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Cobalt-Based Electrode Materials for Sodium-Ion Batteries

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Abstract

The demand for grid-scale energy storage systems has rapidly grown over recent years, to meet the requirements of structural innovation within the energy industry. Due to their inexpensive manufacturing and operating costs, and the similar electrochemical mechanism with the well-established lithium-ion batteries (LIBs), sodium ion batteries (SIBs) have been considered as an attractive candidate for grid-scale energy storage systems. A variety of cobalt-based cathode and anode materials, including cobalt oxides, cobalt chalcogenide and layered sodium cobaltate, have been synthesized and evaluated for sodium storage within the academic literature. In this article, we present a comprehensive review of the recent progress with cobalt-based electrodes (both as an anode and cathode material) used in SIBs. In detail, the electrochemical mechanisms, advantages and disadvantages, the relationship between crystalline structure and electrochemical performance and strategies to enhance the overall electrochemical performance of cobalt-based cathode and anode materials are discussed. Up to now, some cathode materials have already reached a high energy density, which is comparable to commercial LIBs. Furthermore, some cobalt-based materials can maintain a high Coulombic efficiency of over 99% with high reversible capacity during long cycling life. These encouraging results, allow such cobalt-based electrode materials to be a potential solution for grid-scale SIB systems.

Keywords: Sodium-ion batteries; Anode; Cathode; Cobalt oxides; Cobalt chalcogenides

1. Introduction

With the current alarming global pollution problem, the need to develop green renewable energies, and to reduce pollutant emission, is becoming more demanding and is one of the most pressing issues of this generation. As alternatives to traditional fossil energies, solar power, wind power, tidal power and other green energy technologies have rapidly developed over the last decade. As a result, this trend has led to a demand for new energy storage technologies, especially within stationary applications.[1, 2] Among the current energy storage technologies, the lithium-ion battery (LIB) has achieved great success, in particular within portable electronic equipment, and is predicted to dominate the electric vehicle market.[3-5] However, the limited reserves and ever-increasing cost of lithium and other critical raw materials casts doubt over whether this technology is also suitable for large-scale stationary applications. With abundant resource of sodium in both the earth's crust and oceans, the cost of sodium-containing materials is significantly lower than its lithium competitor.[6] For example, one of the most common sodium resource, Trona (Na_2CO_3), is ~ 20 -30 times cheaper than Li_2CO_3 . [7] However, it should be noted that the weight of Na is three times higher than Li. Besides, the standard electrochemical potential of Na is lower than Li (2.71 V for Na and 3.04 V for Li, vs. SHE).[8] These intrinsic properties result in a lower energy density for the sodium-ion battery (SIBs) over that of the LIB under similar conditions. Thus, SIBs have been regarded as a promising candidate for stationary energy storage devices, which is evident in the research of this technology over the last decade. [9, 10]

Unfortunately, however, the Na^+ ion does have a larger radius (1.06 Å) than that of the Li^+ ions (0.76 Å), which in general will cause some problems for SIB materials.[8] The larger radius creates unstable cathodes and anodes during charge/discharge process, leading to a hindered cycling performance.[9, 10] Additionally, the Na^+ ion possesses a larger energy barrier for insertion into many electrode materials, which could conceivably pose a problem of limited capacity and poor rate capability. For example, graphite with a layer spacing of 3.35 Å, only shows a low irreversible capacity for SIBs.[11, 12] Until now, these inferior cycling performances and rate capabilities still hinder the practical application of SIBs. To develop suitable electrode materials with an enhanced electrochemical performance is one of the key issues for the further advancement of SIBs.[13-15] An amount of materials have been studied as electrode materials for SIBs with a few offering acceptable electrochemical performance. For cathode materials, most

research focus upon layered metallic oxides (Na_xMO_2 , $\text{M}=\text{Mn}$, [7] Co , [16, 17] Ni , [18] Fe , [19] Cr , [20] etc), phosphates (NaFePO_4 , [21] $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, [22] NaVPO_4F , [23] $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, [24] $\text{Na}_{1.5}\text{VOPO}_4\text{F}_{0.5}$, [25] $\text{Na}_2\text{FePO}_4\text{F}$, [26] etc), transition metal fluorides (NaMF_3 , $\text{M} = \text{Fe}$, [27] Mn , V and Ni [28]), and organic cathodes [29]. For anode materials, hard carbon, [14] metal alloys, [30] metal oxides [31] and chalcogenides [32, 33] are promising candidates.

Cobalt, the 27th element assigned to group VIII B, is a popular metal within material science. Cobalt-based materials have attracted much attention within many fields, including catalysis, [34] thermopower, [35] ferromagnetic properties, [36] energy storage [37-41] to name a few. Especially, for LIBs, LiCoO_2 is one of the most successful commercialized cathode materials [42]. Similarly, cobalt-based materials can also play an important role in cathode and anode materials for SIBs. [43-48] The SIB cathode material, Na_xCoO_2 is being investigated primarily because of the commercial success of LiCoO_2 in the LIB. [49, 50] With respect to anode materials, cobalt oxides [51-53] and cobalt chalcogenides [54-57] demonstrate a high theoretical capacity for sodium storage. Full cell pairings of stable materials remain to be found and commercialized for SIBs.

We report a detailed review of the most recent advancements in cobalt-based materials for SIBs, with a focus on both cathode and anode electrode materials. This review covers the electrochemical mechanisms, a comparison of advantages and disadvantages, the relationship between crystalline structure and electrochemical performance, and strategies to enhance the overall electrochemical performance of cobalt-based cathode and anode materials. Finally, an overall outlook containing key challenges and perspectives on the future development of SIBs is provided.

2. Cobalt Oxide Anodes

2.1 Co_3O_4

Over the last decade, transition metal oxides (TMOs) have been core materials central to developments in semiconductor technologies, catalysis, sensing and energy storage to name a few. In particular, many TMOs, including Fe_2O_3 , [58] Co_3O_4 , [59] MoO_3 , [60] TiO_2 , [61] etc, are regarded as promising candidates for the replacement of graphite anodes in batteries, due to their high alkaline ion storage capacity, for example Co_3O_4 possesses a high theory capacity of 890 mAh g^{-1} . [62] However, Co_3O_4 does possess an array of limitations, which is currently hindering its

application as an anode material, such as limited electrical conductivity, poor ion diffusion kinetics, large volume expansion during Na^+ ion insertion and so on.[63, 64] Nanocrystallization and protective coating layer are generally considered as an effective methodology to enhance the electrochemical performance of Co_3O_4 . Based on such viewpoint, a large number of nano-sized Co_3O_4 and $\text{Co}_3\text{O}_4/\text{C}$ composites with various morphologies such as nanospheres,[65, 66] nanotubes,[67] hollow octahedra,[68] etc. have been reported within the literature.

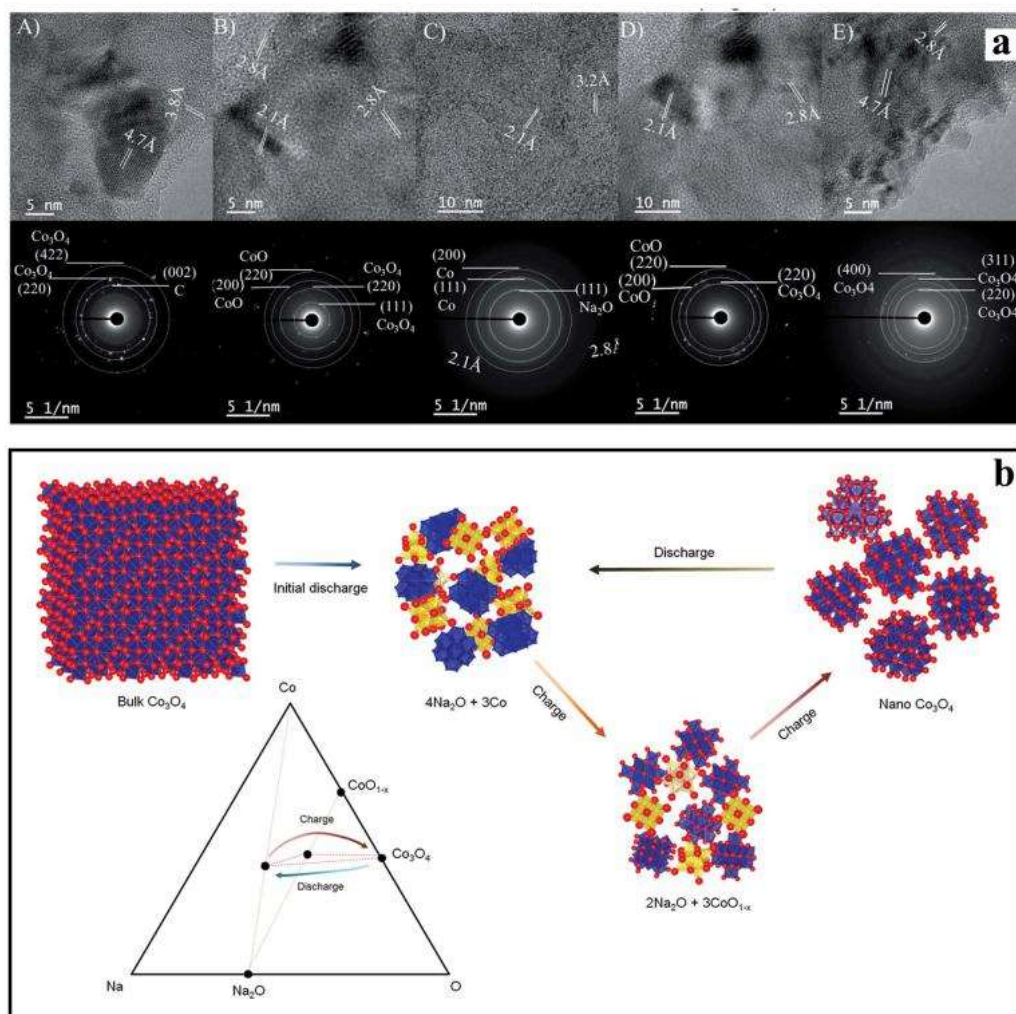
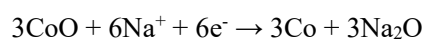
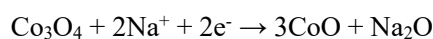


Fig. 1 Structural evolution of the $\text{Co}_3\text{O}_4@NC$ electrode during the electrochemical reaction. (a) TEM images (top) and selected area electron diffraction (SAED) patterns (bottom) at the corresponding points: A) pristine state, B) the discharged state at 0.6 V, C) fully discharged state at 0.01 V, D) the charged state at 1.4 V and E) the fully charged state at 3.0 V.[69] (b) Schematics of conversion and reconversion reaction mechanism for Co_3O_4 in Na rechargeable batteries.[70]

As an anode material for sodium ion battery, Co_3O_4 goes through a conversion reaction during charge/discharge process.[69, 70] As can be seen in Fig 1a, the structural evolution of this material has been investigated systematically by ex-situ TEM and selected area electron diffraction (SAED) at different charge/discharge states. In detail, upon the Na^+ ion insertion, the Co_3O_4 phase gradually turns into a new phase of CoO over the voltage range of 3.0-0.6 V. In the fully discharged state at 0.01 V, only Co and Na_2O can be detected. Upon the subsequent charge process, the phases of CoO and Co_3O_4 emerge at 1.4 V and only the Co_3O_4 phase exists after fully charging at 3.0 V. Based upon these results, the conversion reaction during discharge process of Co_3O_4 with Na^+ ion can be summarized as :



It is well reported that bulk Co_3O_4 material, upon the charge/discharge, undergoes a morphological deterioration as the particle size reduces on the conversion reaction, (as demonstrated in Fig 1b)[70]. This effect lowers the electronic conductivity of the electrode, and can even result in the loss of active material. Such increases in surface area (due to the decreasing particle size) prevent the formation of a stable SEI membrane, often requiring SEI reformation to some degree in every cycle. To understand the morphological-performances correlations of Co_3O_4 materials, micro-sized Co_3O_4 slabs, nano-sized Co_3O_4 needles and nano-sized Co_3O_4 flakes were synthesized by Ruffo's group.[71] It is obvious from their data that the Co_3O_4 needles have the highest capacity and best cycling performance among them. It is believed that smaller size and larger surface area provides a shorter ion diffusion pathway and an increased availability of Na^+ adsorption active sites, which leads to a higher capacity. In this case, the increase in grain boundary resistance with size reduction was not reported as a limiting factor in performance. Presumably, the nanoparticles are capable of withstanding the electrode stress caused by the material expansion.[72]

