal is also widely reported to direct contact or short circuit with anode for presodiation, which has shown exhausted effects. Compared to the pre-cycling method, the activation of anode by direct Na contact avoids the disassembly process, simplifying the fabrication. For example, the Na metal was reported to be placed on the hard carbon anode with direct contact and active in the anode under pressure. Due to the potential difference between the Na metal and the anode material, the activation occurs immediately after the pressing from the inserted Na^+ ions, which increased the reversible capacity and ICE of the presodiated hard carbon (PS-HC) compared to the pristine hard carbon (HC) [Figs. 2(a) and 2(b)].[11] Different from the pre-insertion of Na^+ ions from the Na metal into the hard carbon anode, Liu *et al.*[37] reported the presodiation of Sn anode by the metallic Na foil. As shown in Fig. 2(c), the Sn can form an Sn–Na alloy when direct contact with the Na foil under pressure using a roller, where the bright Sn and Na metal foils became dark gray which confirmed the successful pre-alloying [Fig. 2(d)]. The potential of pre-alloyed anode is below the SEI formation voltage so that the gas formation could be depressed, and the ICE of the Sn–Na anode increased to 75% compared to the pristine Sn anode (25%) in full cell with $Na_3V_2PO_4F_3$ (NVPF) cathode. The Na metal was also reported to be dispersed into organic solvent to make Na powder additive assisted by ultrasonic process, and the solved Na particles enable more homogeneous distribution on the anode.[41]

Interestingly, other than Na metal, Xiao *et al.*[38] found that the Li metal is able to bring similar effect to active the anode by using solved stabilized Li metal powder (SLMP) that is widely used for prelithiation to pretreat the HC anode with homogeneous reaction. The pretreated (prelithiated) HC anodes are also able to deliver increased performance. As shown in Fig. 2(e), the $Na_3V_2(PO_4)_3$ (NVP)//HC full cells can present almost twice of the reversible capacity using the pretreated HC anode compared to the untreated one.

3.3 Chemical Presodiation by Na Complex. To avoid the intensive activity and dangerous handling of Na metal, developing safer and more practical presodiation techniques that can be more easily applied to industrialization, chemical presodiation strategies are regarded as one of the most feasible and promising way towards practical presodiation, which have been earning more and more attention recently.

The chemical presodiation strategies are also learned from the chemical prelithiation.[42–45] Anal-

ogously, chemical presodiation is using the presodiation agents which usually made from Na metal and organics (i.e. naphthalene biphenyl) to form coordination complex in ethers. It is noting that this is different with the physical dispersion of Na metal into organic solvent to make homogeneous solution as previously stated.[41] The Na-naphthalene (Na-Naph) or Na-biphenyl (Na-Bp) compounds with abundant Na free radicals can react with the anodes immediately upon contact due to the potential difference, so that the anode material could be sodiated.

