

Review

A Brief Review of Catalytic Cathode Materials for Na-CO₂ Batteries

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Abstract: As an emerging energy storage technology, Na-CO₂ batteries with high energy density are drawing tremendous attention because of their advantages of combining cost-effective energy conversion and storage with CO₂ clean recycle and utilization. Nevertheless, their commercial applications are impeded by unsatisfactory electrochemical performance including large overpotentials, poor rate capability, fast capacity deterioration, and inferior durability, which mainly results from the inefficient electrocatalysts of cathode materials. Therefore, novel structured cathode materials with efficient catalytic activity are highly desired. In this review, the latest advances of catalytic cathode materials for Na-CO₂ batteries are summarized, with a special emphasis on the electrocatalysts for CO₂ reduction and evolution, the formation and decomposition of discharge product, as well as their catalytic mechanism. Finally, an outlook is also proposed for the future development of Na-CO₂ batteries.

Keywords: Na-CO₂ batteries; CO₂ capture and recycle; energy storage; electrocatalyst; electrocatalysis



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1. Introduction

With the rapid development and wide spread of electric vehicle and consuming electronics, energy storage devices featuring in high energy and power density, low cost, and long cycle life are highly desired [1–8]. Rechargeable batteries, supercapacitors and metal-ion hybrid devices are commonly used, but all of these systems have to deal with some drawbacks in terms of energy density, lifespan, and/or cost [9–14]. In addition, renewable and clean power sources such as wind and solar energy also need high-performance energy storage devices because of their intermittent and unstable characteristics [15,16]. On the other hand, the over consumption of non-renewable fossil fuels have not only caused energy crisis and environmental pollution but also produced large amount of greenhouse gas [17–19]. It is well accepted that CO₂ is the leading greenhouse gas, and its ever-growing emissions will lead to the catastrophic consequences of climate change, sea level rise, and glacier melting [20,21]. Therefore, researchers across the world devote extensive efforts to developing various chemical and physical routes to capture and store CO₂ or convert CO₂ into value-added materials [17,22–30]. However, most of these technologies deliver unsatisfactory performance due to the low efficiency conversion rate and high energy consumption, raising the overall cost and inhibiting the extensive applications.

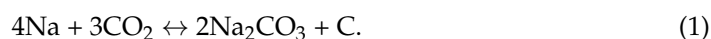
Recently, metal-CO₂ batteries, a type of metal–air batteries, have become one of the most appealing choices due to the unique feature of simultaneously consuming greenhouse gas CO₂ and generating electrical energy [16,18,20,31]. Arther et al. proposed the first prototype of the Li-CO₂ battery, which served as a primary battery and was supposed to capture and utilize CO₂ [32]. Later, Zhang et al. designed the first rechargeable Li-CO₂ battery, and a high capacity was harvested at room temperature by applying a catalytic cathode to promote the decomposition of insulating Li₂CO₃ [33]. Afterwards, a prosperous research field began rising, and various cathode materials, electrocatalysts, and electrolytes have been developed to improve the electrochemical performances of rechargeable Li-CO₂ batteries [34–36]. However, the limited and uneven distribution of lithium resources in the earth boost the price and impede the large-scale utilization of Li-based energy storage systems, motivating researchers to investigate alternatives to Li-CO₂ batteries.

Among various metal-CO₂ batteries, more research attention is being engendered to the Na-CO₂ batteries recently, which show the similar characteristics as their Li-based analogous, including high energy density (1125 W h kg^{−1}) and effective utilization of CO₂ but with low cost (vs. Li) and relatively high working voltage of 2.0 V (vs. Mg and Al, <1.0 V) [37–42]. Moreover, the low free energy ($\Delta rG_m^0 = -905.6 \text{ kJ mol}^{-1}$) for the reaction between Na and CO₂ leads to a smaller charge potential than that of Li ($\Delta rG_m^0 = -1081 \text{ kJ mol}^{-1}$), which is beneficial to suppressing electrolyte decomposition and thus helps to enhance round-trip efficiency and increase the lifespan [37]. Na⁺ as a charge carrier also possesses other advantages compared with Li⁺, such as less polarizing because of larger ion radius and higher coordination number, smaller charge transfer resistance, and faster electrode kinetics due to the lower solvation energy, demonstrating promising potential in Na-CO₂ batteries [43]. Das et al. reported a pioneering work of using a mixture of CO₂ and O₂ as the air cathode in a non-aqueous Na-O₂ battery with the main discharge products of Na₂O₂, Na₂C₂O₄, and Na₂CO₃, proving that CO₂ could be applied as an active material in Na-air batteries [44]. After that, Hu et al. reported a Na-CO₂ battery using multi-wall carbon tubes on Ni mesh as cathode in pure CO₂, and a lifespan of 200 cycles was successfully obtained [37]. Inspired by these exciting and promising investigations, researchers devoted more efforts into the development of novel structured cathodes and efficient catalysts, the anode surface modification as well as the electrolyte regulation for high-performance Na-CO₂ batteries [31,45,46].

However, the practical application of Na-CO₂ batteries is still inhibited by the unsatisfactory electrochemical performance involving limited cycle lifespan, low rate capability, high polarization, and low energy efficiency, which is mainly attributed to the inferior electrocatalyst cathodes [36,47]. Moreover, the reactions occurring at the cathode during charge and discharge processes should also be further explored in order to reveal the underlying mechanism. In this review, after a short introduction of Na-CO₂ batteries, the latest advances of catalytic cathode materials are systematically summarized, with an emphasis on the design of effective electrocatalysts and the corresponding catalytic mechanisms. Finally, an outlook is tentatively presented, and the challenges are also proposed for future development of Na-CO₂ batteries.

2. Na-CO₂ Batteries

Typically, Na-CO₂ batteries are composed of metallic Na anodes, CO₂-involved porous cathodes with sufficient gas-diffusion pathways and effective electrocatalyst, and ion-conducting separators immersing in sodium salts-containing electrolytes, as shown in Figure 1a. Na-CO₂ batteries have a working potential of 2.35 V (vs. Na/Na⁺) and follow a charge/discharge mechanism, as demonstrated in Equation (1): [37]



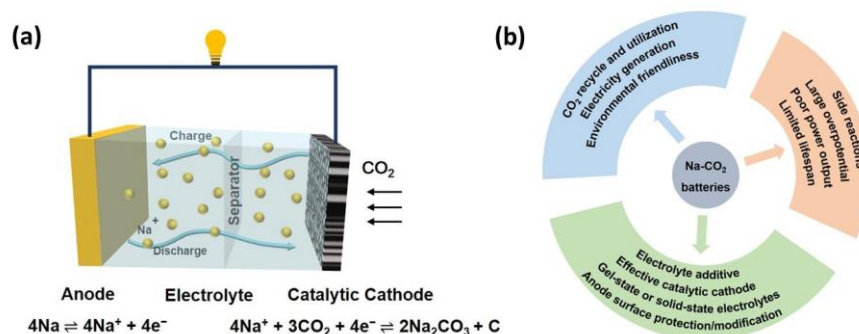


Figure 1. (a) The schematic configuration of rechargeable Na-CO₂ batteries; (b) The importance, existing challenges, and potential solutions for Na-CO₂ batteries.