Another example within the literature to improve the stability of these metal oxides is their growth on conductive carbon substrates.[73-75] Recently, a form of Co_3O_4 mesoporous nanosheets/3D graphene composite (Co_3O_4 MNSs/3DGN), with an average pore size of about 40 nm, was reported.[76] As displayed in Fig 2a-b, the introduction of graphene improves the overall conductivity of the composite and buffers the volume change of the cobalt oxide with the porous

nanosheet structure benefiting the diffusion of Na^+ ions. As a result, this composite demonstrates an improved cycling performance and rate capability compared to Co_3O_4 nanosheets and Co_3O_4 nanoparticles. Using a Co-based MOF as a precursor to synthesize Co_3O_4 /carbon composites is another effective method. For example, several Co_3O_4 with a N-doped carbon coating composites have been reported within the literature.[77]

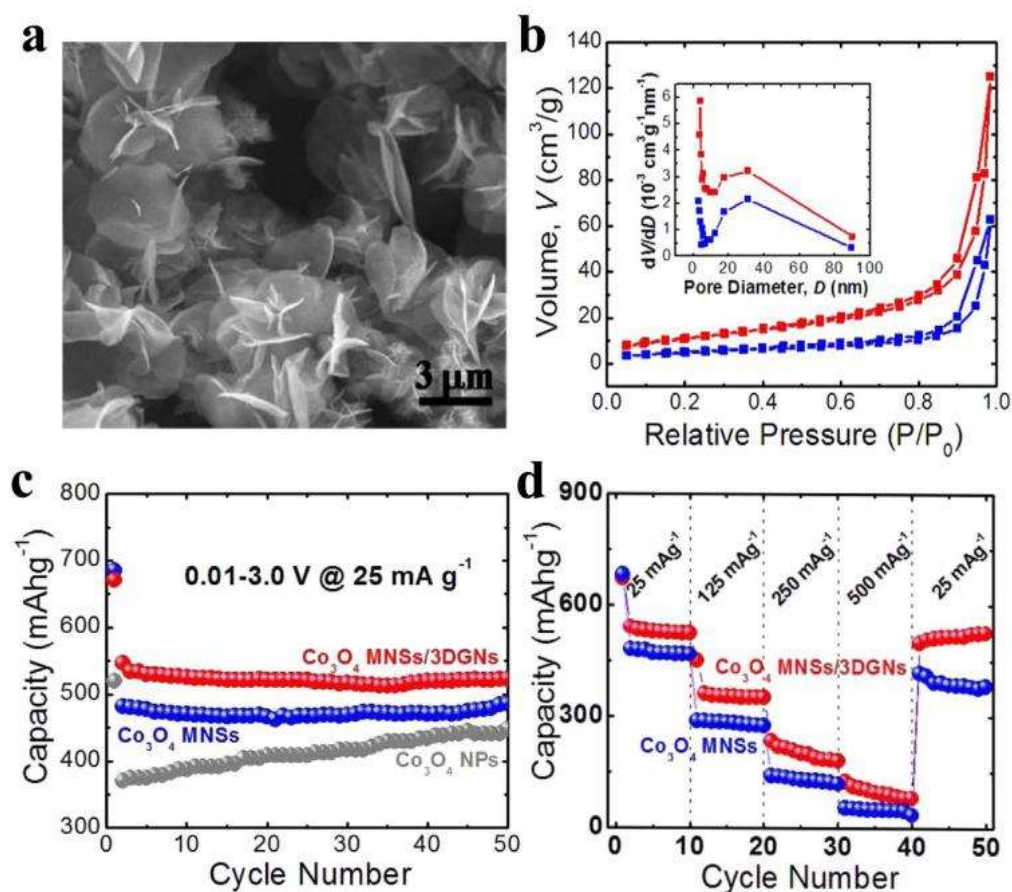


Fig. 2 Structural characterizations and electrochemical performances of Co_3O_4 MNSs/3DGN. (a) FESEM image and (b) Nitrogen adsorption/desorption isotherms for Co_3O_4 MNSs/3DGNs nanohybrids (red lines) and Co_3O_4 MNSs (blue lines). Inset: corresponding pore size distribution curves. (c) The cycling performance of Co_3O_4 - MNSs/3DGNs nanohybrids and Co_3O_4 MNSs. (d) Rate capability of the Co_3O_4 -MNSs/3DGNs nanohybrids and Co_3O_4 MNSs electrodes.[76]

Recently, some papers have proven that Co_3O_4 /metal oxide heterostructures also show good electrochemical performance in sodium ion batteries.[78, 79] is the rationale considered that an oxide heterostructure could potentially improve interfacial and surface charge transfer during

charging and discharging. Thus, the composite with a heterostructure should possess a high electrical conductivity. For example, a novel graphene/SnO₂/Co₃O₄ (GSC) heterojunction material has been reported.[80] In detail, the Co₃O₄ is a p-type semiconductor with a band gap of 2.2 eV and SnO₂ is an n-type semiconductor with a wider band gap of 3.8 eV. In the discharge process, the direction of the internal electric field should point from the SnO₂ side to Co₃O₄ side as an effective p-n junction. Based on the inbuilt depletion region, the accumulation of charge at the interfaces can be reduced. This is beneficial to the Na⁺ ion's diffusion and insertion into this material, as shown in Fig. 3a according to the authors. A smaller charge transfer impedance of the graphene/SnO₂/Co₃O₄ composite compared to the graphene/SnO₂ (GS) can be observed. As a result, graphene/SnO₂/Co₃O₄ demonstrates better cyclic performance than the composite without a heterostructure. The same trend can also be obtained with ZnO/Co₃O₄[81] and Co₃O₄/MnO₂[82] composites. In addition, doping with metallic ions (such as Zn²⁺ and Ni²⁺) is another effective way to enhance the sodium storage properties.[83]

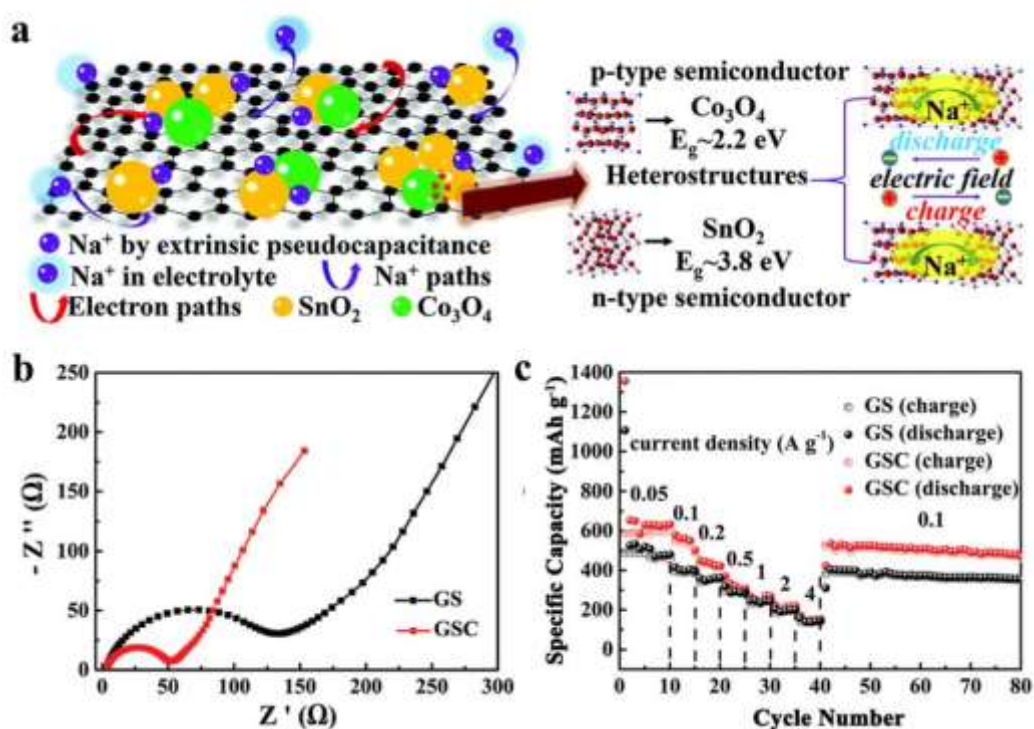
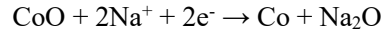


Fig. 3 (a) Summary of the enhanced high-rate capacity mechanism of the GSC anodes in the Na-ion battery system. (b) The Nyquist plots of GSC and GS. (c) Rate performance of GSC and GS at applied various current densities.[80]

2.2 CoO

Besides Co₃O₄, several recent reports have focused on CoO for application in a sodium ion battery. During the Na⁺ insertion process, the electrochemical reaction of CoO can be concluded as the following[84]:



Based on this above reaction, CoO exhibits a sodium storage capacity of 715 mAh g⁻¹. [85] The short cycling life and terrible rate capability also challenge the development of the CoO electrode for the sodium ion battery. To address these limitations, a porous Ni-doped Co/CoO/carbon composite was recently reported.[86] Due to a stated synergistic effect of the carbon coating, highly porous structure, and defect sites caused by Ni-doping, the structural stability, electric and ionic conductivity are improved simultaneously. This material demonstrates a capacity of 307 mAh g⁻¹ at 0.1 A g⁻¹ and a relatively high discharge capacity of about 280 mAh g⁻¹ is observed after 100 cycles at the same current density.

3. Cobalt Sulfide Anodes

3.1 Co₉S₈

Co₉S₈ has attracted great attention over a range of fields of research including catalysis, sensing and energy storage, due to its unique physical and electrochemical properties.[87] As can be seen in Fig 4, cubic Co₉S₈ has a space group of Fm-3m, and a large unit cell parameter of a = 9.926 Å. As shown in Fig 4, its crystal structure comprises two different polyhedra, CoS₆ octahedra and CoS₄ tetrahedra, respectively.[88] In a perfect crystal structure, every CoS₆ octahedron shares its corners with 24 CoS₄ octahedrons. There are three different Co-S bonds with varying bond lengths and energy. This form of structure can not only provide channels for ionic diffusion, but also offers multiple possible routes of bonding-breaking.

