



Exploring the frontiers of catholyte in hybrid Na-CO₂ batteries

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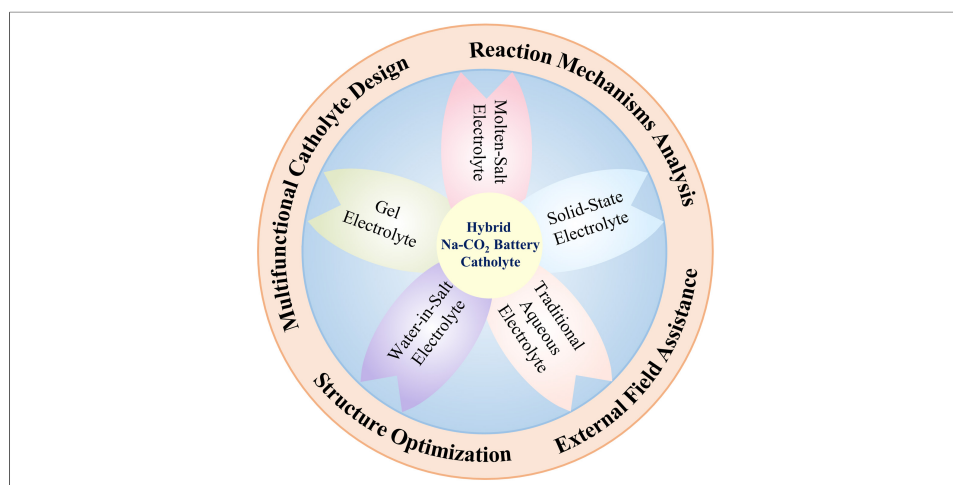
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Abstract

Metal-carbon dioxide (M-CO₂) batteries are a promising dual-function technology for addressing the urgent need for high-energy-density storage and the imperative of carbon capture and utilization. Among them, hybrid Na-CO₂ batteries belonging to the alkali metal-CO₂ family offer unique advantages of resource abundance, enhanced safety, and reaction pathways toward valuable chemicals through a proton-coupled electron transfer mechanism. Among battery components, the catholyte and its nature influence ion transport, establish the micro-reaction environment at the catalyst interface, and directly determine the discharge product speciation and overall cell performance. However, despite growing interest in hybrid Na-CO₂ batteries, review reports thoroughly examining design principles of catholytes, along with their challenges and advances, are still lacking. In this paper, we systematically review the latest progress in catholyte development for hybrid Na-CO₂ batteries, covering aqueous electrolytes, water-in-salt electrolytes, gel electrolytes, molten-salt electrolytes, and solid-state electrolytes. We critically analyze the fundamental

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electrochemical reaction mechanisms, discharge product characteristics, and the corresponding advantages and limitations for each system. Key challenges, such as the narrow electrochemical stability window (ESW), interface compatibility issues, sluggish CO₂ reduction kinetics, and the trade-off between product selectivity and long-term stability, are highlighted. Finally, future research perspectives and directions, emphasizing in-depth mechanistic understanding through advanced operando characterization, rational design of electrolyte-catalyst interfaces, and the development of multifunctional electrolyte systems, are proposed to achieve efficient, durable, and economically viable hybrid Na-CO₂ batteries for practical carbon-neutral energy applications.

INTRODUCTION

The Industrial Revolution and excessive consumption of fossil fuels resulted in increased atmospheric CO₂ concentrations reaching over 425 ppm as of 2024, which, in turn, induced a global warming equivalent to a 1.5 °C rise in global temperature^[1,2]. These compounding pressures of climate change induce extreme weather, ocean acidification, and ecosystem imbalance, posing serious challenges to the sustainable development of human society^[3]. Under these conditions, traditional carbon capture, utilization, and storage (CCUS) technologies, considered a key pathway, have failed due to their high energy consumption and operating costs, especially when considering the continuous rise in carbon emissions, thereby limiting their large-scale application^[4,5]. Alternatively, metal-carbon dioxide (M-CO₂) batteries, deeply integrating energy storage and CO₂ utilization, are innovative systems with unique dual advantages of converting CO₂ as a cathode active material into high-value chemicals, such as carbonates, formates, or carbon monoxide, allowing the realization of *in-situ* resource utilization of greenhouse gases while producing energy with a theoretical energy density of up to 1,880 Wh kg⁻¹, a value significantly better than that of traditional lithium-ion batteries (LIBs, ~250 Wh kg⁻¹)^[6-8]. Among M-CO₂ batteries, alkali metal (Li, Na, and K)-carbon dioxide batteries exhibit unique electrochemical advantages in terms of low electrochemical potentials of its anode metals [-3.04 V vs. standard hydrogen electrode (SHE) for Li, -2.71 V vs. SHE for Na, and -2.93 V vs. SHE for K], as well as excellent theoretical energy densities induced by the multi-electron reduction reaction of the CO₂ cathode^[6,9]. Furthermore, the low free energy generated by the interaction between alkali metals and CO₂ endows the battery with a lower charging potential, helping to suppress electrolyte decomposition, improve round-trip efficiency, and extend battery life^[10,11]. Among the alkali M-CO₂ battery family, Na-CO₂ batteries are synergistically advantageous in terms of resource sustainability and high electrochemical performance. In fact, the resource abundance of sodium with a crustal content of 2.36 wt% is about 3 orders higher than that of lithium (0.0017 wt%), with an even global distribution preventing geopolitical risks and supply chain vulnerabilities from the available sources^[12,13]. Na-CO₂ batteries also operate on a reversible reaction pathway, resulting in a relatively low operating voltage that suppresses electrolyte decomposition and improves cycle efficiency for better electrochemical properties^[14]. The Na⁺ phase, with a small Stokes radius (1.02 Å) and a first ionization energy (495.8 kJ mol⁻¹), also improves the ion transport dynamics of Na⁺ over a wide temperature range, endowing the batteries with excellent low-temperature electrochemical performance^[15,16].