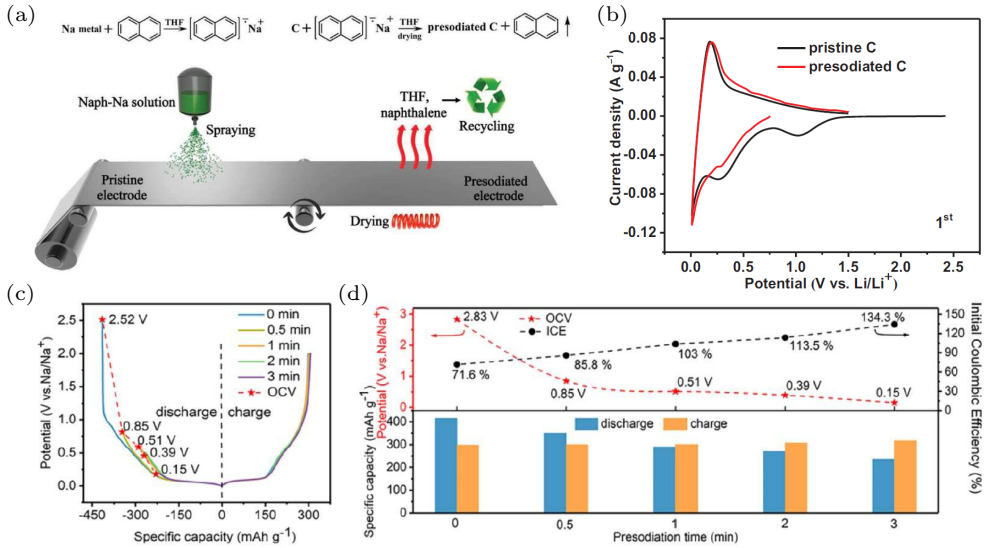

Fig. 3. (a) Schematic illustration of the presodiation process by spraying the Naph-Na solution; (b) 1st cycle CV curves of the pristine and presodiated carbons.[12] (c) Initial discharge/charge curves of the hard carbon anodes with various presodiation durations; (d) initial capacities, OCV and ICE comparisons among the presodiated electrodes.[13]

Liu *et al.*[12] proposed an electrode-level chemical presodiation route using 0.1 M Na-Naph in tetrahydrofuran (THF). As presented in Fig. 3(a), the Na-Naph solution was sprayed at specific dosage (38 μL/cm^2) onto the anode with subsequent drying to evaporate the residual Naph and THF. The ICE of the presodiated electrodes increased to 87% from 67%, and the cyclic voltammetry (CV) curves at the 1st cycles of the pristine and presodiated electrodes in Fig. 3(b) exhibits that the irreversible redox peak at 0.75–1.3 V (vs Na^+/Na) attributed to the irreversible electrode/electrolyte reactions and the SEI formation disappeared. Liu and co-workers[13] used Na-Bp solved in dimethoxyethane (DME) for the chemical presodiation process and claimed that the reduction potential of 0.12 V (vs Na^+/Na), which is the lowest value among all the known polycyclic aromatic hydrocarbon radials, suggesting a strong reduction ability for better presodiation. The presodiation degree could be tuned by controlling the immersing duration of the electrode in the Na-Bp solution. The OCV, ICE and initial capacities were optimized by different presodiation degrees, and 1 min is the best choice [Figs. 3(c) and 3(d)]. The optimized presodiated anode could show ∼100% ICE. When paired with NVP cathodes, the full cell with presodiated anode can deliver a high energy density of 218 Wh/kg compared to the untreated anode with only 120 Wh/kg.

4. Presodiation from the Cathode Side.—4.1 Sacrificial Additives. Apart from the above reviewed presodiation strategies toward anode side, the presodiation could also be applied at cathode side. One of the common used methods is adding sacrificial additives into the cathode. The additives are usually Na-containing salts that can irreversible provide extra Na to offset the initial capacity loss of anode but do not affect the subsequent cycles. This requires the additives proper decomposition potential during charging and enough capacity.

There are also many other sacrificial salts that have been observed for presodiation and for increasing the performance of the NIB full cells such as NaN_3, Na_3P, Na_2NiO_2, and $NaCrO_2$,[36] among which a widely investigated salt for presodiation is $Na_2C_4O_4$ (sodium oxalate), which can be mixed with the active cathode material (together with binder and carbon black, etc.) and can supply extra Na^+ ions upon charging as well as oxidizing the corresponding anions and emitting gases [Fig. 4(a)]. It could be oxidized at around 3.6–4.1 V (vs Na^+/Na) to provide a theoretical capacity of 339 mAh/g.[46] It is reported that 30 wt% $Na_2C_4O_4$ sacrificial salt mixed with $Na_3(VO)_2(PO_4)_2F$ (NVOPF) cathode can lead to an increase of charge capacity around 150 mAh/g in half cell. Paired with HC anode with an initial discharge capacity of 537 mAh/g and a charge capac-

ity of 275 mAh/g (ICE = 51.2%), the use of 30 wt% $Na_2C_4O_4$ can increase the total discharge capacity to 120 mAh/g, which is around 1.5 times the value of 80 mAh/g with the pristine cathode [Fig. 4(b)].[47]