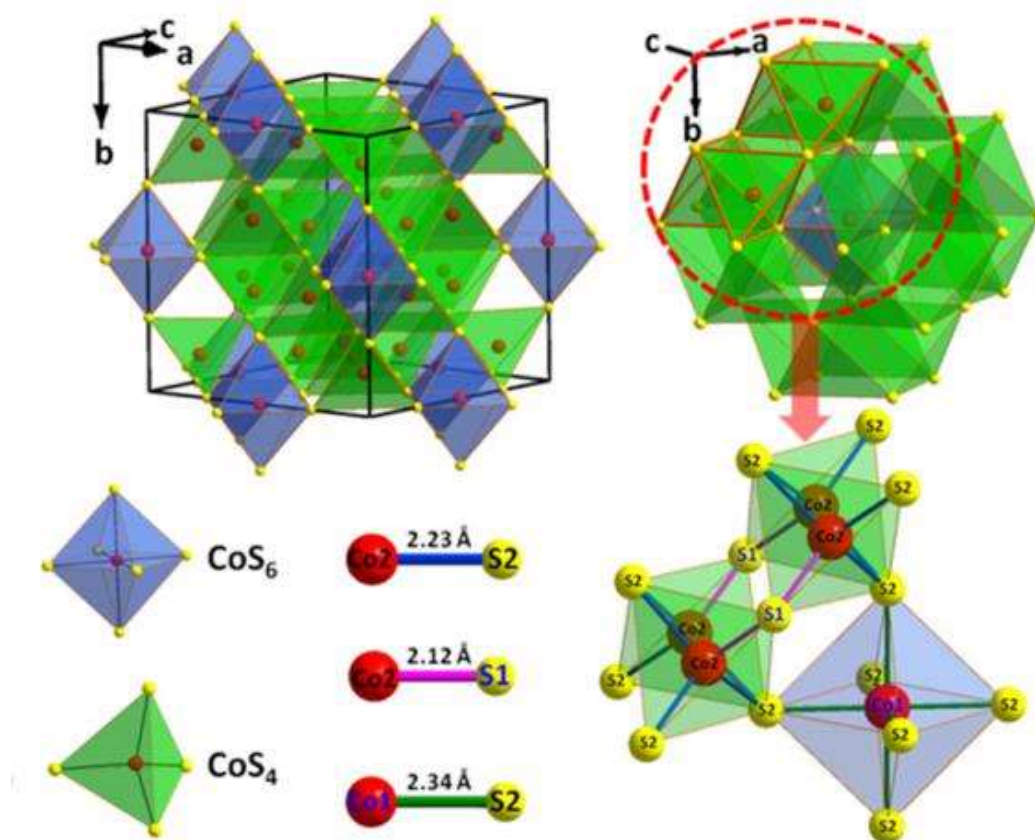


Fig. 4 Schematic structure of cube Co₉S₈. [88]

Through different synthesis methods, such as solvothermal and solid state recrystallization, Co₉S₈-based materials with various morphologies have been obtained.[89, 90] In the energy storage field, engineering these structure to have a large surface area and be capable of high capacity alkaline ion storage properties, nano-sized Co₉S₈ has been widely studied as an electrode material for supercapacitor and lithium ion battery applications. When applied to sodium ion battery systems, Co₉S₈ suffers a conversion reaction according to $\text{Co}_9\text{S}_8 + 16 \text{Na}^+ \rightarrow 9 \text{Co} + 8 \text{Na}_2\text{S}$, which shows a relatively high theoretical capacity of 544 mAh g⁻¹. [91] However, the low degree of reversibility and excessive volume changes caused by the above conversion reaction leads to very poor cycling performance and rate capability, in addition to the unstable solid electrolyte interphase, which also aggravates this problem. [92]

To enhance the electrochemical performance of Co₉S₈ as an anode for sodium ion batteries, several strategies have been reported. For example, hierarchical nanostructuring can play a vital

role for a conductive substrate, buffering the stress caused by the change in volume and offer open channels for Na^+ ion diffusion and for mass transport of other reactants in conversion mode processes. Novel Co_9S_8 quantum dots embedded into hierarchical porous carbon frameworks (3DOM Co_9S_8 -QDs@NC) was obtained by a template method, as shown in Fig 5a.[89] The SiO_2 nanospheres were utilized as a sacrificial template and were etched to form macropores with an average size of 150 nm and the surface-immobilized Co_9S_8 quantum dots are ~ 3 nm (Fig 5b) in size. This composite exhibits an improved cycling performance and rate capability compared to the $\text{Co}_9\text{S}_8/\text{C}$ (Co_9S_8 -QDs@NC) without hierarchical structure by ensuring good interfacial contact and QD access to the electrolyte. In detail, as can be seen in Fig 5c, when the current density reaches to 10 A g^{-1} , this composite still shows a remarkable specific capacity of 253 mAh g^{-1} . Moreover, a capacity of more than 340 mAh g^{-1} is achieved after 2000 cycles with the Coulombic efficiency of over 99%, at a current density of 1 A g^{-1} . Beyond all the above-mentioned reasons of hierarchical structure, the high ratio of diffusion-controlled capacity is another significant reason for the improved electrochemical performance.

Utilizing a Co-based MOF as the precursor is another effective way to synthesize a hierarchical Co_9S_8 -based material. Several studies have proved that ZIF-67 is the suitable precursor for this strategy. For instance, recently, a Co_9S_8 quantum dot/hollow carbon matrix/graphene aerogel was synthesized with the ZIF-67 precursor.[92] This composite demonstrated a stable cycling life over 500 cycles at a current density of 300 mA g^{-1} . Similarly, most capacity is contributed by the diffusion-controlled electrochemical behavior.

Combining with other metal sulfides to form heterostructures can also enhance the sodium storage capacity of Co_9S_8 . MoS_2 is another alternative anode material for SIB. For good wettability with organic electrolyte, MoS_2 can play a role as a useful coating layer for other materials.[93] A type of Co_9S_8 core- MoS_2 shell composite ($\text{Co}_9\text{S}_8/\text{MoS}_2$ -CN) shows more stable cycling life and better rate capability than pure Co_9S_8 or pure MoS_2 , as shown in Fig 5f-g.[94] It is believed that MoS_2 shell can bring such advantages: smaller Ohmic resistance, lower activation energy for Na^+ ion diffusion and larger exposed surface to the electrolyte, which leads to an improved electrochemical performance. In addition, of the choice of electrolyte will have a significant impact on the sodium storage capacity of a Co_9S_8 electrode. It has been reported that an ether-based electrolyte, such as 1.0 M sodium trifluoromethanesulfonate (NaCF_3SO_3) dissolved in

tetraethylene glycol dimethyl ether (TEGDME), can bring a much more stable long-term cycling life and good rate capability.[90]

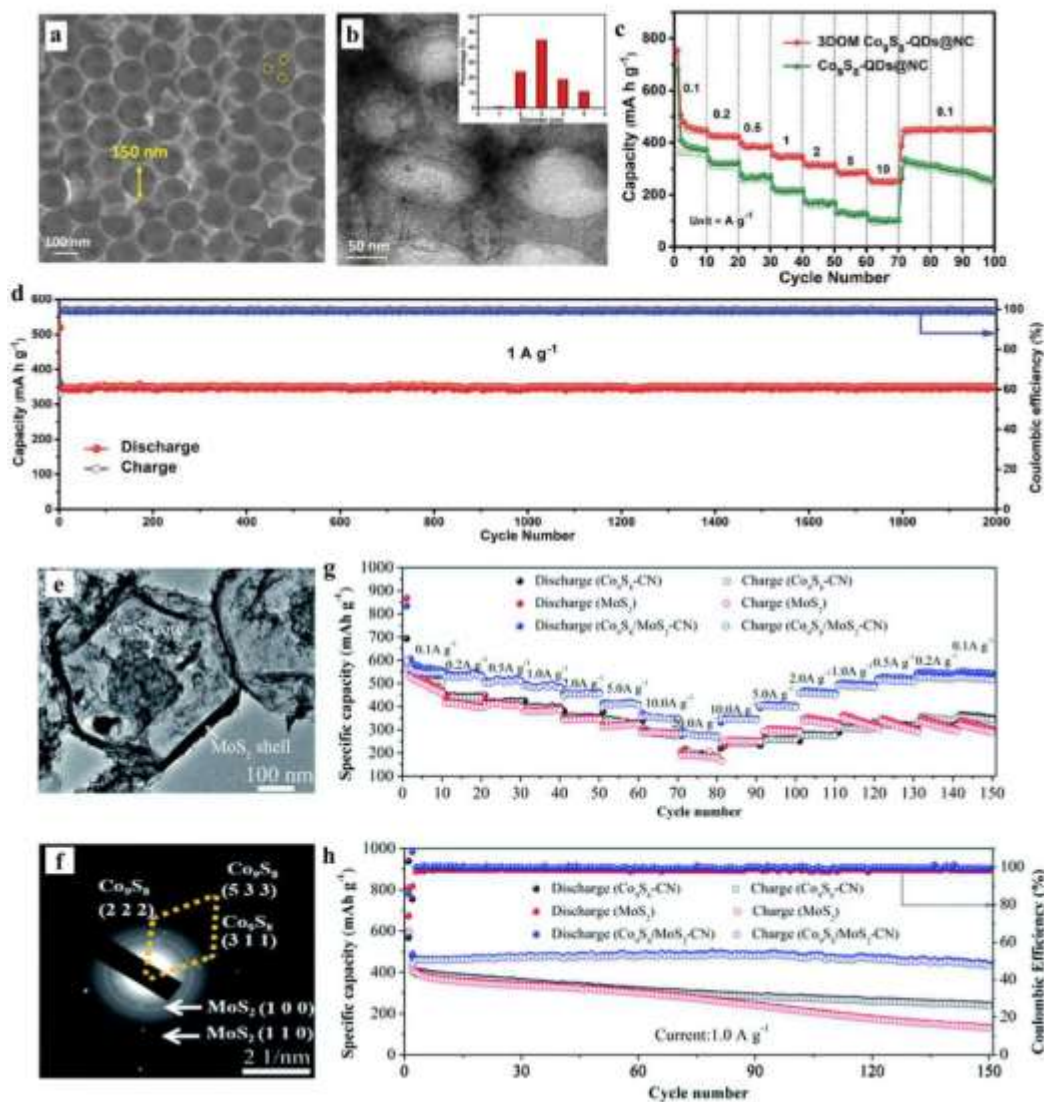


Fig. 5 (a) FESEM images and (b) TEM images with inset of the size distribution of the QDs for 3DOM Co₉S₈-QDs@NC. (c) Rate capability of the 3DOM Co₉S₈-QDs@NC and Co₉S₈-QDs@NC electrode. (d) Cycling performance and Coulombic efficiency of 3DOM Co₉S₈-QDs@NC for 2000 cycles at the current density of 1 A g⁻¹. [89] (e) TEM images and (f) SAED patterns of the yolk-shelled polyhedral Co₉S₈/MoS₂-CN nanocomposite. (g) Rate capability at different current densities and (h) cycling performance at 1.0 A g⁻¹ for the Co₉S₈/MoS₂-CN composite, Co₉S₈-CN and MoS₂ anodes. [94]

3.2 CoS₂

CoS₂ has the same crystal structure as FeS₂, which is called a pyrite phase. The schematic representation of the CoS₂ crystal structure is displayed in Fig 6.[95] A Co atom occupies the central site of an octahedral arrangement with S atoms occupying the corner site the neighboring octahedrons share corners with each other. Besides, CoS₂ is assigned to a cubic phase with the *Pa-3* space group.

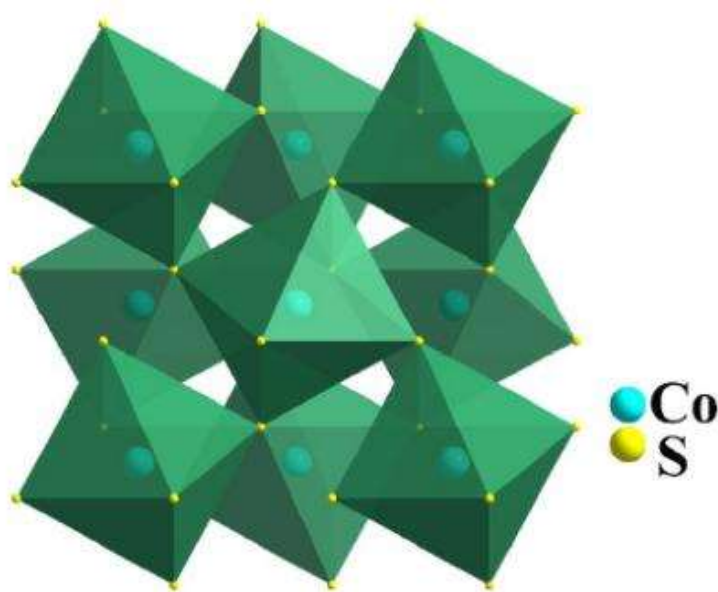


Fig. 6 Crystal structure of CoS₂. [95]

As a promising anode material for SIBs, CoS₂ offers a large theoretical capacity of 870 mAh g⁻¹ and high electronic conductivity.[96, 97] The band gap of CoS₂ is 0 eV, which means this material possesses metallic-like conductivity. According to previous work,[98] as can be seen in Fig 7, each CoS₂ can react with four Na⁺ ions and this electrochemical reaction can be divided into 2 steps. Firstly, when the voltage is above 1 V (vs. Na⁺/Na), no more than two Na⁺ ions inserted into CoS₂ and an intermediate product is formed. Then, with the electrochemical reaction proceeding, Co⁴⁺ is reduced to metallic Co and Na₂S emerged below 1 V (vs. Na⁺/Na). The sluggish kinetics, low reversibility and huge volume change for conversion reaction that takes place in the low voltage range, causes inferior cycling performance. To solve this problem is one of the key issues for CoS₂ as an anode material for sodium ion battery.[99]