A typical Na-CO₂ battery can be configured from a Na anode and a highly porous cathode to facilitate CO₂ gas diffusion and electrochemical reactions. The two electrodes are separated by a polymeric or ceramic membrane and are immersed in an electrolyte^[17-19]. Na-CO₂ battery systems are generally categorized into two main types depending on the nature of the electrolyte. The first has to do with nonaqueous Na-CO₂ batteries (defined as aprotic and solid-state Na-CO₂ batteries), and the second deals with hybrid aprotic/aqueous (referred to as “hybrid”) Na-CO₂ batteries^[20-22]. In nonaqueous electrolyte systems, discharge products of Na-CO₂ batteries, such as Na₂CO₃, are typically insoluble and electrochemically inert^[20]. They can also deposit inside the pores of the gas diffusion electrode, gradually covering the active sites and blocking the CO₂ transport channels, passivating the electrode and degrading battery performance^[23,24]. This bottleneck can be overcome by constructing hybrid Na-CO₂ batteries with the configuration of “Na|aprotic

electrolyte| $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON) solid electrolyte|aqueous electrolyte| CO_2 electrode”^[25], in which the unique dual-chamber structure provides the hybrid Na- CO_2 battery with several significant advantages. The first is highly efficient reaction kinetics, in which the high solubility of CO_2 in aqueous electrolytes enhances CO_2 mass transfer, thereby greatly increasing the positive electrode reaction rate. The second is excellent cycle stability, in which discharge products, such as formate or carbonate, may dissolve in the aqueous electrolyte to effectively prevent their accumulation as solid products in the cathode pores, thereby avoiding electrode passivation and enhancing the long-term activity of the reaction interface and extended battery life. The third advantage has to do with the intrinsic safety, where the NASICON solid electrolyte acts as a physical barrier to completely isolate the aqueous electrolyte and cathode active material from the metallic sodium anode, fundamentally eliminating the side reactions between the active material and the Na anode for significantly improved chemical compatibility and battery safety performance. Last but not least, the fourth advantage relies on product controllability, where the reduction pathway of CO_2 in aqueous solution can be selectively converted by controlling the catalyst and reaction conditions to generate high-value-added chemicals, such as formic acid, carbon monoxide, and methanol, according to the proton-coupled electron transfer mechanism^[21,26]. Together, these advantages have made the hybrid Na- CO_2 batteries very promising for integration into energy storage-carbon sequestration technologies, moving forward from proof of concept to practical application.

So far, significant progress has been made in hybrid Na- CO_2 batteries, as an emerging electrochemical energy storage and carbon fixation technology. For instance, a rechargeable hybrid Na- CO_2 battery with an aqueous cathode electrolyte was reported in 2018 for the first time and was found to continuously generate electrical energy during discharge while producing hydrogen instead of CO_2 during charging^[21]. Further optimization of the battery structure, along with the development of novel cathodes, efficient catalysts, electrolytes, and discharge products, resulted in gradually improved electrochemical performances of the hybrid Na- CO_2 batteries, as depicted in Figure 1A. Among hybrid Na- CO_2 battery components, the catholyte plays a crucial role in connecting the solid electrolyte and the catalyst layer, along with providing a proper micro-reaction environment for CO_2 reduction on the catalyst layer, thereby directly affecting the electrochemical performance of the whole battery^[27–29]. In practice, catholytes not only require basic characteristics, such as high ionic conductivity, good thermal stability, superior chemical/electrochemical stability, environmental friendliness, and low cost, but should also possess easily tunable solvation structures to regulate the interfacial micro-reaction environment^[9,30–33]. However, unfortunately, only a handful of review papers have so far reported the progress on hybrid Na- CO_2 battery catholytes, often as a subsection in general M- CO_2 battery reviews^[29].

Herein, a thorough investigation of the influence of catholyte on the reaction mechanism and electrochemical performance of hybrid Na- CO_2 batteries is performed by focusing on the latest research progress of catholytes [Figure 1B]. A detailed discussion of the electrochemical reaction mechanism of hybrid Na- CO_2 batteries is provided, along with an in-depth analysis of discharge products. The challenges and future development trends of hybrid Na- CO_2 battery cathode electrolytes are also summarized. We believe that this article contributes to providing an in-depth understanding of hybrid Na- CO_2 battery systems and can be used as a reference for future research and development of hybrid Na- CO_2 battery systems.