Recently, Niu *et al.*[16] optimized the use of $Na_2C_2O_4$ as sacrificial salt, which is successfully achieved by tuning the conductive additives, and found that when Ketjenblack (KB) and mesoporous carbon (CMK-3) are used as conductive additives, the oxidation potential of $Na_2C_2O_4$ could reduce to 3.97 V (vs Na^+/Na), which is within the voltage window of common cathode materials to ensure enough capacity released during charge/discharge. It is known that 20 wt% $Na_2C_2O_4$ added in P2-$Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$ cathode can enhance the initial charge capacity to 239 mAh/g, which is mainly contributed from the oxidation of $Na_2C_2O_4$ at 4.25 V (vs Na^+/Na) [Fig. 4(c)]. The extra Na^+ ions can compensate the irreversibility of HC anode and enhance the energy density from 161.5 to 215.9 Wh/kg based on the total mass of cathode and anode active materials. The energy density of the full cell increased from 129.2 to 172.6 Wh/kg based on the mass of the cells [Fig. 4(d)].

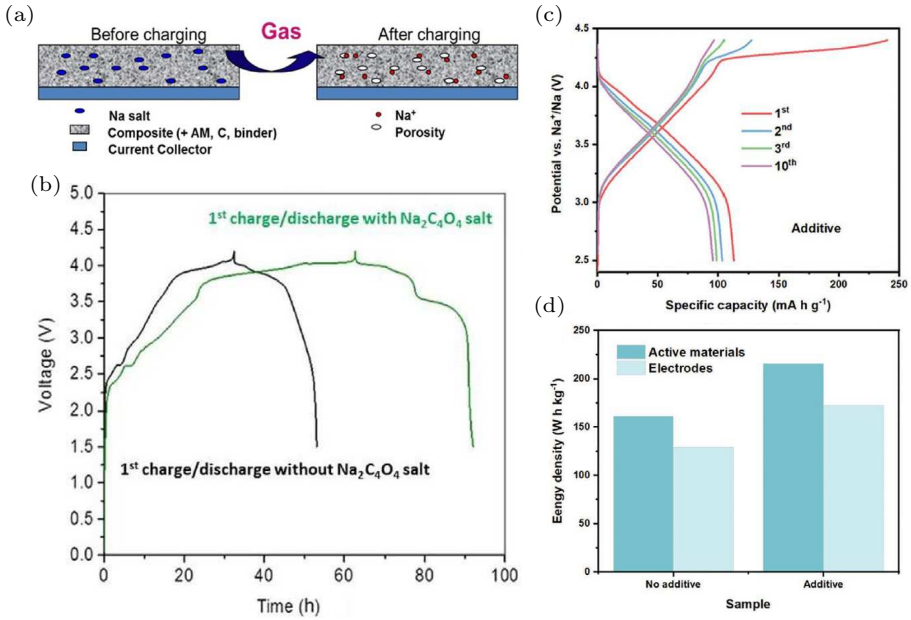

Fig. 4. (a) Scheme of the presodiation concepts as additives in cathode; (b) initial charge/discharge curves of the $Na_3(VO)_2(PO_4)_2F$//HC full cells with and without $Na_2C_4O_4$ additive.[47] (c) Charge/discharge curves of the $Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$ cathode with $Na_2C_2O_4$ additive; (d) comparison of the energy density with and without additive.[16]