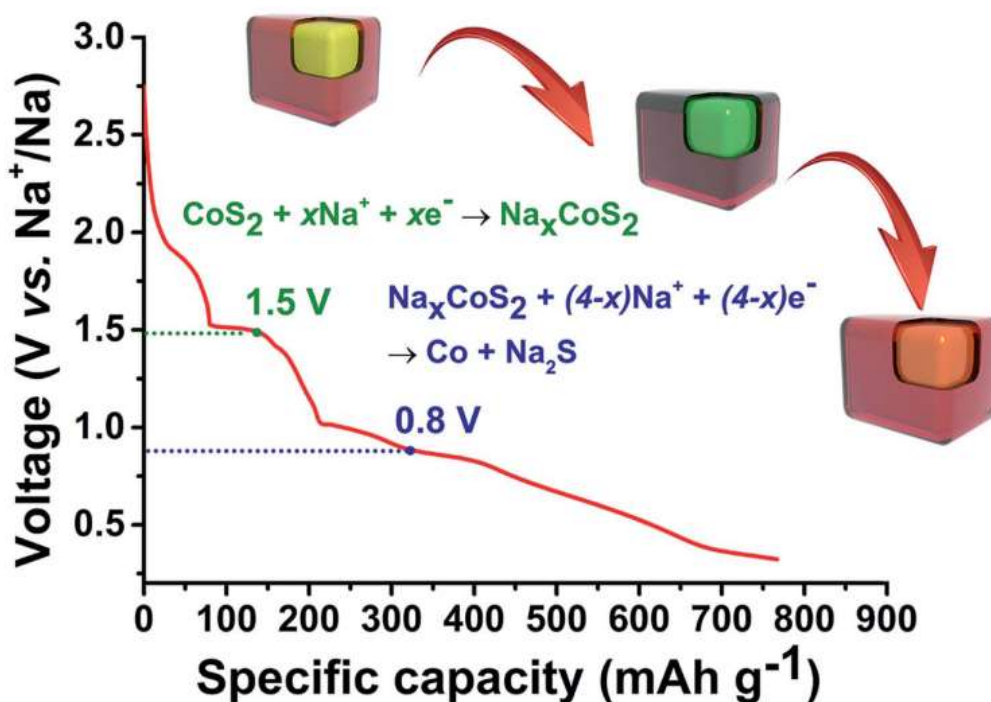


Fig. 7 Reaction mechanisms of CoS₂ in the fully discharged process.[98]

Carbon matrices or coating layers can buffer the volume change of CoS₂ during intercalation-deintercalation of Na⁺ ions and associated reaction phases. Previous work has tried to introduce carbon-based materials to obtain a CoS₂-based composite with good electrochemical performance.[100-102] A kind of flower-like N-doped carbon/CoS₂ spheres (N-C/CoS₂) was synthesized by a solvothermal method followed by sulfurization.[103] As can be seen in Fig 8a, the CoS₂ flowers consist of 2D wrinkled CoS₂ nanosheets with an average thickness less than 5 nm. This open nanostructure can shorten the Na⁺ ion diffusion distance in the CoS₂ crystal in principle. Combined with the carbon matrix, this composite shows a stable cycling life over 500 cycles without obvious capacity decay. In contrast, bare CoS₂ loses most of its capacity after 200 cycles. In another work, combining the template, electrospinning and solvothermal methods, a double-morphology CoS₂-N doped carbon fiber composite was synthesized.[104] As can be seen in Figure 8c, CoS₂ nanosheets were *in situ* formed on the surface of the carbon fiber. Meanwhile, CoS₂ nanoparticles also grew in the channels of these carbon fibers. This form of carbon fiber, with unique its structure, plays the dual role of matrix and coating for CoS₂ nanosheets and nanoparticles, respectively. At 0.1 A g⁻¹, this composite exhibits a high initial discharge capacity of 849.6 mAh g⁻¹, and maintains capacities of more than 700 mAh g⁻¹ over subsequent cycles. In

addition, compared with the bare CoS_2 electrode, double-morphology CoS_2 -N doped carbon fiber composite demonstrate a more stable long-term cycling over 900 cycles.

Similar to Co_9S_8 , heterostructures consisting of CoS_2 and other metal sulfides have also been reported.[105] $\text{SnS}_2@\text{CoS}_2\text{-rGO}$ (reduced graphene oxide) composite shows quite a high discharge capacity and better cycling performance than $\text{SnS}_2\text{-rGO}$ and $\text{CoS}_2\text{-rGO}$ composites.[106] It is believed that a synergetic effect exists between CoS_2 and SnS_2 , which can offer an optimal electrode/electrolyte interface. Using Prussian blue analogues, potassium hexacyanocobaltate as a precursor, a type of $\text{NiS}_2@\text{CoS}_2@\text{C}@\text{C}$ nanocube was obtained.[107] This material also shows a stable cycling life, with more than 600 mAh g^{-1} capacity obtained after 250 cycles, at a current density of 1 A g^{-1} .

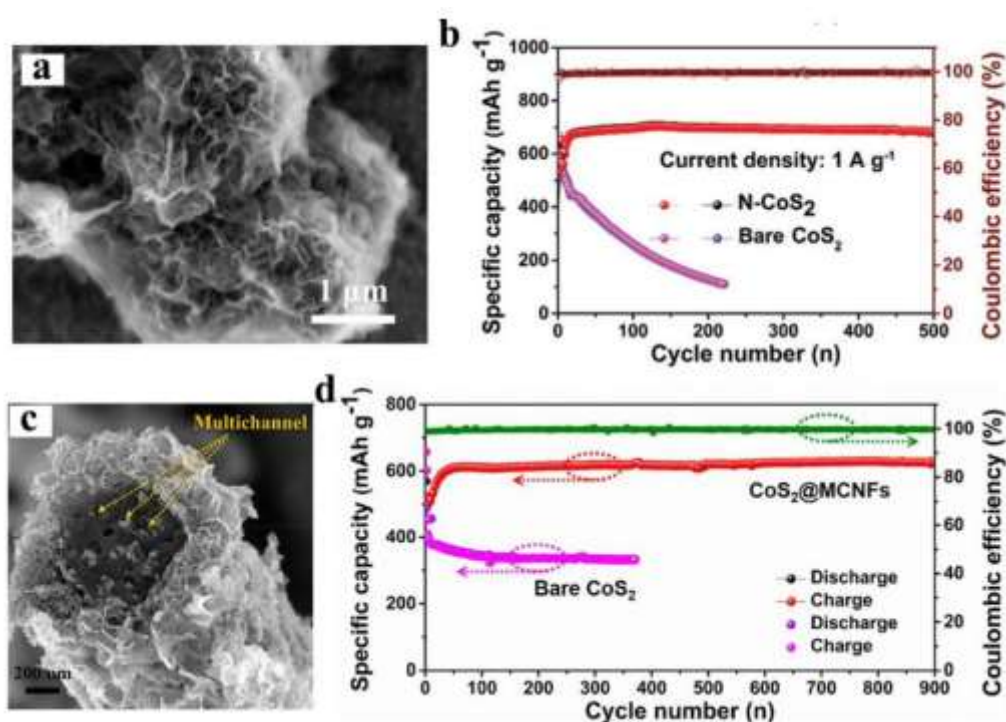


Fig. 8 (a) SEM images of the N-C/ CoS_2 composites. (b) Cycling performance of N-C/ CoS_2 and the bare CoS_2 electrodes at 1 A g^{-1} . [103] (c) High magnification SEM images of the $\text{CoS}_2@\text{MCNFs}$ composites. (d) Cycling life testing of $\text{CoS}_2@\text{MCNFs}$ electrode and bare CoS_2 electrode. [104]

It has been pointed out that when using ether-based electrolyte, CoS_2 -based electrodes show both better cycling stability and rate capability, than with carbonate-based electrolyte.[108] Several factors causing this better performance have been proven, with some mechanistic

similarities for Li-S systems. Firstly, a more stable SEI membrane can form in ether-based electrolyte, which means less consumption of electrolyte and sodium salt. Then, ether-based electrolytes have a better wettability with electrodes than carbonate-based electrolytes. Finally, faster charge-transfer kinetics can be observed in ether-based electrolytes.

3.3 CoS

CoS is another type of cobalt chalcogenide, which has been regarded as another potential anode material for the alkaline ion battery.[109] It appears that almost all of the CoS investigated within the energy storage field is indexed to the hexagonal crystal phase with a $P6_3/mmc$ space group. The corresponding crystal structure is shown in Fig 9.[110] Every crystal cell possesses two Co^{2+} ions and S^{2-} ions. Each Co^{2+} ion occupies the center site of octahedron with six S^{2-} ions coordinate it; the adjacent CoS_6 octahedrons share edges and faces. As an anode material for sodium ion battery, CoS has a theoretical capacity of 588 mAh g^{-1} . In a Na^+ ion intercalation process, each CoS will react with two Na^+ ions. Similarly with CoS_2 , this reaction can be divided into two steps, the insertion step ($\text{CoS} + x\text{Na}^+ + x\text{e}^- \rightarrow \text{Na}_x\text{CoS}$, $x < 2$) and the conversion step ($\text{Na}_x\text{CoS} + (2-x)\text{Na}^+ + (2-x)\text{e}^- \rightarrow \text{Co} + \text{Na}_2\text{S}$). Generally, the conversion step takes place below 0.8 V. [111-113]

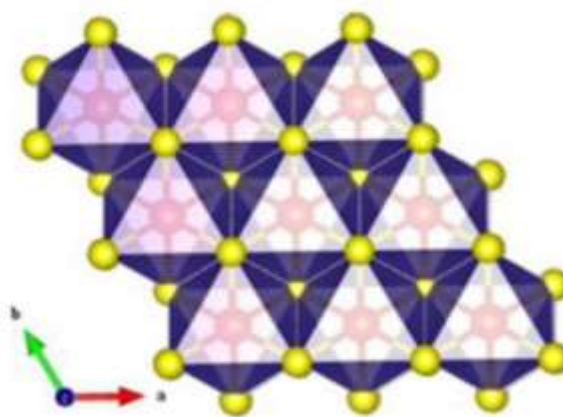


Fig. 9 Crystal structure of hexagonal CoS.[110]

It is well known that the conversion reaction faces similar challenges to other materials discussed previously such as volume expansion, low reversibility and so on.[114-119] Thus, there is no doubt that the conversion step has a remarkable influence upon the electrochemical

performance of CoS. As can be seen in Fig. 10b[114], when the potential window is extended to 0.1-2.9 V, allowing the conversion step to dominate, more than 75% of initial capacity decayed after 500 cycles at 1 A g⁻¹. In contrast, when the cut-off voltage was set to 0.6 V to avoid the conversion step, as shown in Fig. 10a, a high retention rate of 88% could be obtained over 1000 cycles at the same current density. However, although this potential window controlling strategy is highly effective, the capacity provided by conversion step will not be provided. Finally, if the CoS electrode is assembled in a full cell system, the overall reduction of the energy density within this device, will not provide a suitable energy storage platform. Thus, there is a vast requirement to develop methodologies that will alleviate the problems caused by the conversion step.

A method to overcome this destructive conversion step is to use a Co based MOF as a precursor to build porous carbon substrate. For example, through a facile calcination method within inert gas, CoS nanoparticles embedded into porous carbon rods were synthesized by Zhou et al.[110] In the optimized sample, the average size of CoS particles was 7 nm (7-CoS/C). This ultrathin particle suffered more expansion stress than the larger particles with average size of 18.5 nm (18.5-CoS/C). As displayed in Fig. 10c, the composite electrode consisting of 7 nm-sized CoS particles exhibits an improved cycling life than that those containing larger sized active material particles. Additionally, a smaller particle size can also shorten Na⁺ ion diffusion path leading to an increased rate capability. These approaches confirms that the conductive host is important to alleviate increased material resistance from smaller particles with similar tap density to electrode formulations with larger particles, while nanoscaling ensures a better tolerance to volume expansion and accommodation of conversion mode products during cycling.