Overall, the reactions of Na-CO₂ batteries are the reversible reduction and evolution of CO₂ accompanied by the formation and decomposition of Na₂CO₃. Specifically, during the discharge process, the stripping of the Na anode occurs with Na⁺ and electrons moving to the porous cathode where CO₂ is reduced via a carbon dioxide reduction reaction and the products of Na₂CO₃ and amorphous carbon generate, corresponding to the reaction: $4\text{Na}^+ + 4\text{e}^- + 2\text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{C}$. For the charge process, promoting by the catalytic cathode, the discharge products decompose into CO₂ through a carbon dioxide evolution reaction with Na⁺ and electron moving back and depositing on the anode, corresponding to the reaction $2\text{Na}_2\text{CO}_3 + \text{C} \rightarrow 4\text{Na} + 3\text{CO}_2$ [46]. The specific reactions taking place in the cathode and anode are also demonstrated in Figure 1a.

Obviously, as an emerging energy storage system with the merits of low cost and high energy density, Na-CO₂ batteries are of great significance for alleviating the global climate change and energy shortage by CO₂ recycle and utilization as well as electricity generation. Nevertheless, the inherent disadvantages pertaining to large overpotential (resulting in low energy efficiency), limited cycling life, poor rate capability, and serious side reactions hamper their practical applications. All these challenges urgently call for high-performance cathodes with effective catalysts, anode with stable solid–electrolyte interface as well as advanced electrolyte, as demonstrated in Figure 1b and discussed in the following paragraphs.

As one of the key components, cathode materials are in the spotlight in the realm of metal-CO₂ batteries. It is in the cathode where CO₂ is captured and utilized as well as the formation and decomposition of discharge products. Therefore, ideal cathode materials should have merits of high electrical conductivity, effective catalytic activity, excellent mechanical and electrochemical stability, and low cost. Moreover, the structure and porosity of the cathode materials (i.e., morphology, crystalline form, specific surface area (SSA), pore volume, and pore size distribution) also have a great impact on the catalytic effect and thus should be rationally designed. In Li-CO₂ batteries, carbon-based materials [33,48,49] have been widely used as cathodes and sometimes porous gold [50], NiO [51], Ag nanowires [37,52], and platinum net [33,53] have been applied to investigate the reaction products thus far. Similarly, these cathodes/catalysts are quite suitable for Na-CO₂ batteries, too. More importantly, to promote the CO₂ reduction and evolution reactions, highly efficient catalysts are urgently desired. The design strategies of catalytic cathodes and the understanding of their catalytic mechanism are the hottest research topics for Na-CO₂ batteries. In order to achieve high-performance cathode, various preparation techniques including solution-based processing, physical roll pressing and thin film-based technology have been used. Among these, solution-based cathode fabrication featuring mass production and ease of operation is the most commonly utilized. The typical process involves slurry preparing, coating, drying and pressing, which consume large amounts of organic solvents and energy and cause pollution and safety issues. On the other hand, mechanical roll pressing such as dry electrode coating has been developed by physically mixing the raw materials without solvent and then directly pressed into electrode with

desired thickness. Obviously, this emerging technology is pollute-free, energy saving, and much safer [54]. Nevertheless, the uniformity of the electrode prepared by this method needs to further be improved. In addition, other technologies such as vacuum filtration and chemical vapor deposition serve as facile methods to prepare thin film-based electrodes with adjusting thickness, which can be applied to fabricate binder-free and self-standing electrodes for wearable electronics.

Sodium metal is generally used as anode for Na-CO₂ batteries. However, as other sodium metal-based energy storage devices, serious side reactions and uncontrollable dendrite growth during the repeated charge/discharge process are two main obstacles for their practical applications. Therefore, one of the top priorities is to develop an effective way to inhibit the side reactions and form a compatible interface between the electrolytes and Na anode. Normally, both the liquid and solid-state electrolytes are unstable and have serious side reactions with the highly active Na metal, resulting in low Coulomb efficiency, high interfacial resistance, and sluggish Na⁺ ion transfer [55]. In order to form stable interface between Na anode and electrolytes, two strategies are commonly applied, namely, employing Na alloys instead of Na metal as anodes and adding buffer layers on the Na surface [56,57]. Na dendrite formation is another notorious problem for Na metal-based batteries and always leads to short circuit and safety issues. Recently, tremendous efforts have been devoted to solve the annoying problem, and several strategies have been proposed to construct stable dendrite-free sodium metal anodes, including designing effective Na hosts, electrolyte modification, sodium surface protection, or artificial solid electrolyte interface regulation [55,58–61]. Among these methods, special attention should be given to nanostructured framework for the Na anode, which can efficiently homogenize the near surface electric field and regulate the electron transport and ion flux [62,63]. Therefore, the local current density could be sufficiently reduced, and a smooth deposition without dendrite could be obtained.

Organic solvent-based liquid electrolytes are commonly used in Na-CO₂ batteries, but they face the challenges of decomposition because of high overpotential and safety issues such as flammability, volatilization, electrochemical instability and potential leakage risk [55]. In order to enhance the electrolyte stability and suppress the decomposition at high potential, Xu et al. reported an organic–inorganic hybrid liquid electrolyte by adding 10% ionic-liquid-tethered silica nanoparticles [64]. By using this modified electrolyte, the prepared devices could even be operated at a high voltage of 5 V. Furthermore, the quasi-solid- or all-solid-state electrolytes are employed to replace the conventionally used liquid ones due to two main reasons: (i) the safety issues of flammability and leakage of liquid electrolyte because of the open cell configuration of Na-CO₂ batteries can be effectively avoided; (ii) the long-term stability of Na metal anode can be realized by suppressing dendrite growth and inhibiting CO₂ corrosion [55,63,65,66].

However, the development of Na-CO₂ batteries is in a nascent stage, and several big challenges still exist, for instance, the irreversible capacity loss due to the formation of metal carbonates and the unwanted side reactions such as the decomposition of electrolyte and carbon cathode, which impedes the practical applications. Similar to the Li-CO₂ batteries, the sluggish kinetics of CO₂ reduction reaction (corresponding to the formation of Na₂CO₃ during the discharge process) and CO₂ evolution reaction (corresponding to the decomposition of the thermodynamically stable Na₂CO₃) in the cathode are the most critical steps affecting the rate and cycling performance of Na-CO₂ batteries, which is influenced by several factors [67]. For example, the CO₂ reduction and evolution is seriously restrained by the insufficient catalytic activity, resulting in large overpotential and inferior round-trip efficiency. Poor electronic conductivity and slow mass diffusion rate lead to inferior rate performance. Moreover, the surface or porous channels of the cathode materials are easily coated or blocked by the insulating and insoluble discharge products, which can passivate the catalytic centers and thus reduce the electronic conductivity, causing low capacity and unfavorable durability. Hence, advanced cathode materials with high efficiency and robust catalysts are highly needed to reduce the overpotential and

enhance the rate properties and cycling stability. In the following section of this minireview, we will focus on the recent progresses of catalytic cathode materials for Na-CO₂ batteries.

3. Catalytic Cathode Materials for Na-CO₂ Batteries

To realize the commercial implementations of Na-CO₂ batteries, it is of extensive significance to develop efficient cathode materials. During the past decades, fruitful achievements have been made for Na-CO₂ batteries, especially in the design of novel cathodes with highly efficient electrocatalyst materials. Electrocatalysts usually play an important role in promoting the reduction and evolution of CO₂ and the formation and decomposition of carbonates, which has a critical influence on the electrochemical performance of Na-CO₂ batteries.