4.2 Self-Presodiation Cathode Materials. The addition of sacrificial additives leads to increasing the mass of the cathode, and is unavoidably generate some byproducts and gases, which limits its practical application. Therefore, using some self-presodiation or over-sodiated cathode materials can better achieve the presodiation and diminish the negative effects from adding extra components into the slurry and from the byproducts. For example, our group recently reported a self-presodiation cathode material $Na_{0.89}Cu^{2+}_{0.11}Ni^{2+}_{0.11}Fe^{3+}_{0.3}Mn^{3+}_{0.15}Mn^{4+}_{0.23}Ti^{4+}_{0.10}O_2$ (Ti1-QC) via a quenching process.[17] Compared to the natural cooled material $Na_{0.84}Cu^{2+}_{0.11}Ni^{2+}_{0.11}Fe^{3+}_{0.30}Mn^{3+}_{0.10}Mn^{4+}_{0.28}Ti^{4+}_{0.10}O_2$ (Ti1-NC), the quenched sample preserves more Mn^{3+} and Na^+ contents, which can provide extra Na^+ ions by Mn^{3+} oxidation during the initial charging to compensate the Na loss. As shown in Fig. 5(a), there is voltage plateau at around 3 V (vs Na^+/Na) at both the 1st and 2nd cycles, while an extra plateau at 2.4 V (vs Na^+/Na) for around 17 mAh/g at only the 1st cycle which corresponds to the Mn^{3+}/Mn^{4+} oxidation for Ti1-QC, leading to an enhanced charge capacity to 132.8 mAh/g compared to 122.5 mAh/g for Ti1-NC. When paired with HC anode in full cell, the Ti1-QC cathode delivers higher reversible capacity of 104.3 mAh/g than Ti1-NC of only 94 mAh/g [Fig. 5(b)], corresponding to an increased energy density from 233 to 256 Wh/kg. In addition, the cycling performance is also improved for the full cell using Ti1-QC which retained 84% of the capacity after 300 cycles at 0.3 C [Fig. 5(c)].

4.3 Other Presodiation Strategies for Cathode Materials. Another presodiation strategy is to insert extra Na into the Na-poor cathode materials to enhance the capacity rather than to compensate the irreversible capacity lose in anode. As introduced in section 3.2, in the work of Moeez *et al.*,[11] the Na metal was not only used to sodiate the anode but also directly pressed onto the P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ cathode (NFMO). As presented in Figs. 5(d) and 5(e),

when charged/discharged in half cells between 1.5 V and 4.3 V (vs Na^+/Na), the pristine NFMO delivers an initial charge capacity of 109 mAh/g, corresponding to ~0.42 Na^+ extraction. Upon the presodiation process via the Na metal press, the presodiated NFMO (PS-NFMO) can deliver a higher initial charge capacity of 200 mAh/g, which corresponds to the extraction of ~0.77 Na^+. Herein, in a full cell paired with HC anode, the PS-NFMO could provide a reversible discharge capacity of 102 mAh/g, which is much higher than 64 mAh/g for the pristine NFMO cathode. Zhou *et al.*[48] also reported the chemical method using the Na-Bp/DME solution to treat $Na_{0.44}MnO_2$ and to transform it to a Na-rich cathode $Na_{0.66}MnO_2$. The presodiated cathode material can have improved initial charge capacity from 56.5 to 115.7 mAh/g.