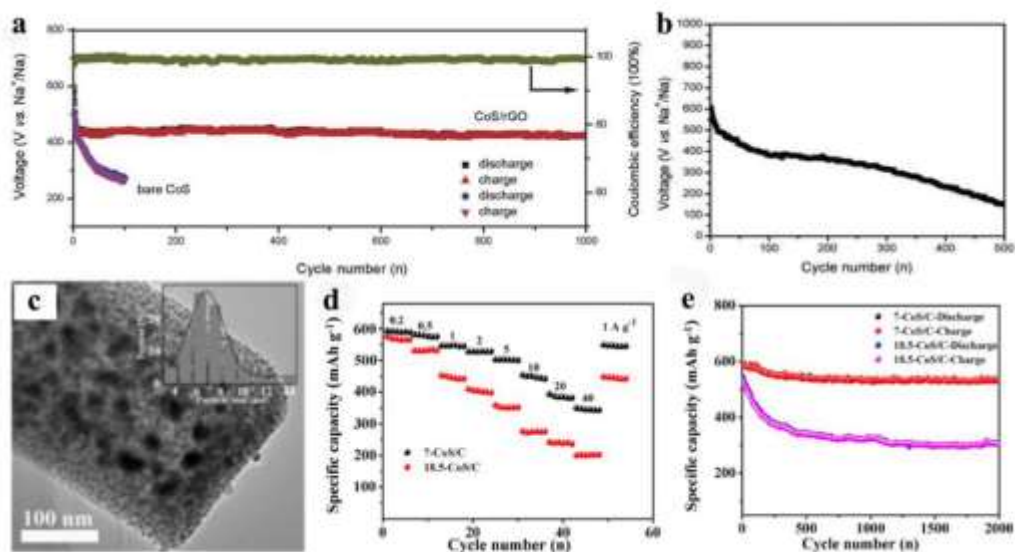


Fig. 10 (a) Cycling performance (left) and Coulombic efficiency (right) of the CoS@rGO composite at a current density of 1 A g⁻¹ over a voltage window of 0.6-3.0 V. (b) Cycling performance of CoS/rGO at a current density of 1 A g⁻¹ over a potential window of 0.01-2.9 V.[114] (c) High-resolution TEM with inset of particle size distribution diagram for 7-CoS/C. (d) Rate capability and (e) cycling performance at a current density of 1 A g⁻¹ in the voltage range of 0.6-3 V (vs. Na⁺/Na) for 7-CoS/C and 18.5-CoS/C electrodes.[110]

The construction of a yolk-shell structure can also address the aforementioned problems. Recently, Mai's group reported a self-adaptive CoS@C with yolk-shell microsphere composite was obtained by SiO₂-templated method.[120] Briefly, as shown in Fig. 11a, the silica and resorcinol formaldehyde (RF) was coated on the CoS precursor. After an annealing process, the resulting SiO₂ particles were etched by HF and the yolk-shell structure was obtained. The resulting morphologies of the cycled samples were also investigated. The CoS micron spheres without carbon shells deteriorated after 10 cycles and were totally pulverized after 50 cycles. Nonetheless, the yolk-shell CoS@C composite can maintain its structural integrity even after 50 cycles. The gap-space was states as the reasons why this material could accommodate the volume expansion of the products during the conversion step (Co and Na₂S), with the carbon shell preventing the loss of active material.

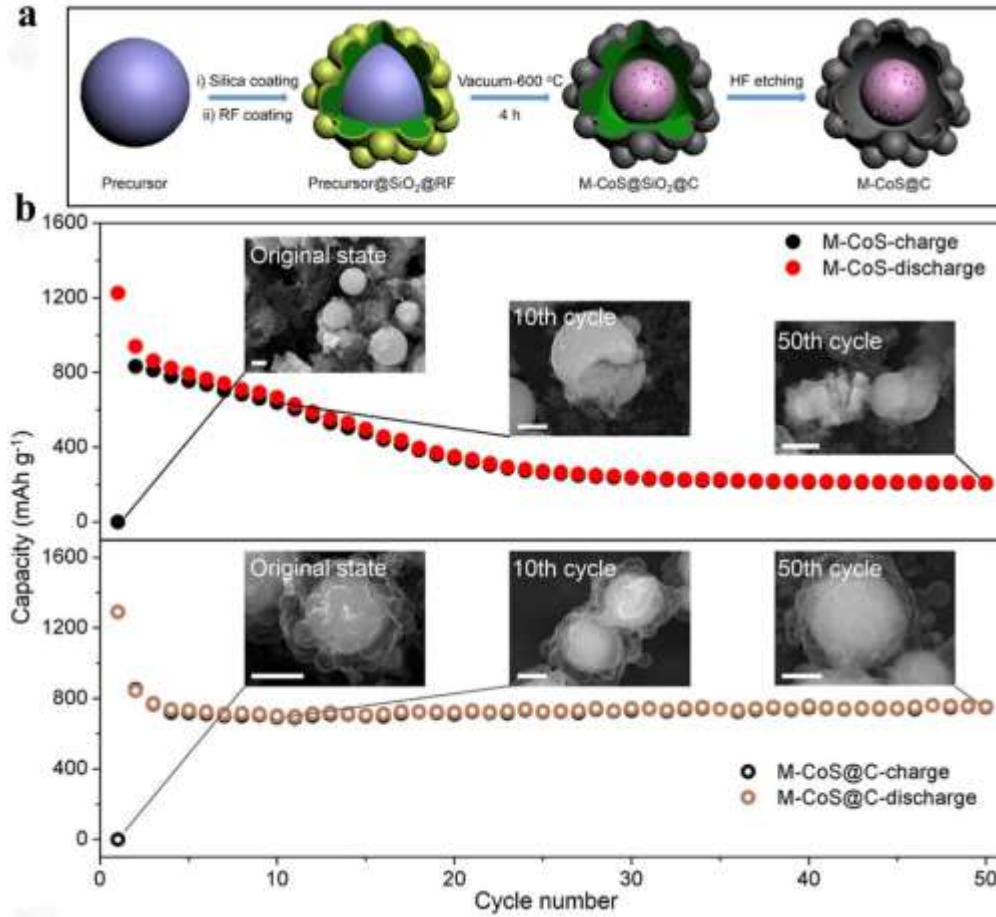


Fig. 11 (a) Schematic illustration of the synthesis of yolk-shell M-CoS@C. (b) The SEM images of the M-CoS and yolk-shell M-CoS@C at 0, 10th and 50th cycle (full charge state) respectively, and their corresponding cycling performances at 1 A g⁻¹. Scale bar, 1 μ m.[120]

4. Cobalt Selenide Anodes

4.1 CoSe₂

Generally, compared with other metal oxides and sulfides, metal selenides possess higher volumetric capacity and electrical conductivity, and have been routinely applied within SIBs.[121, 122] Generally, metal selenides have similar properties with metal sulfides, resulting in the wide range of investigations of CoSe₂, as a promising anode for SIBs. CoSe₂ has two different phases, namely the trogtalite and hastite phases. The first belongs to an orthorhombic marcasite phase with a space group of *Pnmm* and the second is the cubic phase with a space group of *Pa3*. Both of these phases of CoSe₂ have been studied as anode materials for SIBs.[123, 124] For example, the crystal structure of hastite phase is shown in Figure 12a, and, six Se anions coordinate to a Co²⁺

ion, which occupies the center site of the octahedron. The adjacent Se anions forms a Se_2^{2-} anion via a covalent Se-Se bond.[123]

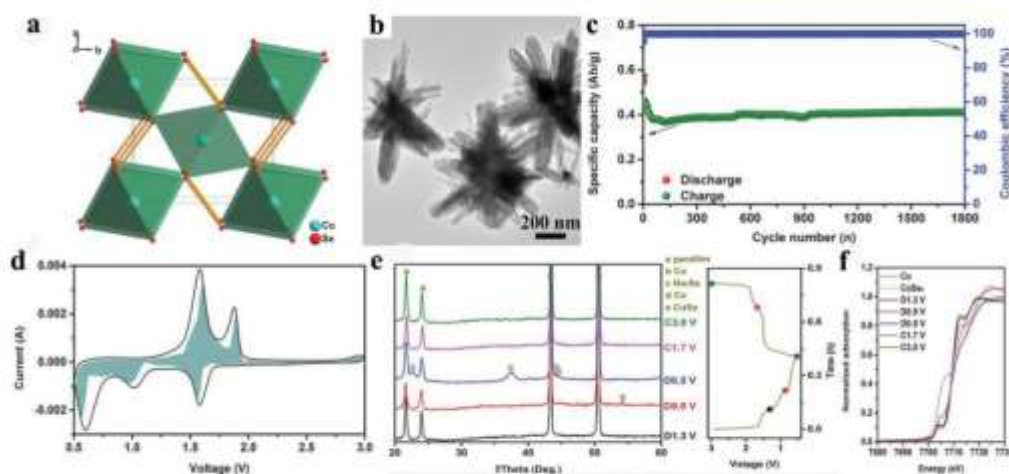
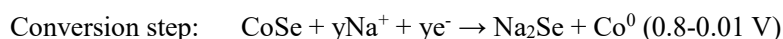
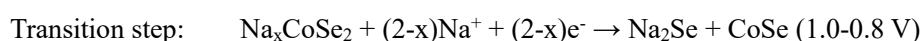
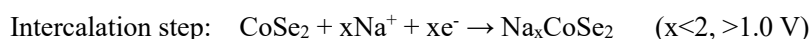


Fig. 12 (a) Crystal structure of the marcasite-type CoSe_2 . (b) TEM and (c) cycling life of the CoSe_2 at a current rate of 1 A g⁻¹. CV curve with the pseudocapacitive fraction shown by the darkly cyan region at a scan rate of 1 mV s⁻¹. (e) Reaction mechanism: *ex situ* XRD analysis of the CoSe_2 electrodes at different charge-discharge states with the corresponding charge-discharge curve and parafilm was used to protect the CoSe_2 electrodes when testing XRD. (f) Near-edge X-ray absorption spectroscopy of the CoSe_2 electrodes at different cycling states and the reference Co and CoSe_2 . [123]

Ou and co-workers focused on the mechanism for Na^+ ion intercalation reaction with CoSe_2 . It has been proven that this electrochemical reaction can be divided into three steps and CoSe forms as an intermediate product. In detail, the three steps are as follows[125]:



Based upon this electrochemical reaction with four electrons, CoSe_2 exhibits a theoretical capacity of 494 mAh g⁻¹. However, as with CoS_2 , the application of CoSe_2 is hindered by its poor cycling performance due to the volume change and structural pulverization.[126, 127]

Chen's group synthesized a kind of urchin-like CoSe_2 , which consists of multiple nanorods as

shown in Fig. 12b,[123] with pseudocapacitive behaviors (Fig. 12d) that can lead to a stable cycling life. This material shows a high reversible capacity of 410 mAh g⁻¹ after 1800 cycles, at a current density of 1 A g⁻¹, over a potential window of 0.5-3.0 V as displayed in Fig. 12c. Upon incorporation into a Na₃V₂(PO₄)₃/CoSe₂ full cell, the urchin-like CoSe₂ still exhibits a high capacity of 380 mAh g⁻¹. However, there is a huge capacity loss between the 1st and 2nd cycles, which could be due to the irreversible formation of SEI. To further understand this phenomenon, as exhibited in Fig. 12e-f, *ex situ* XRD analysis and near-edge X-ray absorption spectroscopy determined that, after the first discharge process, even upon charging to 3.0 V, the anode material did not return to its original pristine state, as some Na⁺ ions were not extracted from the anode material. Thus, upon subsequent cycles, the reversible electrochemical reaction starts and ends with the state of Na_xCoSe₂, which unavoidably hinders the capacity of the anode material.