Several figures of merit should be emphasized to obtain effective catalytic cathodes, which are exhibited in Figure 2. Firstly, materials with high electrical conductivity, rationally designed porous structure and large pore volume are preferable to enable fast electron transport, facilitate the mass (Na⁺ and CO₂) diffusion, and accommodate the insulating discharge products, aiming to reduce the impedance and thus to improve rate capability. Secondly, it is of equal importance for the cathode materials to possess strong binding affinity with CO₂, helping to decrease the reaction barriers at the gas/electrolyte/solid interfaces [65]. Last but not the least, ideal cathodes should have highly efficient catalytic activity to promote the CO₂ reduction and evolution and the decomposition of discharge products, which is beneficial to reduce the overpotential during charge and discharge and lead to high electrochemical performance. Therefore, high SSA with abundant and accessible catalytic sites is extremely desired [67]. Other factors about the catalytic cathodes, including resources abundance, environmental friendliness, and facile preparation process, are also vital for the practical applications of Na-CO₂ batteries.

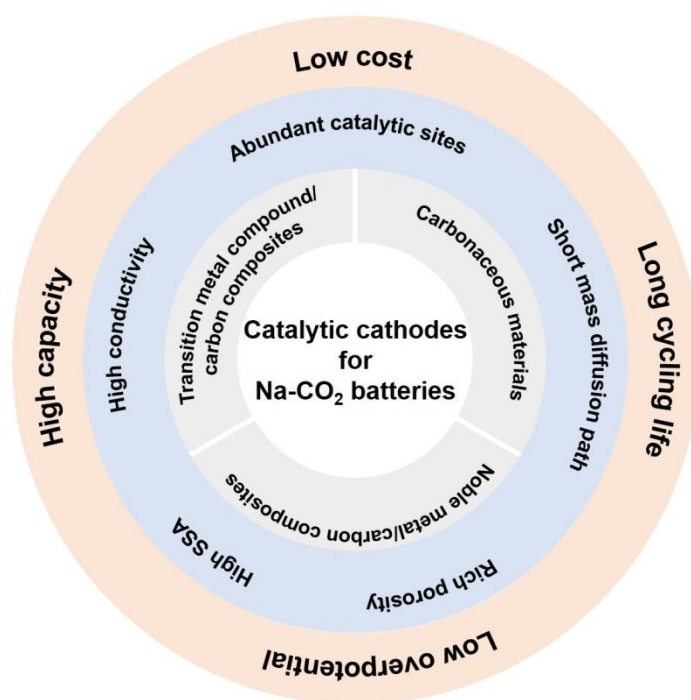


Figure 2. Effective catalytic cathode materials for high-performance Na-CO₂ batteries.

Typical catalytic cathode materials for high-performance Na-CO₂ batteries include carbon-based materials, noble metal/carbon-based materials, and transition metal oxide/carbon-based composites, as demonstrated in Figure 2. In this section, the latest achievements of catalytic cathode materials for Na-CO₂ batteries are reviewed with a special focus on the synthetic methods, structures, and catalytic mechanisms.

3.1. Carbonaceous Materials

Due to their appealing advantages of inherently high electronic conductivity, abundance, tunable pore structure, rich surface chemistry, and high SSA, carbon-based materials (i.e., commercial carbon black, carbon nanotubes, and graphene) have been extensively applied as active materials, conductive additives, or supports in various energy conversion and storage devices, including metal-CO₂ batteries [15,33,49,64,68–71].

Commercially available carbon materials such as Super P, ketjen black (KB) carbon and activated carbon have been adopted as cathode composites and/or catalysts in metal–air batteries because of their low cost and mature and scalable preparation processes [44,64,72,73]. For instance, Super P was used as the cathode material by Das et al. in the first report of CO₂ involved Na-air batteries [44]. Unfortunately, commercial carbons show unsatisfactory electrocatalytic performance because of their relatively low electronic conductivity, low SSA, small pore volume, and limited active centers. Therefore, heteroatom-doped carbons and novel nanostructured carbon materials have been developed to improve the catalytic property.

It has been corroborated in the realm of Li-CO₂ batteries that heteroatom dopants can be benefit to the CO₂ reduction and evolution reactions by adjusting the charge distribution of the carbon framework, enforcing the nearby carbon atoms positively charged and enhancing CO₂ adsorption affinity [69,74,75]. Doped carbons also serve well as cathodes in Na-CO₂ batteries. For example, Hu et al. reported an all-solid-state Na-CO₂ battery with zeolitic imidazolate frameworks (ZIF-8) derived N-doped nanocarbon as cathode, a Na metal anode, and a liquid-free PEO-based polymer electrolyte (Figure 3a) [65]. The cathode was facilely synthesized by calcinating ZIF-8 at a certain temperature and then washed by using diluted HCl. As revealed in Figure 3b, the as-prepared N-doped samples achieve a higher uptake of CO₂ than carbon black, although they have relatively smaller SSA. According to the calculation results, the N-doped surface shows stronger bond interaction with CO₂ than the undoped carbon surface (Figure 3c), which is expected to promote the reduction of CO₂ and the formation of discharge products. With the optimized N-doped nanocarbon (NC900), all-solid-state Na-CO₂ batteries were assembled, which demonstrated large discharge capacity (10,500 mAh g^{−1}), much reduced overpotential, longer cycling (320 h), and higher energy density (up to 180 Wh kg^{−1}). Particularly, as demonstrated in electrochemical impedance spectroscopy (Figure 3d), the impedance of the battery with NC900 cathode shows only a slight increase after 80 cycles resulting from the gradual accumulation of insulating discharge products, which was much better than that of a battery with carbon black cathode (around six times increase after seven cycles). The sharp contrast could be ascribed to the effective catalytic effects of the porous and highly conductive N-doped nanocarbon. Furthermore, the X-ray photoelectron spectroscopy (XPS) presents that the signals of CO₃^{2−} are clearly detected on the NC900 cathode after discharge and disappear after charge, confirming the reversible formation and decomposition of Na₂CO₃ (Figure 3e). It should be noted that doping is a feasible, facile, and low-cost strategy to enhance the electrochemical performance of pristine carbon materials, making it become a very promising method to prepare superior non-metal cathodes for Na-CO₂ batteries.