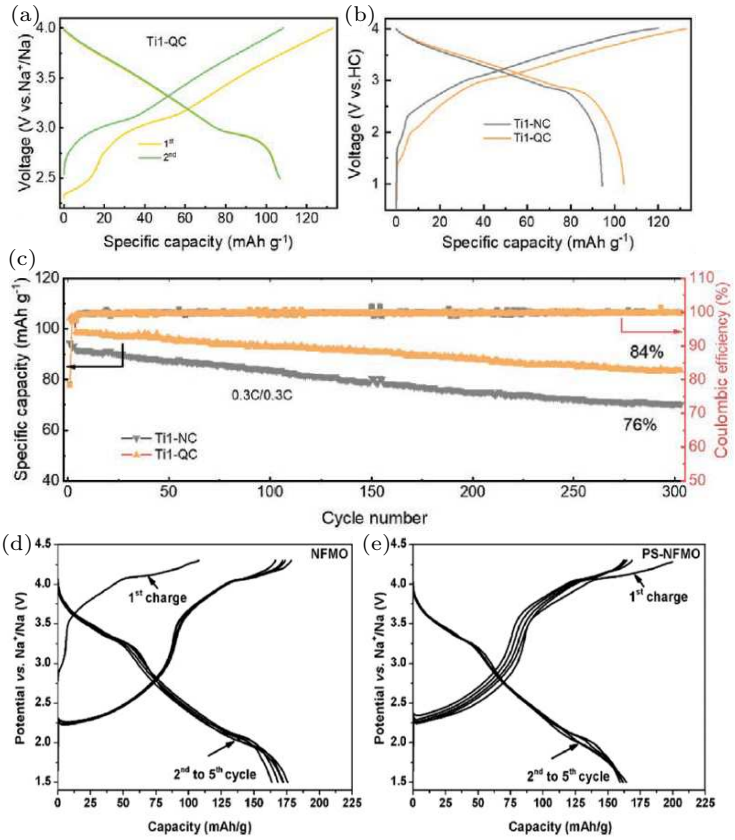

Fig. 5. (a) Charge/discharge curves of the Ti1-QC electrode. [(b), (c)] Initial charge/discharge curves and cycling performance of the full cells with HC as anode and Ti1-NC or Ti1-QC as cathode.[17] [(d), (e)] Charge/discharge profiles of the pristine and presodiated NFMO cathode in half cells.[11]

5. Perspectives and Discussion. The recent progress in presodiation strategies towards both cathode and anode sides has been introduced in the previous text. As summarized in Table 1 and Fig. 6, different strategies have different pros and cons, which need to be well chosen for different situations, and some challenges still require further study and optimization so as to be finally utilized in practical industrialization.

In terms of the electrochemical presodiation to precycle in half cell, this is the easiest way to get the anode presodiated in a real cell circumstance. The sodiation process is involved in the normal electrochemical cycling so that the Na storage behavior and the SEI formation are exactly the same as the pristine process, which does not involve any extra effect. The presodiation is also easy to be tuned by simply setting the cut-off voltage during discharging. However, the pre-cycling strategy undergoes cell disassembly before constructing full cells, complexing the total procedure of battery fabrication, which is impractical for industrialization. Meanwhile, both the pre-cycling at half cells and the direct Na metal contact require the handling of Na metal, which is dangerous under ambient condition or even in the dry room, further limiting the application. Although the passivated Li metal (i.e. SLMP) has been used for prelithiation, the passivation for Na metal is difficult and is in lack of study, making this strategy regarded as only a lab-level strategy for the presodiation study but hard to be applied to real situation.[49]

In contrast, chemical presodiation strategy has much greater potential to be used in commercial electrode fabrication due to its simple presodiation procedure via immersing the electrodes into the presodiation agents or spraying without cell disassembly.

The presodiation degree is also controllable by tuning the immersing duration. The chemical presodiation agents such as Na-Naph/Na-Bp in THF or DME solutions are also reported to be stable in dry air and safe when adding water.[13,42] The biggest challenge of this strategy is that the presodiated electrodes with active Na are sensitive in air and will cause serious capacity decay during cycling, which requires further exploration of the passivation of the presodiated electrodes or active materials. Furthermore, the chemical presodiaiton will also lead to different Na storage behaviors, and the irreversible side reactions with the chemical sodiated Na are also different from the normal electrochemical cycling. Meanwhile, without the participation of electrolyte during the sodiation process, the SEI formation of the presodiated electrode after contacting electrolyte in cells will also be different from the normal case, which is lack of systematically study.[36] The investigations of the unexplored fundamental mechanisms of the chemical presodiation of the anode materials are urgent and significant to better guide the presodiation strategy design as well as deep understanding of the Na storage mechanisms of anode materials such as hard carbons.

Table 1. Comparison of the advantages and disadvantages of different presodiation strategies.