OVERVIEW OF HYBRID NA- CO_2 BATTERY

Mechanism of hybrid Na- CO_2 batteries

Despite the relatively early development of non-aqueous Na- CO_2 batteries, the separator’s inferior physicochemical properties and inability to effectively prevent the crossover of active species have led to severe anode corrosion and dendrite growth [Figure 2A]. These issues significantly compromise both the

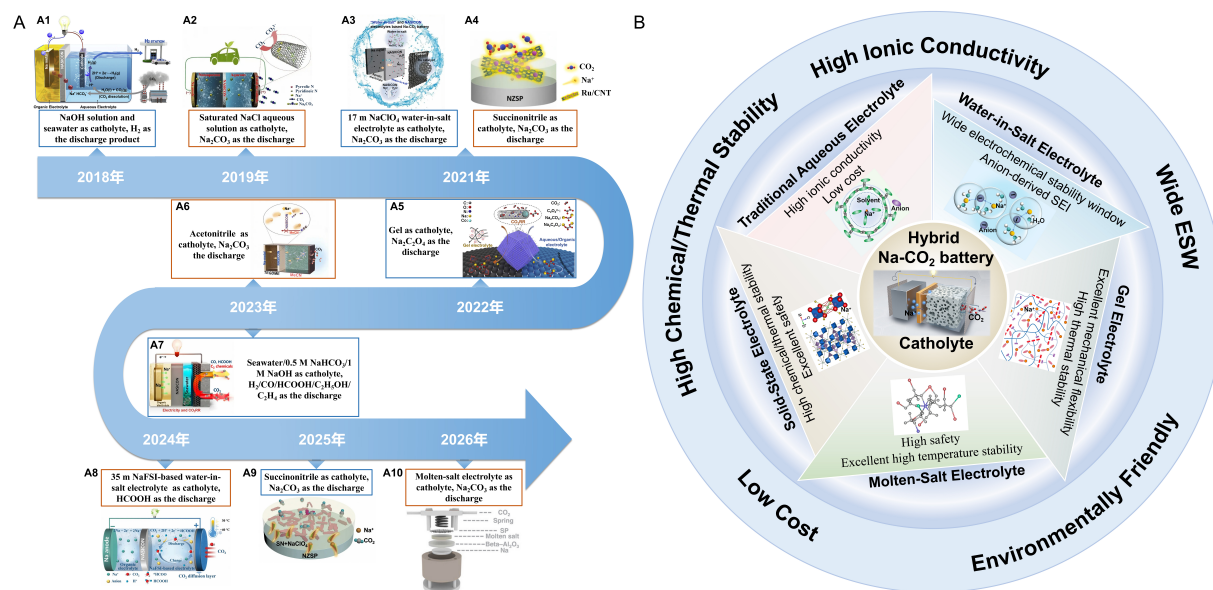


Figure 1. (A) Progress of hybrid Na-CO₂ batteries with various catholytes, (A1) Reprinted with permission from Ref.^[21]. Copyright © 2018 Elsevier. (A2) Reprinted with permission from Ref.^[25]. Copyright © 2019 Elsevier. (A3) Reprinted with permission from Ref.^[30]. Copyright © 2021 Elsevier. (A4) Reprinted with permission from Ref.^[31]. Copyright © 2021 Elsevier. (A5) Reprinted with permission from Ref.^[32]. Copyright © 2022 Elsevier. (A6) Reprinted with permission from Ref.^[33]. Copyright © 2023 Elsevier. (A7) Reprinted with permission from Ref.^[34]. Copyright © 2023 American Chemical Society. (A8) Reprinted with permission from Ref.^[28]. Copyright © 2024 John Wiley & Sons. (A9) Reprinted with permission from Ref.^[35]. Copyright © 2025 Elsevier. (A10) Reprinted with permission from Ref.^[36]. Copyright © 2026 John Wiley & Sons; (B) Schematic illustration of the catholyte in hybrid Na-CO₂ batteries. NASICON: Na₃Zr₂Si₂PO₁₂; SEI: solid electrolyte interface.

electrochemical performance and safety of non-aqueous Na-CO₂ batteries, and can be addressed by constructing hybrid Na-CO₂ battery alternatives. Such systems typically comprise a sodium metal anode in contact with an organic anolyte, a NASICON solid electrolyte separator, and a catalytically active porous cathode in contact with an aqueous catholyte, as depicted in Figure 2B. The NASICON solid electrolyte allows the diffusion of only Na⁺ between the cathode and anode electrodes, while effectively blocking the diffusion of active materials to the anode to prevent corrosion of metallic sodium. During discharge, metallic sodium oxidizes to Na⁺ by losing one electron, which is then driven by the voltage difference to migrate toward the cathode through the organic electrolyte and solid electrolyte^[28]. At the cathode, CO₂ gains electrons at the reaction interface and reduces to different forms of carbon-containing discharge products (solid products, liquid products, and gaseous products) depending on the different micro-reaction environments composed of the electrolyte and the catalyst. During the charging process, the solid and liquid products decompose, releasing Na⁺ and CO₂^[8,10]. When gaseous products are generated, the charging process is the oxygen reduction step of water oxidation in the electrolyte. Thus, the catholyte not only acts as a transport medium for Na⁺ but also determines the electrochemical reaction pathway and may even directly participate in the whole electrochemical reaction of the battery. Therefore, proper electrolytes with stable electrochemical properties and high conductivity may yield better results, thereby being the focus of current research and development.