Carbon nanotubes are typical carbon-based nanostructured materials with high electronic conductivity, high SSA, and a unique one-dimensional structure, making them excellent cathode materials in Na-CO₂ batteries [52,66,76]. For example, Hu et al. designed rechargeable room-temperature Na-CO₂ batteries by using a Na-foil anode, an ether-based electrolyte, and a tetraethylene glycol dimethyl-treated multi-walled carbon nanotubes (t-MWCNT) cathode on Ni mesh [37]. The treated cathode has high electron conductivity, a three-dimensional tri-continuous porous structure to facilitate CO₂ adsorption, and favorable wettability to electrolyte, greatly benefiting the reaction in the gas/electrolyte/cathode boundary (Figure 4a). The as-prepared t-MWCNT-based devices deliver an extremely high capacity of up to 60,000 mAh g^{−1} (Figure 4b) and could run for 200 cycles with an initial discharge/charge voltage gap of only 0.6 V, which gradually increased to 1.3 V after 200 cycles (Figure 4c), demonstrating the excellent electrochemical properties of the catalytic t-MWCNT-based cathodes. More importantly, they first proposed and verified the

reaction mechanism and discharge product in the Na-CO₂ batteries. As we can see from the transmission electron microscope (TEM) image in Figure 4d, the grape-shaped discharged nanoparticles (50 nm) were randomly deposited on the t-MWCNT surface, which can be confirmed as polycrystalline Na₂CO₃ and amorphous graphite carbon by the clear fringes in the selected area electron diffraction (SAED, Figure 4e) and the high-resolution transmission electron microscopy (HRTEM) image (Figure 4f). The grape-like discharge products of Na₂CO₃ and C vanished after charge (Figure 4g). These results are consistent with diverse spectrum analysis. As shown in Raman spectra in Figure 4h, the peak of Na₂CO₃ (1180 cm⁻¹) initially appeared and increased during discharge, while it decreased and disappeared during charge. XPS exhibit the same trend (Figure 4i), implying the reversible formation and decomposition of Na₂CO₃. Electron energy loss spectroscopy (EELS) was applied to confirm the existence of carbon in the discharge products. As can be seen in Figure 4j, the visible edges at 280.8 eV correspond to the core-loss K edges of carbon atoms. For the discharge product, the peak intensity is much stronger, and the visible edge location is 3 eV lower than that of the standard Na₂CO₃ sample, demonstrating that the signals mainly stem from carbon. The peak disappears after charge, clearly indicating the excellent reversibility of the product carbon. Later, the same group also reported all-solid-state Na-CO₂ batteries with the MWCNTs cathode and NaF-modified anode [55]. To increase the adsorption ability of CO₂, MWCNTs were treated by acid to introduce the -COOH and -OH groups prior to use. Combining the succinonitrile-based plastic-crystal electrolyte and in situ generated NaF-rich interface on Na anode, the as-obtained devices show a high specific capacity (7624 mAh g⁻¹ at 50 mA g⁻¹), remarkable rate capability (2689 mAh g⁻¹ at 500 mA g⁻¹), and outstanding durability. Furthermore, an overpotential increase of only 0.33 V was received, demonstrating the unique design of the batteries.

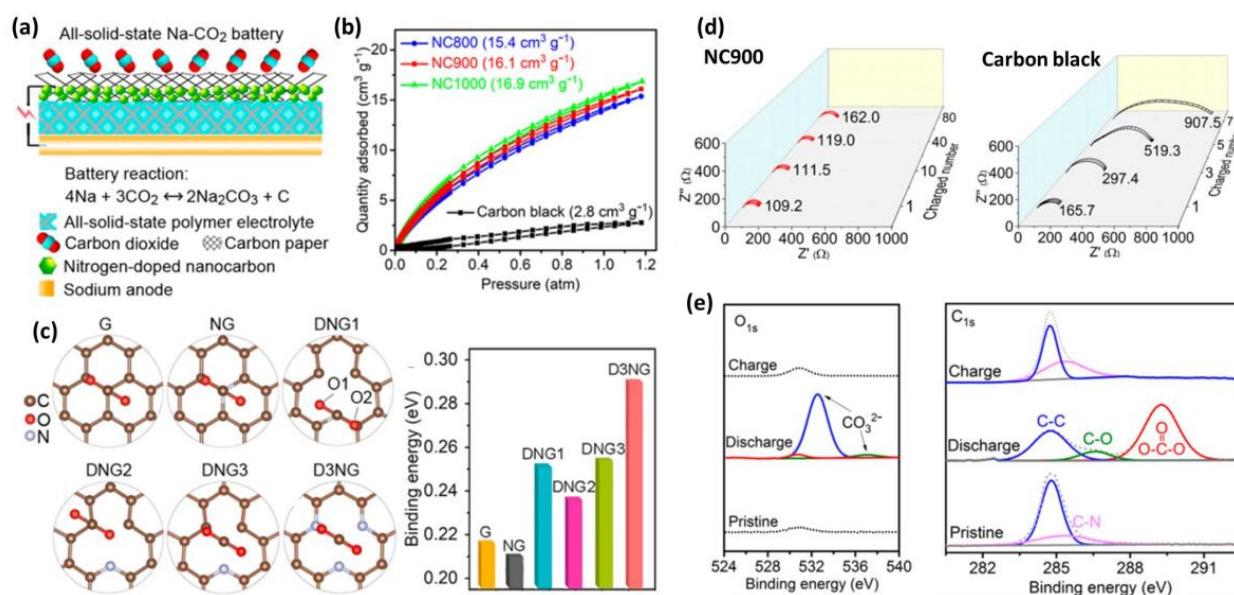


Figure 3. (a) All-solid-state Na-CO₂ battery configuration with N-doped carbon cathode; (b) Low-pressure CO₂-adsorption isotherms for N-doped nanocarbons and carbon black at 273 K with; (c) DFT calculations of undoped, graphitic N-doped, and pyridinic N-doped nanocarbon interacted with a CO₂ molecule and the calculated binding energies of one CO₂ molecule adsorbing on the undoped and doped nanocarbons; (d) Nyquist plots of Na-CO₂ batteries with NC900 cathodes and carbon black cathodes at different charged states; (e) XPS characterizations to confirm the reversible formation and decomposition of Na₂CO₃ in discharged and charged progress. Reproduced with permission from [65]. Copyright 2021, American Chemical Society.