Another methodology that has been considered is the synthesis of a novel type of CoSe₂@C bridged with carbon nanotubes (CoSe₂@C/CNTs) reported by Qiu et al..[127] As can be seen in Fig 13, the precursor, ZIF 67, was annealed in H₂/Ar mixed gas and the Co²⁺ was reduced to form Co metallic nanoparticles. These metal particulates act as a catalyst promoting the formation of the carbon nanotubes. In this hierarchical structure, the CNT can construct a cross-linked conductive network and prevent the agglomeration of the active material. This composite demonstrates a high reversible specific capacity of about 470 mAh g⁻¹ at a current density of 0.2 A g⁻¹. After 1000 cycles, a superior capacity retention closing to 100% can be observed (calculated from the 70th cycles).

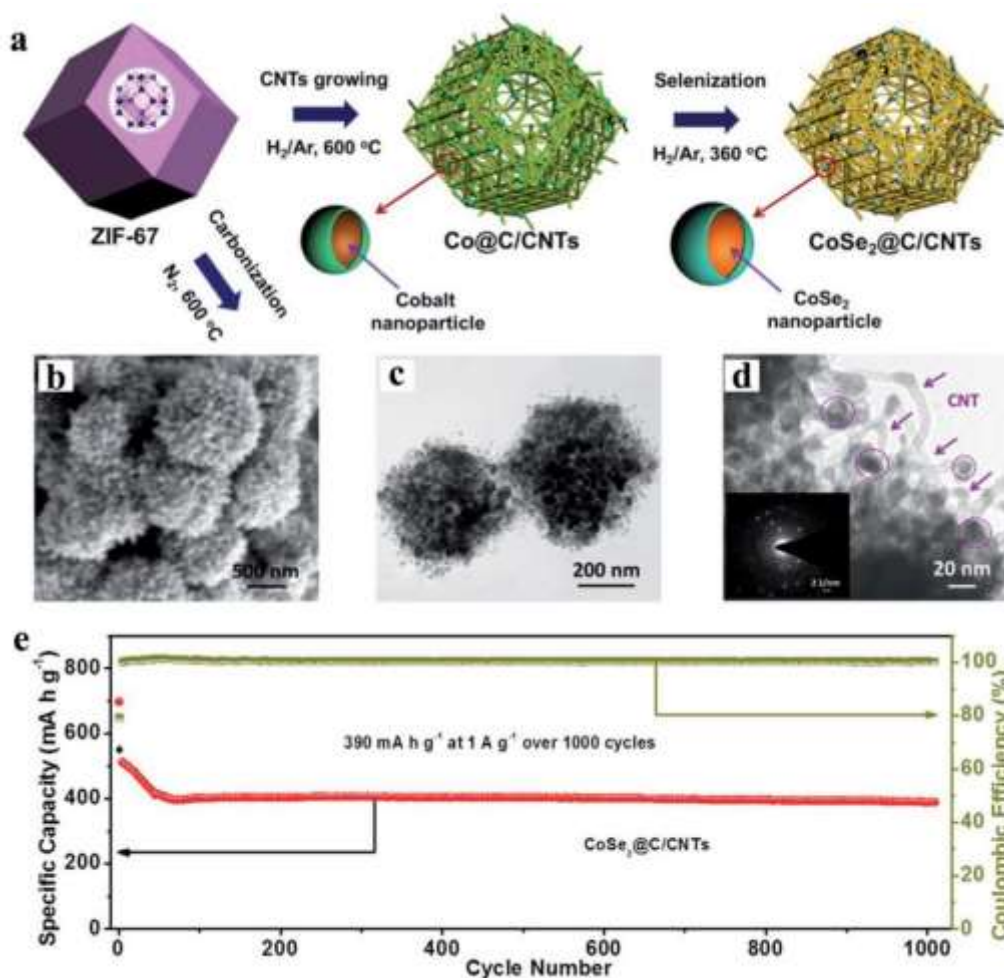


Fig. 13 (a) Synthetic processes of the CoSe₂@C/CNTs and CoSe₂@GC. (b) FESEM images and (c) TEM images exhibiting the polyhedral CoSe₂@C/CNTs integrated with tangled CNTs and carbon-coated CoSe₂ nanospheres; (d) TEM image of the CNTs (shown by purple arrows) on CoSe₂ particle surface; the SEAD patterns (inset) suggest the polycrystalline structure of CoSe₂ nanospheres in the hybrid. (e) Long-life cyclability of the CoSe₂@C/CNTs anode.[127]

The structural design of coating other kind of metal sulfides to form heterostructure has been also applied for optimizing the electrochemical performance of CoSe₂. [128, 129] Through a facile synthesis route combining hydrothermal coating and selenization processes, CoSe₂ particles with MoSe₂/C shells were developed as a composite (CoSe₂@MoSe₂/C). [130] This MoSe₂/C hybrid shell was reported to simultaneously enhance the transition of both ions and electrons, alleviating the volume change during alkaline ion insertion/extraction processes. Combining this with a capacitive contribution, this composite shows a specific capacity of 450 mAh g⁻¹ over 100 cycles

at 0.1 A g⁻¹, and maintains more than 300 mAh g⁻¹ capacity at 1 A g⁻¹ after 200 cycles, respectively.

4.2 Other cobalt selenides

Recently, Chen's group reported the utilization of porous Co_{0.85}Se ultrathin nanosheets anchoring on rGO composite as an anode for SIB. The morphology of as prepared Co_{0.85}Se nanosheets is shown in Fig 14a.[131] As can be seen in Fig. 14b-c, this composite shows superior capability and stable cycling life over 800 cycles at 1 A g⁻¹. This hierarchical nanostructure can provide enough active sites for Na⁺ ions adsorption and reserve space to accommodate the volume change. Importantly, the unequal content of Co and Se elements in Co_{0.85}Se leads to the formation of defects. As shown in Fig. 14d-e, the band gap calculation by using density function theory (DFT), shows that the Co_{0.85}Se has a narrower band gap (0.68 eV) than that of the CoSe (1.36 eV), meaning an enhanced electronic conductivity. These defects also provide suitable Na⁺ ion diffusion pathways, which can lead to a lower migration energy barriers of Co_{0.85}Se than for CoSe as displayed in Fig. f-g, respectively. Additionally, the possible Na⁺ ion diffusion trajectories in above two kinds of materials are shown in Fig. 14h. The bond length of Co-Se in Co_{0.85}Se is longer than that in CoSe, leading to faster reaction kinetics for the Co_{0.85}Se conversion to Co and Na₂Se.

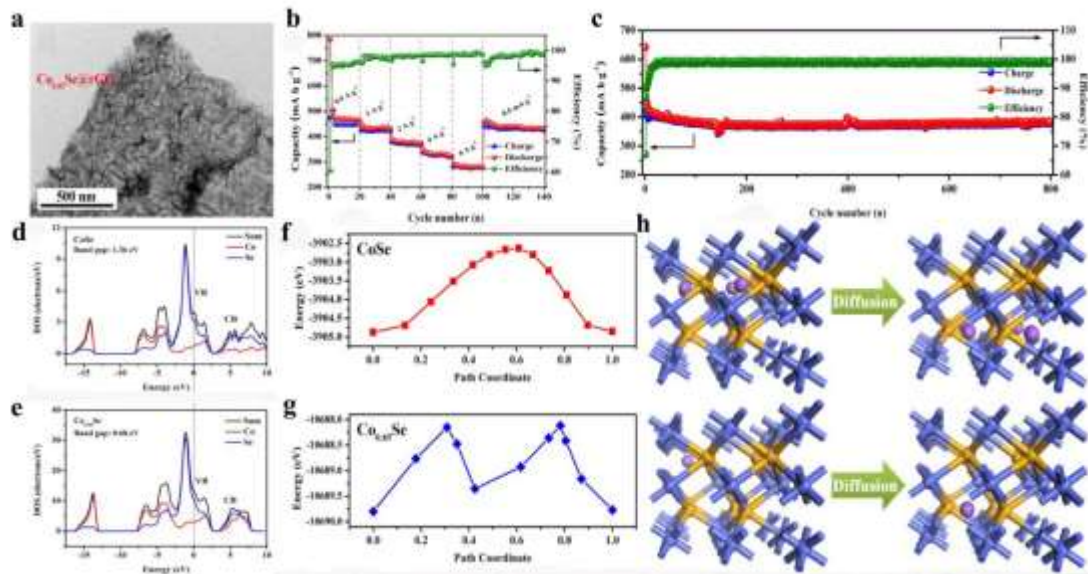


Fig. 14 (a) TEM images of Co_{0.85}Se NSs@rGO. (b) Rate performance at different current densities and (c) long-cycling performance at 1 A g⁻¹ for Co_{0.85}Se NSs@rGO electrode. (d-e) DOS and

PDOS spectra of CoSe and Co_{0.85}Se. (f-g) The calculated migration energy barriers of the single Na⁺ ions along the described paths. (h) Possible Na⁺ ion diffusion trajectories in CoSe (upper schematics) and Co_{0.85}Se (lower schematics) through the vacancy site.[131]

Another Co_{0.85}Se/graphene composite has been reported by Zhou's group, as a binder-free anode electrode for alkaline ion battery.[132] As can be seen in Figure 15, the Co_{0.85}Se nanosheets anchored on graphene stably and this "sheet-on-sheet" nanostructure with strong interfacial interaction can self-assemble to form a flexible film electrode without any conductive additive and binder. It is believed that the strong interfacial interaction between different parts of the composite can effectively enhance the electron transfer. Graphene can not only play a role of conductive matrix, but also protect the Co_{0.85}Se from agglomeration after the charge-discharge test. Besides this, the binder-free strategy can improve the volumetric specific capacity of this electrode. When applied to SIBs, this novel electrode exhibits a preferred stable cycling performance and better rate capability than pure Co_{0.85}Se nanosheet electrode.

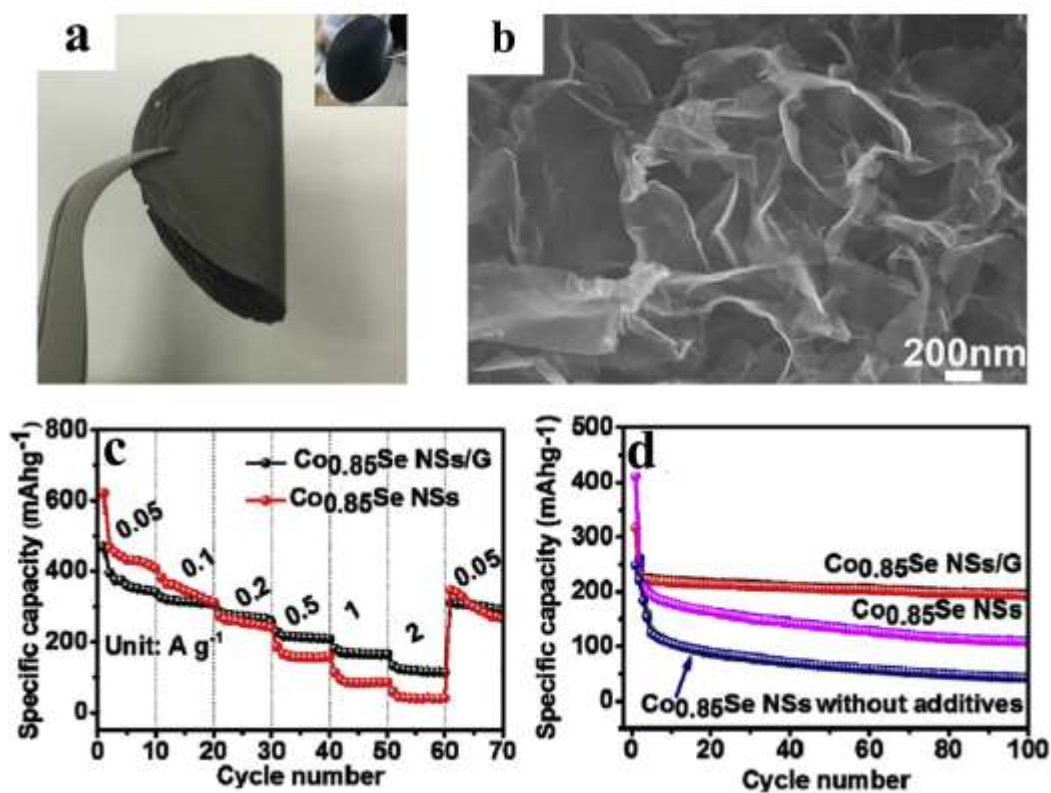


Fig. 15 (a) Optical images of the Co_{0.85}Se NSs/G film with the inset of Co_{0.85}Se NSs/GO film. (b) SEM images of Co_{0.85}Se NSs. (c) Sodium storage rate performance of the Co_{0.85}Se NSs and the