Electrolytes and catalyst interface micro-reaction environment chemistry

The core advantage of hybrid Na-CO₂ batteries resides in the catholyte, which not only serves as an ion-transport medium but also actively participates in regulating interfacial reaction chemistry. Through synergistic interaction with the catalyst, a micro-reaction environment can be precisely constructed at the

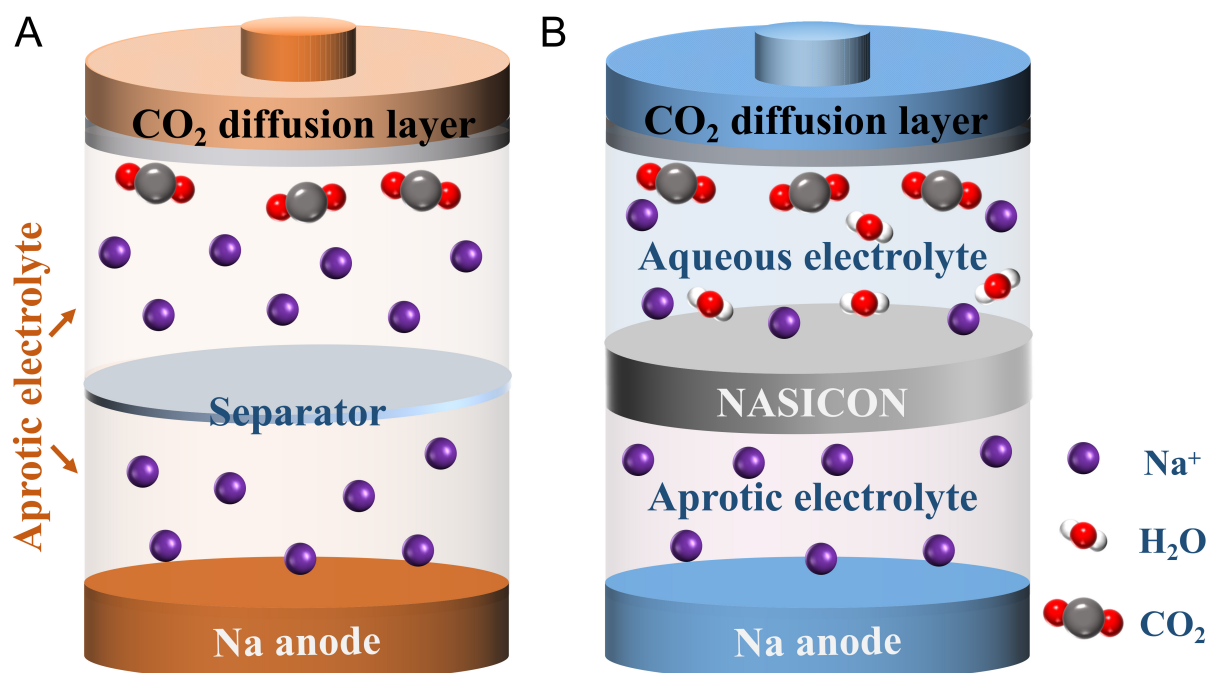


Figure 2. (A) Non-aqueous Na-CO₂ battery structure, (B) hybrid Na-CO₂ battery structure. NASICON: Na₃Zr₂Si₂PO₁₂.

solid/liquid/gas three-phase interface to control the pathway and final products of the electrochemical CO₂ reduction.

The electrolyte dictates the chemical potential and the kinetics of proton supply at the interface. For aqueous electrolytes, water serves not only as a solvent but as a crucial proton source directly participating in CO₂ reduction. The proton-coupled electron transfer mechanism allows CO₂ reduction to overcome the constraints of simple electron transfer, thereby surmounting various energy barriers to generate various chemical products ranging from formic acid (HCOOH) and CO to multi-carbon products (such as C₂H₄ and C₂H₅OH)^[34]. However, an excessive proton supply may not necessarily be advantageous, rendering the precise regulation of proton activity and concentration vital for successful reactions. For example, the relatively low H/O atomic ratio at the electrolyte/catalyst interface in sodium bis(fluorosulfonyl)imide (NaFSI)-based electrolytes may create a highly favorable chemical environment for CO₂ adsorption and subsequent hydrogenation steps^[28]. This environment stabilizes key intermediates, such as *HCOOH or HCOO*, ultimately leading to the highly selective production of HCOOH.

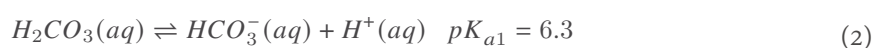
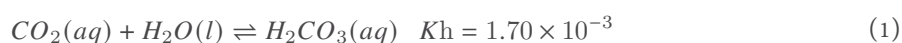
Electrolytes can also directly regulate the stability and evolutionary pathways of reaction intermediates through their unique bulk and interfacial structures. For instance, organic cations, such as those derived from imidazolium-based ionic liquids in gel electrolytes, can interact with both the electrode surface and reaction intermediates via strong coordination or π - π stacking, effectively stabilizing the key intermediate C₂O₄²⁻ and inhibiting its disproportionation into the thermodynamically stable CO₃²⁻^[32]. In this fashion, the discharge products might be directed towards the highly reversible Na₂C₂O₄, rather than the insulating and difficult-to-decompose Na₂CO₃. Hence, highly reactive intermediates can be “captured” and stabilized by the intrinsic molecular properties of the electrolyte components, enabling the rational manipulation of reaction pathways. The interfacial contact configuration between the electrode and the solid electrolyte also plays a crucial role in the electrode reactivity. Optimizing the traditional “point-to-point” contact into a more efficient “face-to-face” configuration not only reduces interfacial charge-transfer impedance but also establishes a more continuous and stable three-phase reaction channel for the transport of Na⁺ and CO₂^[35].