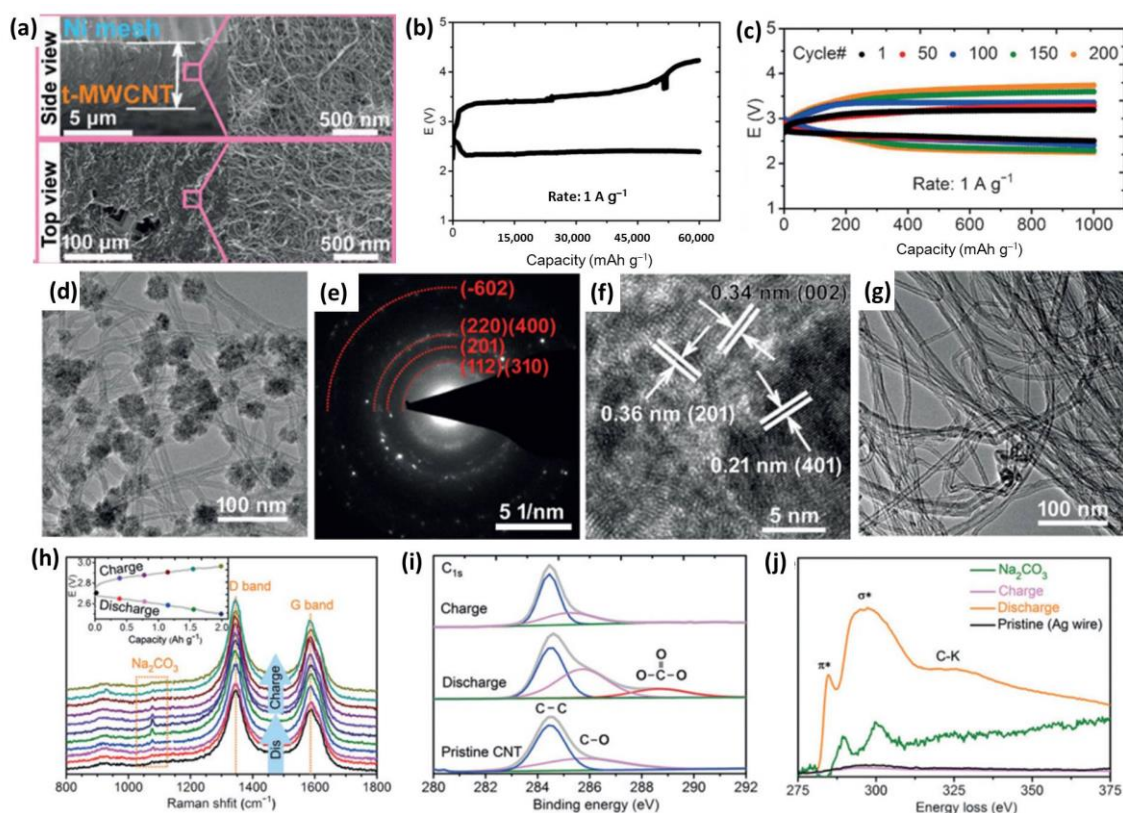


Figure 4. (a) SEM images of the t-MWCNT cathode from top and side views for the room temperature Na-CO₂ batteries; (b) Full discharge/charge curves at 1 A g⁻¹; (c) Discharge and charge profiles at 1 A g⁻¹; (d) TEM image, (e) SAED image, and (f) HRTEM image of t-MWCNT cathode after discharge for 4 h at 1 A h⁻¹; (g) TEM image of charge state of t-MCNT cathode; (h) In situ Raman spectrum and corresponding discharge/charge profiles with 11 selective points; (i) XPS and (j) EELS of Ag wire cathode at different states. Reproduced with permission from [37]. Copyright 2016, Wiley-VCH.

Overall, carbon-based materials are one of the most commonly used catalysts in Na-CO₂ batteries because of their extraordinary features of large SSA, high intrinsic electronic conductivity, high chemical and electrochemical stability, low cost, renewability, and rich surface chemistry. Nevertheless, as a catalytic cathode, carbon-based materials are far from reaching the requirements. To our best knowledge, the commercial carbons exhibit the unsatisfactory electrochemical performance among the carbon-based materials due to their inferior catalytic activity such as less active centers, relatively smaller SSA, and lower conductivity. Heteroatom-doped carbons show improved properties because of the stronger affinity of CO₂ by regulating the charge distribution of the carbon network, thus promoting the reduction and evolution of CO₂. However, big challenges still exist, including the uneven dopants distribution and the unexposed doped sites. Recently, nanostructured carbons such as CNTs and graphene are drawing more attention in metal–air batteries due to their novel structure, outstanding conductivity, and high SSA. However, both the serious agglomeration arising from strong π – π interaction and the high cost inhibit their practical application. In conclusion, carbon-based materials face the drawback of moderate catalytic effects, requiring effective strategies to tune the microstructure, porosity, defects, and dopants.

3.2. Noble Metal/Carbon Composites

Although carbon-based porous materials possess superior performance in electron and mass transfer, their catalytic activity is relatively low in terms of CO₂ reduction and evolution reactions and reversible conversion of the thermodynamically stable discharge products [77]. In other words, they can not effectively catalyze the formation and decom-

position of Na_2CO_3 . Therefore, various noble metal-based cathode materials have been designed, and their catalytic capability has been investigated in Na- CO_2 batteries [78]. For example, Guo et al. designed a cathode composite by depositing ruthenium (Ru) nanoparticles on the porous ketjen black carbon [79]. The Ru@KB composite was facilely prepared via in situ reduction of RuCl_3 in ethylene glycol in the presence of KB. Benefiting from the high catalytic activity of Ru nanospheres and the porous structure of KB, the reversibility of discharge product was greatly enhanced and the as-fabricated Na- CO_2 batteries with Ru@KB composite cathode delivered much improved discharge capacity (11537 mAh g^{-1}) as well as good cycling stability (over 130 cycles) with reduced overpotentials. Raman spectrum, X-ray diffraction (XRD), and XPS were used to analyze the Ru@KB at different states in the first cycle and the reversible formation and decomposition of Na_2CO_3 was confirmed, revealing the effective catalytic activity of Ru. Recently, Ru nanoparticles deposited onto CNTs (Ru/CNT) as a cathode composite were adopted by Thoka et al. to investigate and compare the mechanism, stability, overpotential, and energy density of Li- CO_2 and Na- CO_2 batteries [80]. As shown in the XRD patterns (Figure 5a), the peaks belonging to Na_2CO_3 were both observed after discharge in the 1st and 15th cycles, indicating the formation of Na_2CO_3 . In the charge state, the peaks related to Na_2CO_3 completely disappeared for the 1st cycle, while they remain for the 15th cycle, indicating incomplete decomposition. This result was also displayed and confirmed in SEM images (Figure 5b), XPS (Figure 5c), and Raman spectra. Furthermore, the catalytic ability of the Ru/CNT composite to promote the evolution of CO_2 was verified through in situ gas chromatography–mass spectrometry (GC–MS) during the charge process. As demonstrated in Figure 5d, only CO_2 evolution was revealed, with no obvious change in the evolution curves of O_2 and electrolyte decomposition, successfully proving that the efficient catalytic effect of Ru/CNT for the reversible decomposition of Na_2CO_3 to CO_2 . Similar trends were also presented in Li- CO_2 systems. Interestingly, the authors find that the reduction and evolution reaction of CO_2 are easier to perform for Na- CO_2 than for Li- CO_2 and the charge transfer resistance values in the Na- CO_2 systems are much lower than those in the Li- CO_2 systems at all states, demonstrating that the Ru/CNT-based catalytic cathode is more effective for Na- CO_2 batteries. Platinum (Pt)-based materials have also been used as the catalysts for energy conversion and storage devices [81–83]. Zhu et al. successfully constructed a Na- CO_2 nanobattery with a single Pt atom deposited on nitrogen-doped carbon nanotube (Pt@NCNT) as a cathode and probed the morphology evolution and phase transformations of the products during charge/discharge process using in situ environmental transmission electron microscopy [84]. As expected, thanks to the introduction of a single-atom Pt catalyst, the discharge rate was significantly boosted, and the cycling performance was largely promoted.

Compared with the pure carbon-based materials, noble metal-based catalysts supported by carbon materials demonstrate excellent catalytic activity in promoting the electrochemical reactions involved in Na- CO_2 batteries and thus enhanced the discharge/charge capacity; smaller overpotential and higher energy efficiency could be obtained. Typically, noble metal-based catalysts could help to decrease the active energy needed by the reduction of CO_2 and the decomposition of discharge products. Unfortunately, the high cost and the limited resources seriously impede the commercial applications of noble metal-based catalysts. In view of this, rational strategies should be explored, such as designing nanostructured materials and developing single-atom-based catalysts. In addition, other inexpensive and abundant metal-based catalysts are highly expected.

