

Catalytic Cathodes for Na-CO₂ Batteries

Subjects: Electrochemistry

Contributor: Dong Sui

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.

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

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][2][3][4][5][6][7][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][10][11][12][13][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][18][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][23][24][25][26][27][28][29][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][35][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.

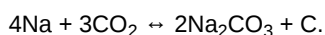
Among various metal-CO₂ batteries, more research attention is being engendered to the Na-CO₂ batteries recently, which show the similar characteristics as their Li-based analogous, including high energy density (1125 W h kg⁻¹) and effective utilization of CO₂ but with low cost (vs. Li) and relatively high working voltage of 2.0 V (vs. Mg and Al, <1.0 V) [37][38][39][40][41][42]. Moreover, the low free energy ($\Delta G^0_m = -905.6 \text{ kJ mol}^{-1}$) for the reaction between Na and CO₂ leads to a smaller charge potential than that of Li ($\Delta G^0_m = -1081 \text{ kJ mol}^{-1}$), 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].

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]



(1)

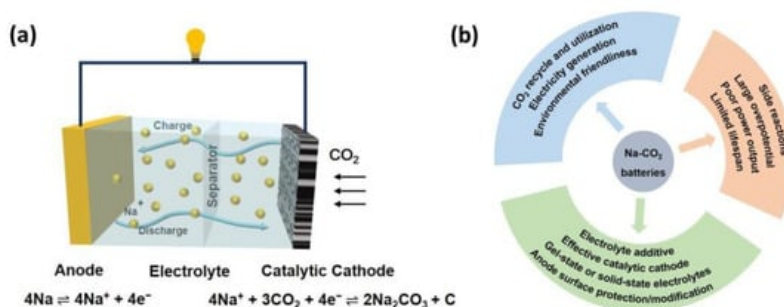


Figure 1. (a) The schematic configuration of rechargeable Na-CO₂ batteries; (b) The importance, existing challenges, and potential solutions for Na-CO₂ batteries.

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, idea 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][59][60][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 CO_2) 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 CO_2 , 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 CO_2 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- CO_2 batteries.

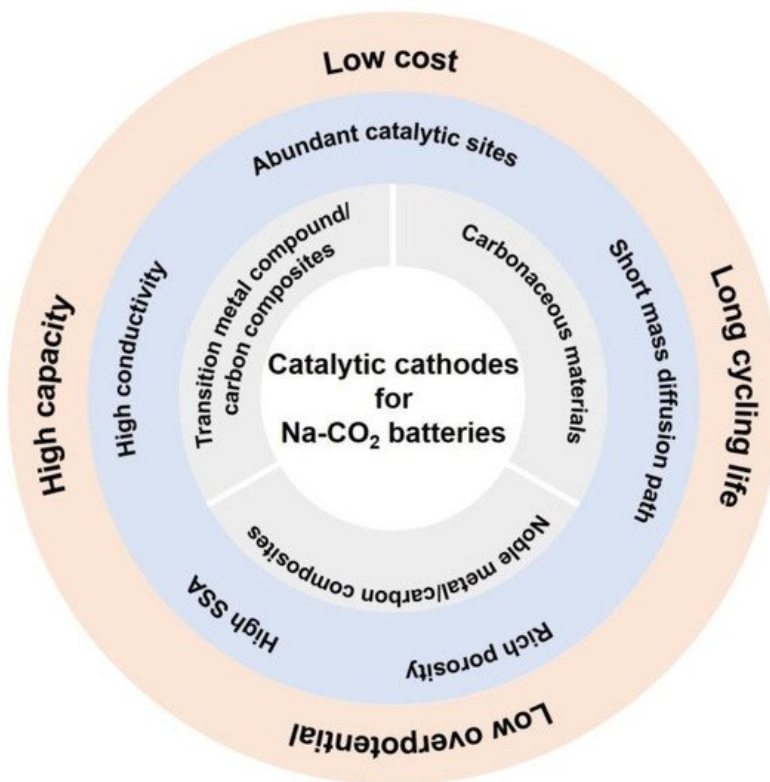


Figure 2. Effective catalytic cathode materials for high-performance Na- CO_2 batteries.

Typical catalytic cathode materials for high-performance Na- CO_2 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- CO_2 batteries are reviewed with a special focus on the synthetic methods, structures, and catalytic mechanisms.

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