Co_{0.85}Se NSs/G film. (d) Cyclic properties of the Co_{0.85}Se NSs with and without the addition of a binder and conducting additives and of the Co_{0.85}Se/G film at a current density of 0.5 A g⁻¹. [132]

5. Na_{0.7}CoO₂ SIB Cathodes

Sodium cobaltates, Na_xCoO₂ (0.5 ≤ x ≤ 1), are a significant cathode material for SIBs. Researchers have paid much attention to this type material for two main reasons. [133-135]¹³³⁻¹³⁵ Firstly, several transition-metal oxides cathodes for SIBs, such as Na_xVO₂, Na_xCrO₂, Na_xMnO₂, several sodium cobaltates, Na_xCoO₂ (0.5 ≤ x ≤ 1), have been routinely examined for the electrochemical sodium intercalation as early as the early 1980s. [136] Secondly, the success of LiCoO₂ as the cathode for lithium-ion battery, also promotes research on Na_xCoO₂ for SIBs. [137]

Na_xCoO₂ has a layered structure that can be described as OCONOCON..., where the O represents oxygen, C represents cobalt and N represents sodium. According to the various sodium coordination, there are four different phases that can be identified within the sodium composition range from 0.5 to 1.⁸ Following the traditional nomenclature, these four phases are denoted as O3, O'3, P'3 and P2 phases. Briefly, O is the octahedral coordination and P represents the trigonal prismatic coordination of the sodium ions; the number two (2) or three (3) implies the number of distinguishable sodium layers within the structure. These various phases can be obtained by controlling the sodium concentration. Specifically, NaCoO₂ is an O3 structure, Na_{0.77}CoO₂ is an O'3 structure, Na_{0.64} ≤ x ≤ 0.77 CoO₂ is a P2 structure and Na_{0.55} ≤ x ≤ 0.6 CoO₂ is a P'3 structure, respectively. Various crystal structures lead to differing electrochemistry and electrochemical performances. For example, the O3-phase cathode will transform into O'3 or P'3 phase. If the electrochemical reaction starts with the O'3 or P'3 phase, the value of 'x' can increase and the O3 phase material is always obtained, as shown in Fig. 16a. Many previous studies reported that the phase transition between the above three phases can easily take place at room temperature. [137, 138]

In contrast, when the electrochemical reaction starts with the P2 phases, the pristine structure can be preserved over the whole electrochemical process, as displayed in Fig. 16b. [139] Although this type of sodium cobaltate also undergoes a complex electrochemical reaction, the multiple plateaus upon charge-discharge are caused by the redistribution of Na⁺ during

intercalation-deintercalation process, not by the phase transitions. As a result, an improved structural stability leads to an overall better electrochemical performances. As far back as 1981, Delmas and co-workers¹³⁸ found that the P2 phase sodium cobaltates possess the highest capacity ($\sim 95 \text{ mAh g}^{-1}$) among the different types of sodium cobaltates. Besides, P2 phases offer longer cycle life and higher energy efficiency. Thus, P2 type sodium cobaltates have attracted much attention and have been regularly studied. In the following paragraphs in this section, P2 type sodium cobaltates will be discussed in detail.

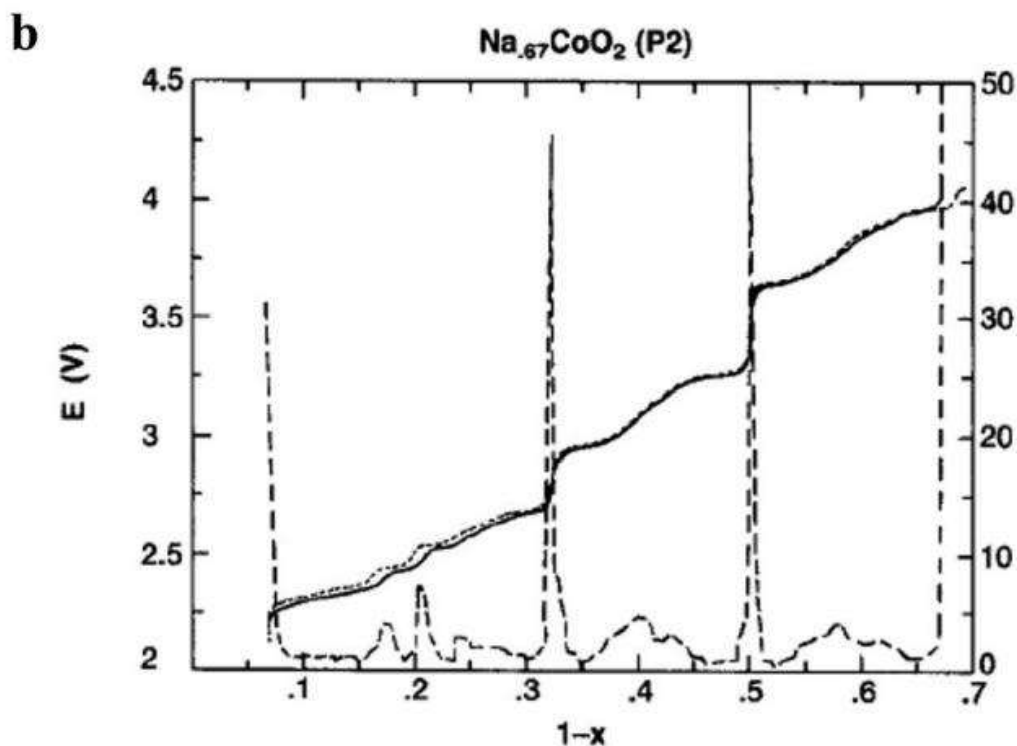
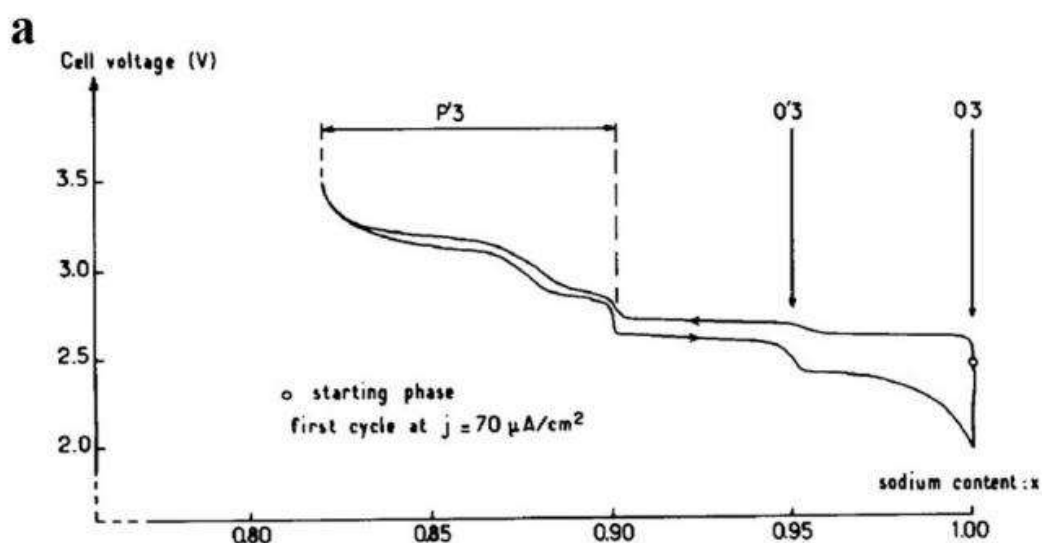


Fig. 16 (a) Emf composition curve obtained from NaCoO_2 (O3).¹³⁸ (b) Open-circuit potential vs. composition for $\text{P2-Na}_{0.67}\text{CoO}_2$ during ion intercalation (solid curve) and deintercalation (dotted curve).[139]

To understand the electrochemical behaviour of $\text{P2-Na}_x\text{CoO}_2$, the materials with different Na^+ compositions were investigated systematically. Three main factors cause the cationic redistribution, including the electrostatic repulsion between Na^+ ion in different planes, the repulsion between Na^+ and Co^{3+} through the common face of different polyhedra and the electronic interaction in the Co layer. The schematic of cationic redistribution in $\text{P2-Na}_x\text{CoO}_2$ is described in Fig. 17. The experimental result shows that the distribution of cationic ions has a significant impact on the electronic properties. Even a slight deviation (about 1% or 2%) can form a new distribution of the Na^+ ions. Thus, the investigation of $\text{P2-Na}_x\text{CoO}_2$ materials and their electrochemical performances is varied and interesting.[137]

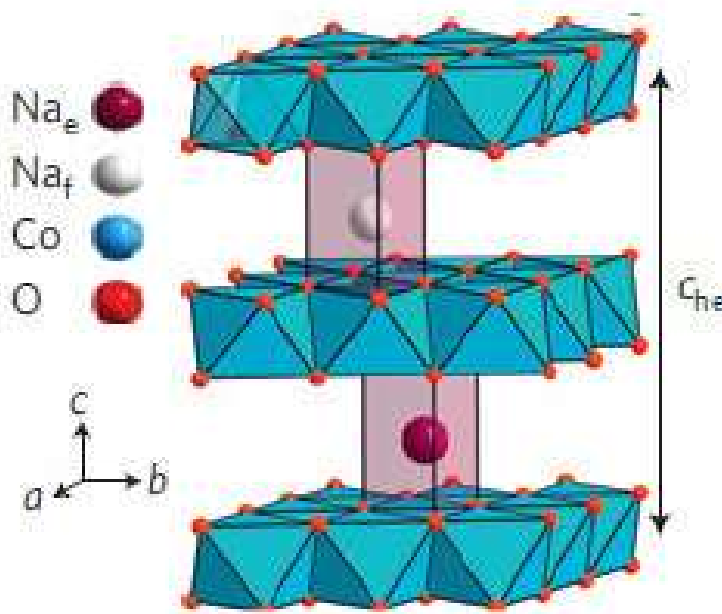


Fig. 17 Na^+ /vacancy ordering in the interslab space of the lamellar structure of $\text{P2-Na}_x\text{CoO}_2$ phases.[137]

As cathode material for SIB, the main disadvantage of $\text{P2-Na}_x\text{CoO}_2$ is its poor cycling performance.[140]¹⁴⁰ To solve this problem, several methods have been introduced such as morphology controlling, introduction of conductive substrate and cation doping. Recent work by

Lou's group proved that regular morphology and microsize can prolong the cycling life and improve the volumetric energy density of $\text{Na}_{0.7}\text{CoO}_2$. [141] Such $\text{Na}_{0.7}\text{CoO}_2$ was synthesized by a facile strategy. As shown in Fig. 18, regular sized CoCO_3 was used as the precursor, with the final product, regular- $\text{Na}_{0.7}\text{CoO}_2$ (r-NCO), maintaining a spherical morphology with a size of about 5 μm . Between the operating voltage range of 2.0-3.8 V (vs. Na/Na^+), this material offers a high specific capacity of 125 mAh g^{-1} at 0.04 C (about 5 mA g^{-1}). After 300 cycles, at 0.4 C, 86% capacity is preserved for the regular $\text{Na}_{0.7}\text{CoO}_2$, which is remarkably higher than that of the irregular version (only a low capacity retention of 46% after 200 cycles can be observed for irregular $\text{Na}_{0.7}\text{CoO}_2$). Even at a large rate of 16 C (about 2 A g^{-1}), regular $\text{Na}_{0.7}\text{CoO}_2$, still demonstrates a high specific capacity of 64 mAh g^{-1} , presenting excellent rate capability.