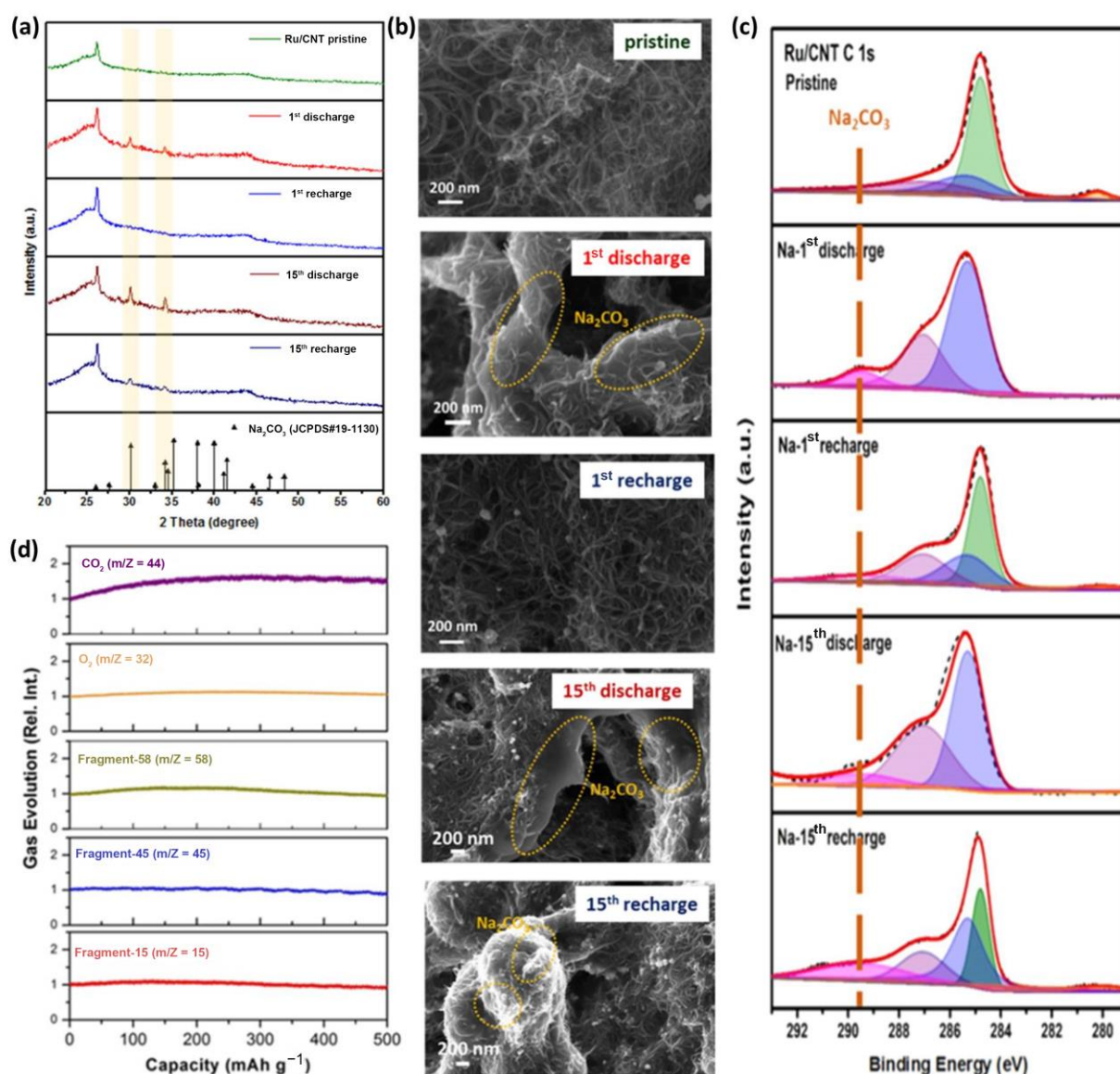


Figure 5. (a) XRD patterns, (b) SEM images, and (c) XPS spectra of Ru/CNT electrodes of the 1st and the 15th discharge–charge cycles in Na–CO₂ batteries; (d) In situ GC–MS characterization to detect gas evolution during the charging of Na–CO₂ batteries with the Ru/CNT cathode. Reproduced with permission from [80]. Copyright 2021, American Chemical Society.

3.3. Transition Metal Compound/Carbon Composites

In light of the moderate performance of carbon-based materials and high-cost of noble metal-based compounds, transition metal-based compounds of cost-effectiveness and natural abundance, especially Co-based catalysts, have been explored in metal-CO₂ batteries and other fields [48,85–88]. For example, Fang et al. proposed a facile method to screen efficient cathode catalysts through Na₂CO₃ activation experiment [89]. Through the in situ growth of Co₂MnO_x on carbon fibers and then followed by annealing at high temperature, flexible, and free-standing catalytic cathodes (CMO@CF) were prepared (Figure 6a). As revealed in XPS spectra (Figure 6b), both Co and Mn exist with a mixed valence state, which is expected to show excellent electrocatalytic activity. Not surprisingly, compared with pure cobalt oxide (CO@CF) and manganese oxide (MO@CF), Co₂MnO_x-based cathode can promote Na₂CO₃ decomposition at the lowest voltage and also exhibits higher discharge voltage plateau due to the co-existing hybrid Co²⁺/Co³⁺ and Mn²⁺/Mn³⁺ redox couples, proving the outstanding catalytic performance. As expected, the as-assembled Na–CO₂ batteries based on CMO@CNF show higher capacity (8448 mAh g⁻¹) with initial Coulombic

efficiency of 80.2% (Figure 6c), lower overpotential (1.77 V) (Figure 6d), and better cycling stability (Figure 6f), which is much better than that of the cathodes based on pristine CF and other metal oxides decorated CF. Thoka et al. fabricated a composite cathode of spinel ZnCo_2O_4 porous nanorods on MWCNT to decompose the insulating Na_2CO_3 [90]. Theoretical calculation results revealed that the three faces of [001], [111] with only exposed Co atoms and [111] of exposed Co and Zn atoms with decreased coordinate number had strong adsorption energy for CO_2 , Na, and Na_2CO_3 , which was favorable for catalyzing the reactions. Thus, the as-assembled Na- CO_2 batteries held a high reversible capacity of 12475 mAh g^{-1} , improved lifespan (over 150 cycles) and low overpotential.