Finally, the physicochemical properties of electrolytes, particularly their CO₂ solubility and ionic transport characteristics, establish the fundamental kinetic framework for interfacial reactions, in which highly concentrated electrolytes significantly restrict the free water content. This not only broadens the electrochemical stability window (ESW) but also suppresses side reactions, such as the hydrogen evolution reaction (HER), facilitating the electrochemical CO₂ reduction across a wider potential range^[30]. For instance, the low donor number (DN) and high polarity of the solvent in acetonitrile (MeCN)-based gel electrolytes, coupled with the low solvation-desolvation energy barrier for Na⁺, synergistically facilitate CO₂ enrichment and accelerate reaction kinetics at the electrode interface^[33]. In high-temperature molten-salt systems, the exceptionally high ionic conductivity and the unique molten ionic environment significantly enhance interfacial charge transfer and accelerate the oxidative decomposition kinetics of discharge products, such as Na₂CO₃^[36]. As a consequence, tailoring the physical state of the electrolyte can effectively decouple and optimize the crucial processes of ionic transport and interfacial reactions.

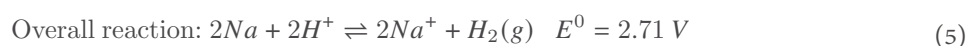
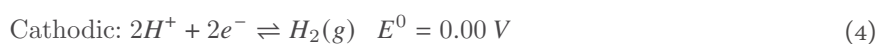
Product analysis of hybrid Na-CO₂ battery

The discharge products of hybrid Na-CO₂ batteries are closely related to the nature of the catalyst, atmosphere, and electrolyte^[37,38]. Depending on the properties of key materials and reactants, the discharge products of the battery may include gaseous, liquid, and solid products. To better understand reaction mechanisms, various experiments and analyses have been performed on different cell configurations. For example, Kim *et al.*^[21] constructed a hybrid Na-CO₂ battery using metallic sodium as the anode, CO₂ as the cathode, and NaOH solution as the catholyte, with the sodium metal anode kept in the organic electrolyte and separated from the aqueous electrolyte by a NASICON separator.

In this battery, the overall reaction mechanisms included chemical reactions and electrochemical reactions. The chemical reaction of the CO₂ dissolution mechanism was as follows:



As shown in Figure 3A, the gas chromatography (GC) analysis of the generated gases during discharge confirmed H₂ as the only gaseous product. The corresponding electrochemical reaction that took place in the battery can be summarized as follows:



During the charging process, the qualitative GC analysis detected the evolution of oxygen, as evidenced by Figure 3B, with the corresponding electrochemical reactions that can be written as follows:



Xu *et al.*^[25] further investigated the discharge reaction mechanism of the hybrid Na-CO₂ battery using *in-situ* Raman spectroscopy [Figure 3C] and *ex-situ* X-ray diffraction (XRD) [Figure 3D]. Their study aimed to confirm Na₂CO₃ and C as discharge products of the Na-CO₂ battery based on a saturated NaCl aqueous solution as a catholyte. The relevant reactions can be summarized as follows:

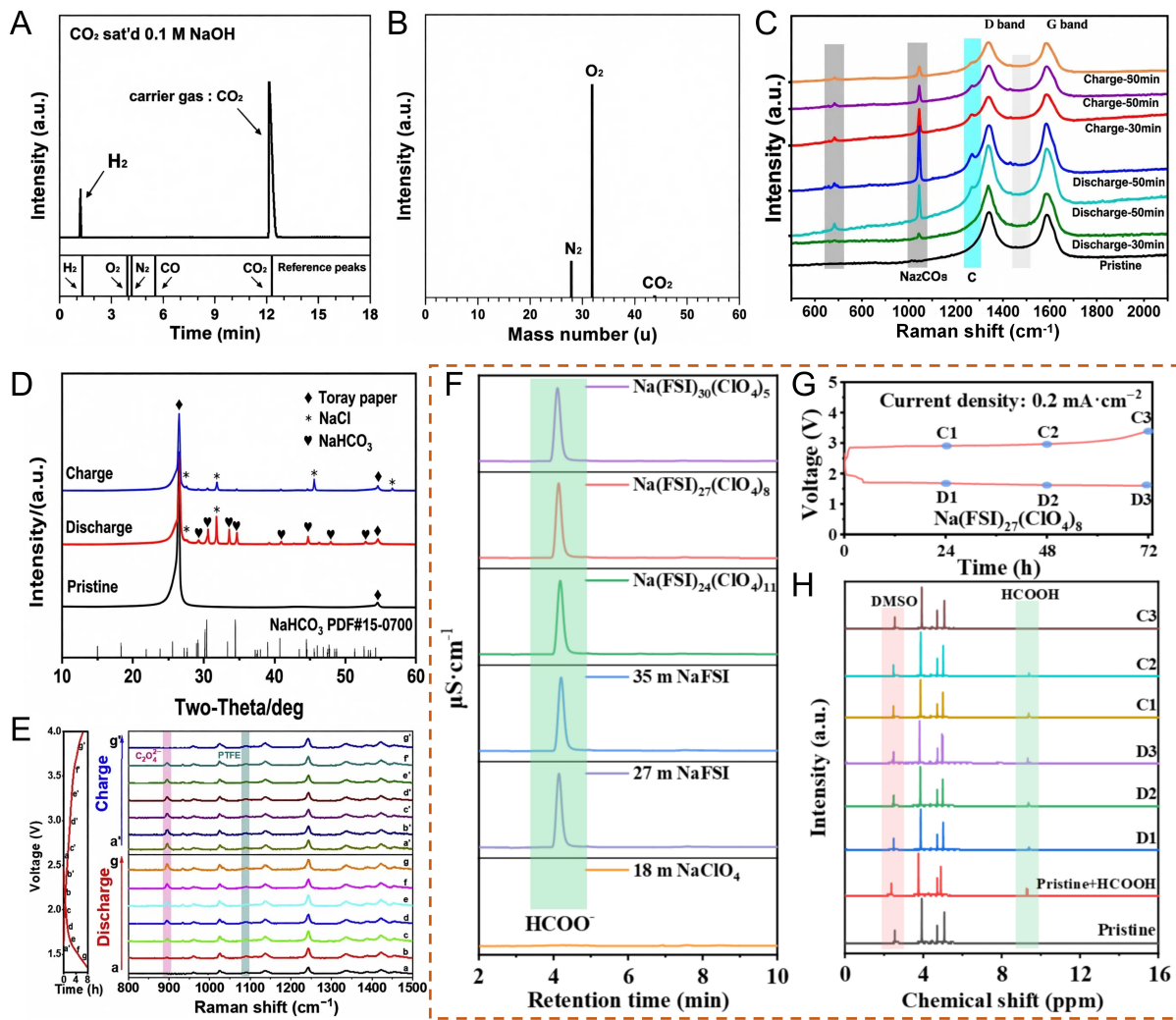
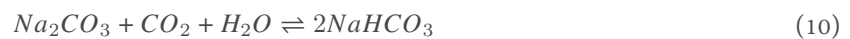
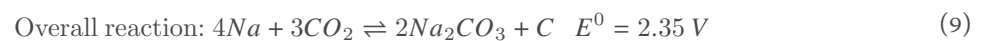


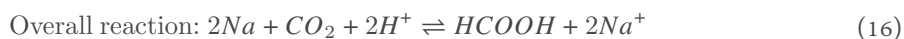
Figure 3. Gas chromatography (GC) profiles of gases evolved during the (A) discharge and (B) charge processes. (A and B) Reprinted with permission from Ref.^[21]. Copyright © 2018 Elsevier; Characterization of the hybrid Na-CO₂ battery electrode during discharge and recharge: (C) *in-situ* Raman spectra and (D) *ex-situ* X-ray diffraction (XRD) patterns. (C and D) Reprinted with permission from Ref.^[25]. Copyright © 2019 Elsevier; (E) *In-situ* Raman spectra of quasi-solid-state Na-CO₂ batteries. (E) Reprinted with permission from Ref.^[32]. Copyright © 2022 Elsevier; (F) Ion chromatography (IC) analysis of the catholyte after discharge, (G) discharge/charge profiles, and (H) *quasi-in-situ* ¹H nuclear magnetic resonance (NMR) characterization of the catholyte at different discharge/charge stages. (F-H) Reprinted with permission from Ref.^[28]. Copyright © 2024 John Wiley & Sons. PTFE: Polytetrafluoroethylene.



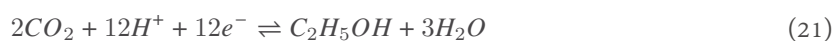
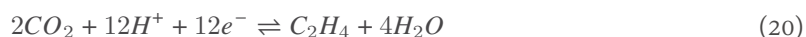
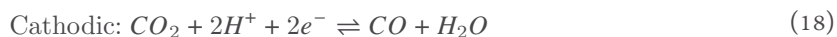
Using *in-situ* Raman spectroscopy, Xu *et al.*^[32] confirmed Na₂C₂O₄ as the discharge product of the hybrid Na-CO₂ battery based on gel electrolyte, as displayed in Figure 3E. In gel electrolyte, Na₂C₂O₄ surrounded by imidazole-like organic cations significantly reduced the charge on its surface, preventing the disproportionation reaction of C₂O₄²⁻ to CO₃²⁻ to ensure Na₂C₂O₄ as the final discharge product, as follows^[32]:



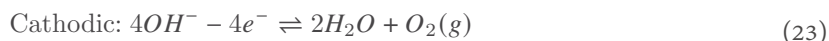
In our previous study^[28], we employed a water-in-salt electrolyte as a catholyte to enable the successful generation of HCOOH in the hybrid Na-CO₂ battery. The ion chromatography (IC) analysis of the electrolyte after discharge revealed the formation of substantial amounts of HCOO⁻ in the electrolyte, as evidenced by Figure 3F. The *quasi-in-situ* ¹H-nuclear magnetic resonance (¹H-NMR) characterization during the discharge/charge process confirmed the production of large quantities of HCOOH during discharge, which gradually disappeared during the charging process, corroborating HCOOH as a discharge product of the battery [Figure 3G and H]. The corresponding battery reactions can be summarized as follows:



Using different combinations of aqueous electrolytes and catalysts, Kim *et al.* successfully generated chemical substances, such as CO, HCOOH, and C₂ in a hybrid Na-CO₂ battery^[34], with relevant reactions during discharge that can be summarized as follows:



During the charging process, the electrochemical reaction can be written as follows:



In aqueous electrolytes, the continuous supply of protons (H) allows effective control over the battery reaction pathway to generate diverse discharge products, providing a foundation for the functional design of batteries and the resource utilization of CO₂.