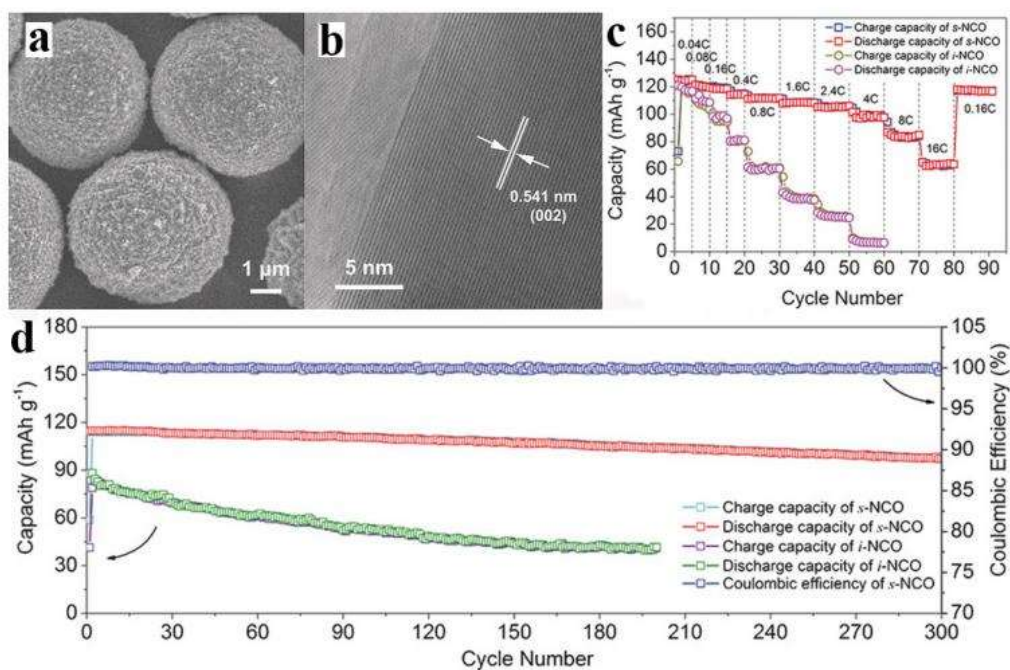


Fig. 18 (a) FESEM images and (b) HRTEM image of P2- $\text{Na}_{0.7}\text{CoO}_2$ microspheres. (c) Rate performance of s-NCO and irregular-NCO (i-NCO), and (d) Cycling performance of s-NCO and i-NCO at a current rate of 0.4 C and the corresponding Coulombic efficiency of s-NCO. (Note: $1\text{C}=125 \text{mAh g}^{-1}$). [141]

Nanocrystallization is another effective strategy to improve the electrochemical performance of electrode materials. Engineering $\text{Na}_{0.7}\text{CoO}_2$ arrays upon Ni foam can control the size and morphology of this sodium cobaltates. [142] As shown in Fig. 19, open architecture $\text{Na}_{0.7}\text{CoO}_2$

nanosheets can orderly grow on Ni foam. This composite shows a high areal capacity of 1.16 mAh cm⁻² at 1 C, with a prolonged cycling life being obtained. More than 50 mAhg⁻¹ capacity can be preserved after 1100 cycles, at 6 C. Furthermore, at a larger rate of 15 C, a capacity of 57.8 mAhg⁻¹ maintains. However, although the Ni foam substrate can bring significant advantages, such as binder free, high conductivity, open ion diffusion pathway, it will also reduce the energy density because Ni does not offer capacity.

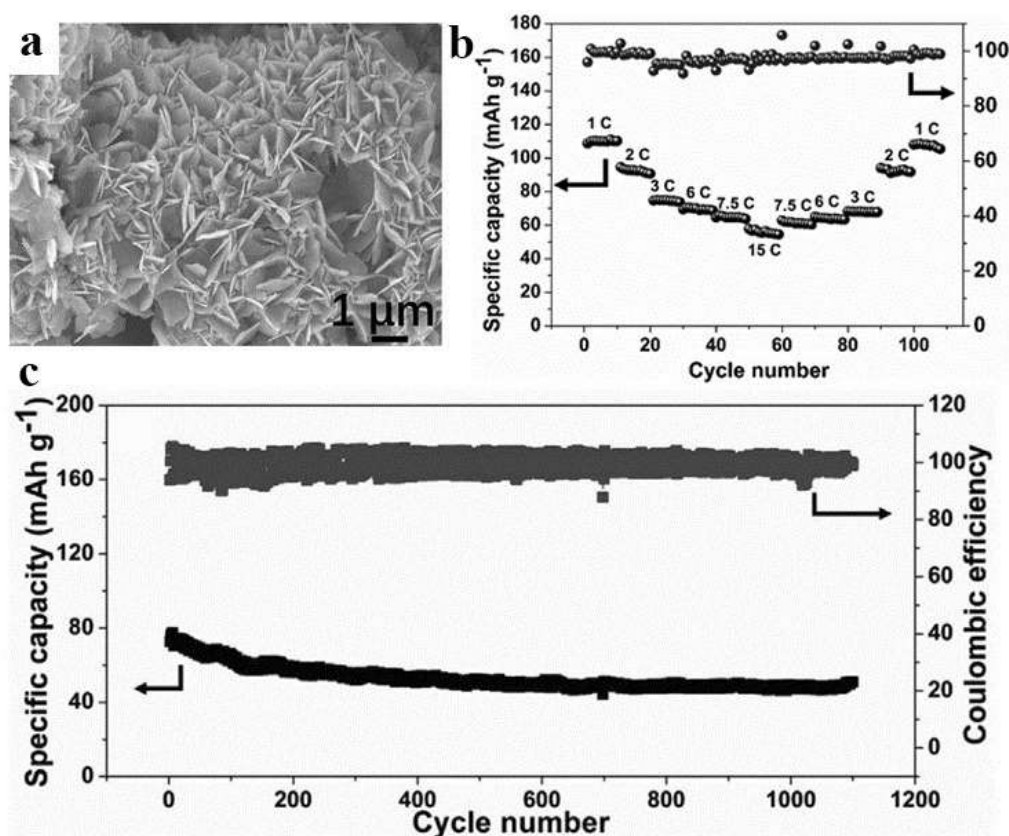


Fig. 19 (a) SEM images of Na_{0.7}CoO₂ arrays. (b) Rate performance at various current rates and Cycling performance of the Na_{0.7}CoO₂ electrode at a current rate of 6 C.[142]

It is believed that the cationic substitution improves the cycling life due to the suppression of the Na⁺/vacancy ordering condition.[143-145] Theoretical calculation results suggest that the P2-Na_xNi_yCo_{1-y}O₂ cathodes ($x=0.66$ or 0.75 , and $0 \leq y \leq 0.33$) are thermodynamically stable or metastable.[146] Therefore, a new type of P2-type layered transition metal oxide, Na_{0.75}Ni_{0.22}Co_{0.78}O₂, has been synthesized by Bianchini and co-workers. The introduction of nickel can increase the capacity and raise the average discharge voltage to ~3V. However, the cycling performance and Coulombic efficiency of this material should be further optimized.

Further investigations by Kang et al. have considered the effect of titanium substitution upon the $\text{P2-Na}_x\text{CoO}_2$.^[147] However, the content of Ti should not be higher than 10%, otherwise an unfavorable crystal phase is formed. Compared with pristine, the $\text{Na}_{0.67}\text{CoO}_2$, $\text{Na}_{0.67}\text{Co}_{0.90}\text{Ti}_{0.10}\text{O}_2$ possesses an improved cycling life and larger energy density. It should be noted that if the content of Ti increases more than 10%, the rate capability will decrease.

Over recent years, $\text{P2-Na}_x\text{CoO}_2$ has been regarded as an available cathode material for solid state SIBs. For example, a novel solid state sodium polymer battery consisting of a $\text{Na}_{0.7}\text{CoO}_2$ cathode, PEO-based electrolyte and Na metal anode has been reported by Singh et al.^[148] Under the optimized conditions, this battery exhibits a specific capacity of $\sim 138 \text{ mAh g}^{-1}$ at 0.1 C with a Coulombic efficiency of 99%. To further enhance the electrochemical performance, $\text{Na}_{0.7}\text{CoO}_2$ material that can be combined with some sodium oxyacids.¹³³ Briefly, $\text{Na}_{0.7}\text{CoO}_2$ when ball-milled with several sodium oxyacids (including NaNO_3 , Na_2SO_4 , Na_3PO_4 , NaBO_3 or Na_2CO_3), can form an amorphous cathode material. It should be pointed that when tested in a cell with a Na_3PS_4 solid electrolyte, the sodium oxyacids can enhance the malleability and ionic conductivity of $\text{Na}_{0.7}\text{CoO}_2$. In particular, $\text{Na}_{0.7}\text{CoO}_2\text{-NaNO}_3$ hybrid cathodes shows the highest ionic conductivity and capacity of 170 mAh g^{-1} in the 5th cycle. However, the rate capability of solid sodium battery assembled by $\text{P2-Na}_{0.7}\text{CoO}_2$ cathode should be further improved.

6. Conclusion and Outlook

As a promising candidate for grid-scale energy storage, SIBs have attract great attention due to the low-cost of sodium resources and electrochemical characteristics similar to those of LIBs. From the commercialization perspective, the primary parameters are the production and operation costs and long-term cycling capability. During the past few years, some achievements have already built upon the electrode material for SIB with high energy density and long cycle stability comparable to LIB counterparts. In addition, some new understanding of the Na^+ ion intercalation chemistry offers new design ideas for novel electrode materials that are potentially low-cost and scalable for manufacture. As a result, some classic materials with a long research history have been revitalized, including cobalt-based materials. Cobalt-based materials, as cathode or anode materials, are promising candidates for achieving high-performance SIBs for large-scale energy storage applications. The structure and specific capacities (practical and theoretical values) of

representative cobalt-based materials reported in recent years for SIBs are a foundation of SIB development based on LIBs and the knowledge from conversion mode systems and Li-S systems.

The layered $P2-Na_xCoO_2$, which has a longer history than $LiCoO_2$, faces the challenge of sufficient cycling stability because of the unavoidable intrinsic complex structural redistribution during Na^+ insertion/extraction. Using a strategy of suitable element doping/substitution, the fast degradation in the capacity may be mitigated or suppressed. This is a promising way to overcome the inherent defects of $P2-Na_xCoO_2$. Combined with rational structure design, the future of this layered metal oxide and its isostructural counterparts are expected to be useful in SIB electrode development.

For anode materials, various cobalt oxides, sulfides and selenides are all hindered by the conversion reactions, which creates shortcomings such as low reversibility, sluggish kinetics and large volume change especially when deep discharged to lower voltages. Although conversion reactions can deliver high theoretical capacities, most of the electrodes exhibit reversible capacities (in a limited voltage window) far lower than the theoretical values, indicating that oxide-based anodes require alternative material developments to offset low voltage influence on energy density for SIBs, as is the case for LIBs. One approach that tackles Na^+ insertion and volumetric expansion is carbon coating and electrical wiring. Another is the development of binder and conductive additive-free formulations that offset energy density loss to some degree, in cases where the lower voltage range is limited to avoid conversion reactions. This approach saves weight in the electrode formation. Cobalt chalcogenides have the higher conductivities than their metal oxide counterparts do. Thus, they are more promising than cobalt oxides for SIBs. It should be noted that the final products of the conversion reaction, Na_2S and Na_2Se , are similar to the Na-S battery and Na-Se battery. Maybe a successful strategy in these two fields are also effective to enhance the electrochemical performance of cobalt chalcogenides. In addition, the relationship between an ether-based electrolyte and the electrochemical behaviors of the cobalt-based anode should be studied more systematically in future.

By increasing the detail of the electrode design, such as with carbon decoration and nanostructuring, the cycle stability and rate capability can still be improved. Although many significant challenges lie ahead, the rapid advances in recent years by many researchers, together with the sustained interest from industrial and academic communities, indicate that cobalt-based

electrode materials are worth further investigation in the pursuit of low-cost, long-term life of SIBs.

Acknowledgements

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