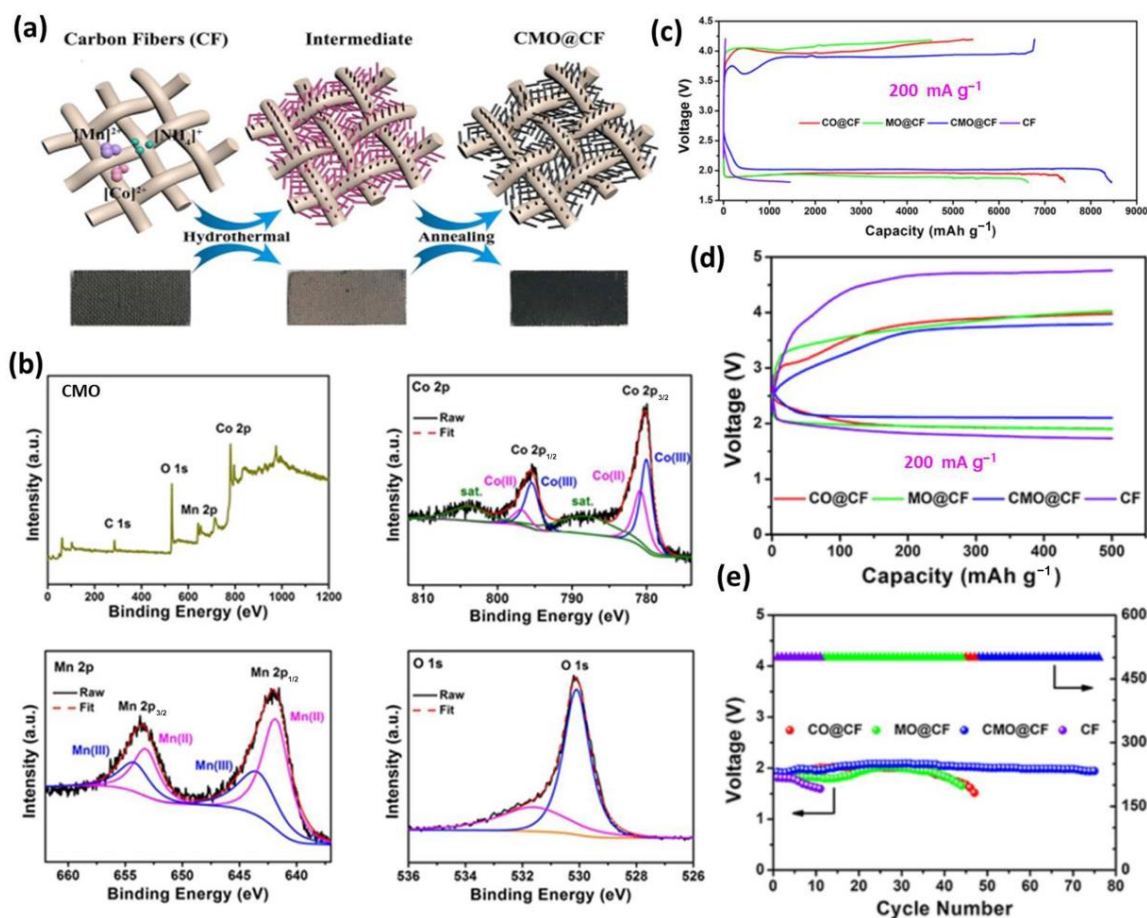


Figure 6. (a) Schematic illustration of preparation process of CMO@CF electrodes; (b) XPS spectra of CMO sample, Co 2p, Mn 2p, and O 1s; (c) Galvanostatic charge–discharge curves of the TMO@CF and CF cathodes with the cut-off voltage of 1.8–4.2 V; (d) Galvanostatic discharge–charge curves of the TMO@CF and CF electrodes at first cycles with a capacity limitation of 500 mAh^{-1} ; (e) The terminal discharge potential vs. the cycling number of the TMO@CF and CF at 500 mAh^{-1} . Reproduced with permission from [89]. Copyright 2018, American Chemical Society.

Loading Co-based compounds into a heteroatom-doped carbon matrix is another strategy to enhance the catalytic performance for Na- CO_2 batteries. For instance, Xu et al. reported a highly efficient catalytic cathode through encapsulating evenly dispersed Co/ Co_9S_8 nanoparticles into biomass-derived S,N-codoped hierarchically porous carbon (Co/ Co_9S_8 @SNHC) [67]. The cathode composites were prepared as depicted in Figure 7a. Firstly, areca catechu was washed and dried; then, it was carbonized at 500°C and activated by KOH at 800°C to obtain biomass-derived hierarchically porous carbon. Secondly, S and N dopants were introduced by annealing the porous carbon in the presence of $(\text{NH}_4)_2\text{S}$. Finally, the final Co/ Co_9S_8 @SNHC samples were collected via a hydrothermal reaction of doped porous carbon with Co source in combination with high-temperature treatment. Several advantages were obviously demonstrated because of the elaborate struc-

tural design. The highly conductive and hierarchically porous structure of the composite could facilitate electron and mass transport, electrolyte infiltration, and CO_2 diffusion, and provide sufficient voids to accommodate the discharge products. Moreover, the overgrowth and agglomeration of Co_9S_8 could also be suppressed so that more active centers could be exposed (Figure 7b). As clearly displayed in Figure 7c–e, as expected, Na- CO_2 batteries with $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$ as the cathode delivers a high discharge capacity of 7421 mAh g^{-1} (vs. 6025 mAh g^{-1} for SNHC), narrower overpotential gap, and long lifespan of over 200 cycles. The excellent electrochemical performance was ascribed to the synergistic effect of S and N dopants, carbon defects, and the Co_9S_8 loaded in the robust and highly porous carbon skeleton of the catalytic cathode, which promoted the CO_2 reduction and evolution and Na_2CO_3 formation and decomposition.