HYBRID NA-CO₂ BATTERY ELECTROLYTES

Traditional aqueous electrolytes

The use of aqueous electrolytes in Na-CO₂ batteries is advantageous in terms of intrinsic safety, excellent ion transport performance, environmental friendliness, and the unique CO₂ reduction mechanism^[39,40]. Water solvent is non-flammable and thermally stable, preventing fundamental safety hazards of flammability and explosion related to the use of organic electrolytes. The low viscosity and high dielectric constant of water also endow aqueous electrolytes with higher ionic conductivity when compared to organic systems, enabling rapid charging and discharging of the battery at low-temperatures. Using water as a solvent also avoids the strict assembly environment associated with organic solvents, significantly reducing material costs and environmental impact for better economic efficiency and sustainability. More importantly, the application of water solvent in hybrid Na-CO₂ batteries not only acts as an ion transport medium but also serves as a direct source of protons, enabling the occurrence of a proton-coupled electron transfer mechanism, suitable for a more flexible and controllable CO₂ reduction process, as well as directional generation of various value-added chemicals, such as formate and C₂H₄. The formation of soluble products in water solvent also effectively prevents the deposition and passivation of solid products on the electrode surface, benefiting the cycle stability and energy efficiency of the battery. The combined effect of these advantages of using water as a solvent enables hybrid Na-CO₂ batteries to achieve synergistic energy storage and CO₂ resource utilization under mild conditions, demonstrating unique technological value and application prospects of aqueous solvents in hybrid Na-CO₂ battery assemblies.

As presented in Figure 4A, Kim *et al.*^[21] constructed a hybrid Na-CO₂ battery with metallic sodium as the anode in contact with an organic electrolyte as the anolyte, and a noble metal as the cathode catalyst (Pt/C + IrO₂) in contact with an aqueous NaOH solution as the catholyte, with the organic electrolyte and aqueous electrolyte separated by a NASICON membrane. In this configuration, CO₂ spontaneously dissolved in the aqueous electrolyte, resulting in electrolyte acidification. During discharge, the battery underwent a HER to generate H₂ gas and deliver electrical energy. Since the cathode reaction potential was significantly affected by the pH of the aqueous solution, the spontaneous dissolution of CO₂ helped improve the kinetic performance of HER due to the decrease in pH, as shown in Figure 4B. The H₂ generated during the discharge process naturally escaped from the electrode surface, forcing the occurrence of an oxygen evolution reaction (OER) from water oxidation during the charging process without CO₂ generation [Figure 4C]. The resulting system exhibited a stable charge-discharge platform and a stable cycle life of 700 h, fully demonstrating its good rechargeability, as confirmed by Figure 4D.

Kim *et al.*^[34] explored different combinations of catalysts and electrolytes in similar battery structures, overcoming the limitations of traditional hybrid Na-CO₂ batteries in terms of C₂ product generation and power density, as illustrated by Figure 4E. When applied to an H-cell type hybrid Na-CO₂ battery composed of a 0.5 M NaHCO₃ catholyte and Ni-N-C catalyst with an average particle diameter of 1 μm, products based on formic acid, CO, and H₂ were generated simultaneously during discharge, as shown in Figure 4F. The highest amount of HCOOH [70.4% Faradaic efficiency (FE)] was obtained at a current density of 15.0 mA cm⁻², followed by FE_{H₂} at 13.9% and FE_{CO} at 13.7%^[34]. Furthermore, the battery showed stable cyclability for more than 24 h at a current density of 5 mA cm⁻². In a flow cell-type hybrid Na-CO₂ battery configuration, the use of a Ni-N-C catalyst in combination with a 1 M NaOH electrolyte delivered a battery power density reaching 25.0 mW cm⁻² at a current density of 29.7 mA cm⁻², as revealed by Figure 4G. In this flow cell-type hybrid Na-CO₂ battery, using cubic Cu₂O nanoparticles as the catalyst and a 1 M NaOH aqueous solution as the catholyte resulted in a variety of discharge products, such as H₂, CO, formate, ethylene, and ethanol, as shown in Figure 4H. Under 25 mA cm⁻², the highest FE was recorded with C₂ compounds, consisting of 37.6% (ethanol: 18.1% and ethylene: 19.5%). In addition, this work also constructed an anode-free hybrid Na-CO₂ battery using Ni-N-C nanoparticles as cathode catalyst in contact with