Side	Strategy	Category	Agent	Advantage	Disadvantage
Anode	Pre-cycling in half cell	Electrochemical	Na metal	Similar to the real cycling	Dangerous Na handling; complex cell disassembly
	Direct contact with Na metal	Chemical	Na metal	Simply control the presodiation degree	Dangerous Na handling
	Chemical presodiation by Na complex	Chemical	Na complex (i.e. Na-Naph/Na-Bp) in ethers (i.e. THF, DME)	Relatively safe; controllable presodiation degree;	Air-sensitive upon presodiation
Cathode	Adding sacrificial additives	Electrochemical	Na salts (i.e. NaN_3, $Na_2C_2O_4$, $Na_2C_4O_4$)	Safe; air-stable; simple fabrication	Extra component to the electrode; unexpected gas formation
	Self-presodiation materials	Electrochemical	Cathode materials with self-presodiation properties	Safe; no extra component required	Confined by the limited materials selections

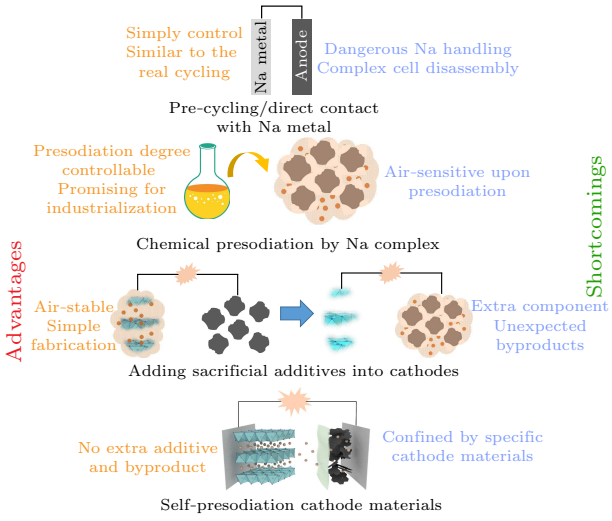

Fig. 6. Scheme of the presodiation strategies and their advantages/disadvantages.

Aside from the presodiation methods at anode side, the ones from the cathode sides have also been widely explored, where the most popular topic is the sacrificial additives to compensate the irreversible Na loss at anode. This is also a simple strategy without any complex procedures such as cell disassembly with only physically mixing the additives with the active cathode materials, binders and conductive additives. There is also no air-sensitive issue that needs to be considered. However, the oxidation of the sacrificial salts will unavoidably generate some byproducts and gases, which will influence the electrochemical performance or cause some safety issues. In addition, this strategy is principally to decrease the ICE of the cathode, and the addition of the extra component into the cathode will also lead to the increase of weight, which is not conductive to the improvement of energy density. Therefore, satisfied sacrificial additives are the key to seek to provide proper capacity to compensate the Na loss at anode with least byproducts.

The self-presodiation cathode materials are regarded as a superior method compared to sacrificial additives as no extra component is needed and the byproducts could be avoided as well. However, this is confined in many cases because it strongly depends on the cathode materials themselves, and proper high-performance cathode materials with the self-presodiation characteristic should be designed and synthesized.

6. Conclusions and Outlooks. This review systematically summarizes the recent progress in the presodiation technique for NIBs and provides a general insight of the state-of-the-art presodiation strate-

gies, aiming at making researchers preliminarily understand the significance and the methods of presodiation. The presodiation could be classified into several sections including the electrochemical presodiation (pre-cycling in half cells), direct contact with Na metal, chemical presodiation by spraying or immersing the anodes into chemical presodiation agents, sacrificial additives addition into cathodes and synthesizing specific cathode materials with self-presodiation characteristic. Different strategies have their own pros and cons, which are also discussed at the end of this review. Generally, the current presodiation strategies are still staying in the academic level and still need further exploration to pave the way from lab to industrialization. Furthermore, some fundamental studies such as the Na storage behaviors of the chemical sodiation and the different SEI formation are also importantly clarified to better guide the optimization of presodiation technique. We believe that the presodiation is a very important technique that should be combined with materials and electrolytes design, which must contribute to the improvement of NIBs in the future.

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