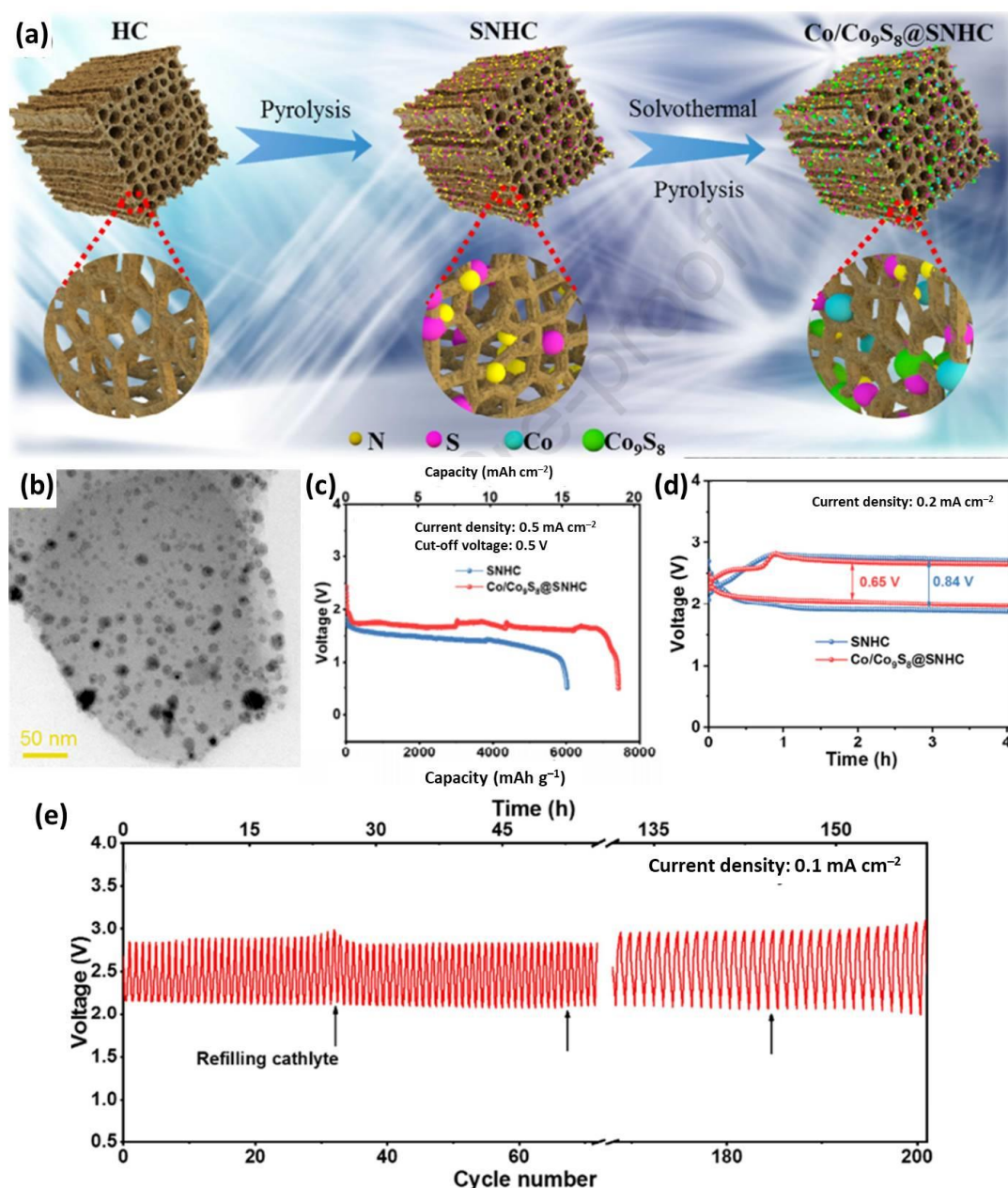


Figure 7. (a) Schematic illustration of synthesis procedures for $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$; (b) TEM images of $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$; (c) Discharge capacity of Na- CO_2 batteries with $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$ or SNHC; (d) Discharge-charge curves at a current density of 0.2 mA cm^{-2} of Na- CO_2 batteries with $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$ or SNHC; (e) Cycling performance of Na- CO_2 battery with $\text{Co}/\text{Co}_9\text{S}_8@\text{SNHC}$ as the catalyst. Reproduced with permission from [67]. Copyright 2021, Elsevier.

Obviously, by forming composites with carbon, transition metal-based materials are considered to be the most appealing catalytic cathodes for Na-CO₂ batteries due to the combination of merits of the two components, i.e., the high SSA and electronic conductivity of carbon and the effective catalytic effects of metal compounds. Hence, more attention should be devoted to design composites of carbon and transition metal-based compounds with novel structures and to investigate the interaction between them in future studies. Another future research direction of transition metal-based catalytic cathodes is their controllable and large-scale production, which is of paramount significance for commercial applications.

As discussed above, the design and fabrication of advanced catalytic cathodes has been the research hotspot in Na-CO₂ batteries due to the sluggish kinetics of reactions occurring at the cathode such as the reduction and evolution of CO₂ and the decomposition of discharge products. These reactions have crucial effects on the discharge capacity, overpotential, rate capability, energy efficiency, and cycling life. Thus, these challenging problems promote researchers to develop advanced catalytic cathodes for Na-CO₂ batteries, and exciting progresses have been achieved, as summarized in Table 1.

Table 1. Summary of recent progress in catalytic cathodes for Na-CO₂ batteries.

Cathode	Overpotential (V)	Discharge Capacity (mAh g ⁻¹)	Cycling Stability	Ref.
t-MWCNT	0.6 (1 A g ⁻¹)	60,000 (1 A g ⁻¹)	200 cycles (2000 mAh g ⁻¹)	[37]
MWCNTs	1.53 (50 mA g ⁻¹)	7624 (50 mA g ⁻¹)	50 cycles (1000 mAh g ⁻¹)	[55]
a-MCNT	0.74 (100 mA g ⁻¹)	5000 (50 mA g ⁻¹)	400 cycles (1000 mAh g ⁻¹)	[63]
N-doped nanocarbon	1.5 (200 mA g ⁻¹)	10,500 (300 mA g ⁻¹)	100 cycles (400 mAh g ⁻¹)	[65]
Ru@KB	1.5 (200 mA g ⁻¹)	11,537 (100 mA g ⁻¹)	130 cycles (1000 mAh g ⁻¹)	[79]
Ru@CNT	≈1.6 (100 mA g ⁻¹)	19,533 (100 mA g ⁻¹)	100 cycles (500 mAh g ⁻¹)	[80]
Ru/CNT	1.4 (100 mA g ⁻¹)	28,830 (100 mA g ⁻¹)	70 cycles (500 mAh g ⁻¹)	[78]
CMO@CF	1.47 (100 mA g ⁻¹)	8448 (200 mA g ⁻¹)	75 cycles (500 mAh g ⁻¹)	[89]
ZnCo ₂ O ₄ @CNT	1.5 (100 mA g ⁻¹)	12,475 (100 mA g ⁻¹)	150 cycles (500 mAh g ⁻¹)	[90]
Co/Co ₉ S ₈ @SNHC	≈0.32 V (0.2 mA cm ⁻²)	≈18.9 mAh cm ⁻² (0.5 mA cm ⁻²)	200 cycles (0.1 mA cm ⁻²)	[67]

4. Conclusions and Outlook

As a potential solution for energy crisis and climate change, rechargeable Na-CO₂ batteries have emerged as a promising technology due to their combination of CO₂ capture and utilization with electric energy generation in addition to low cost and high energy density. In this review, recent achievements of catalytic cathode materials for Na-CO₂ batteries have been briefly reviewed, and the material preparation routes, structures, and catalytic mechanisms have been also specially emphasized. Nevertheless, despite great progress, the research of Na-CO₂ batteries is still in its infancy compared with other energy storage systems, and big challenges remain in this realm such as inferior cyclability, poor rate capability, large discharge/charge overpotential gap, and low round-trip efficiency. All these drawbacks could be ascribed to the cathode-related electrochemical reactions, namely, CO₂ reduction/evolution and Na₂CO₃ formation/decomposition. To develop high-performance Na-CO₂ batteries, we tentatively propose the following perspectives:

(i) Exploring effective catalytic cathode materials should be given top priority. In view of the cost and performance, it is a very promising strategy to fabricate composites with porous carbons and transition metal-based compounds. Moreover, heteroatom doped carbon and single-atom catalysts should be also given more attention.

(ii) The highly reactive Na foil could cause serious side reactions by reacting with electrolyte and the Na dendrite formation during repeated charge/discharge processes, resulting in low Coulomb efficiency and intractable safety issues. Therefore, feasible surface coating materials and/or techniques should be investigated for Na anode to suppress the dendrite growth. In addition, great efforts are required to develop quasi-solid-state or all-solid-state electrolytes to replace the flammable and volatile liquid electrolyte to further enhance the safety of Na-CO₂ batteries [78].

(iii) Novel device configurations need to be proposed. For example, Xu et al. proposed hybrid Na-CO₂ batteries with an Na Super Ionic Conductor structured ceramic separator separating the aqueous electrolyte and organic electrolyte [91]. Notably, the aqueous electrolyte provides a possible method to solve the accumulation and blockage of discharge products, which are insoluble in organic electrolyte systems.

(vi) With regard to the abundance of K and its similar electrochemical properties as Na, K-CO₂ batteries can also serve as a promising alternative to Na-CO₂ batteries [92,93]. Moreover, more efforts should be also devoted to other metal-based CO₂ batteries such as Al-CO₂, Mg-CO₂, and Zn-CO₂ systems because of their merits of low reactivity anodes, abundant reserves, and high theoretical specific capacities [39,40,94,95].

In conclusion, Na-CO₂ batteries are one of the most promising technologies to solve the energy and environmental problems simultaneously in spite of the remained scientific and technical challenges. The rational design of electrocatalysts toward high activity can act as a feasible strategy for the construction of high-performance Na-CO₂ batteries. Along this line, fruitful achievements have been attained to date. However, the commercial application of Na-CO₂ batteries is still waiting to be enabled by continuous efforts and long-term endeavors from both theoretical and practical explorations.

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