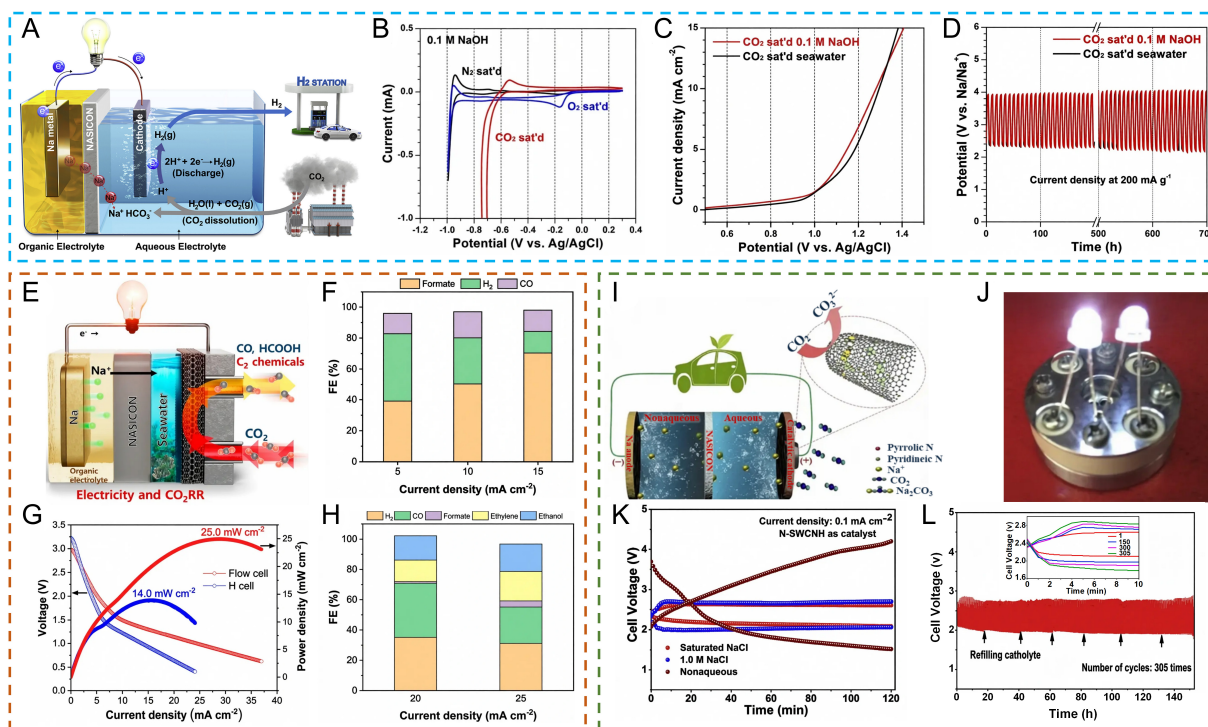


Figure 4. (A) Schematic illustration of the hybrid Na-CO₂ system and its reaction mechanism, (B) cyclic voltammetry (CV) profiles, (C) anodic rotating disk electrode profile, and (D) cycle performance of the hybrid Na-CO₂ battery. (A-D) Reprinted with permission from Ref.^[21]. Copyright © 2018 Elsevier; (E) Flow cell type hybrid Na-CO₂ battery and its discharge product, (F) FE_{formate} , FE_{CO} , and FE_{H_2} at different current densities, (G) discharge polarization curves and power density curves, (H) FE of discharge products at different current densities. (E-H) Reprinted with permission from Ref.^[34]. Copyright © 2023 American Chemical Society; (I) Schematic illustration of the proposed hybrid Na-CO₂ battery, (J) photograph of a practical hybrid Na-CO₂ battery, hybrid Na-CO₂ battery performance: (K) discharge-charge voltage curves with different catholytes, and (L) cycling performance. (I-L) Reprinted with permission from Ref.^[25]. Copyright © 2019 Elsevier. NASICON: Na₃Zr₂Si₂PO₁₂.

seawater as the catholyte. During the discharge process, CO and H₂ were recorded as the positive electrode discharge products. Under a current density of 20.0 mA cm⁻², FE_{CO} reached a highest value of 85%^[34]. Mechanistic studies revealed that the OER reaction from water oxidation takes place during the charging reaction, while the discharge products do not directly participate in the electrochemical process, limiting the long lifespan of the hybrid Na-CO₂ battery.

Xu et al.^[25] designed a reversible hybrid Na-CO₂ battery using a saturated NaCl aqueous solution as the catholyte in contact with N-doped single-walled carbon nanohorns (N-SWCNHs) as the catalyst, and a NASICON solid electrolyte as the separator, as shown in Figure 4I and J. The *in-situ* Raman spectroscopy and *ex-situ* XRD characterization of the cathode catalyst layer during the discharge process revealed the reduction of CO₂ to C and Na₂CO₃, while the generated Na₂CO₃ further reacted with water in the electrolyte to form NaHCO₃ [Equation 10]. The high solubility of the discharge product Na₂CO₃ in aqueous solution and the unique catalytic activity of N-SWCNHs greatly improved the battery round-trip efficiency and cycle capability, as shown in Figure 4K and L. Further improvement of the electrochemical performance of the hybrid Na-CO₂ battery can be achieved by using saturated NaCl aqueous solution as the catholyte in combination with proper design and optimization of catalysts^[41].

Together, the above results show great progress in the hybrid Na-CO₂ batteries based on aqueous electrolytes, yet several significant challenges remain to be solved during battery operation. First, aqueous electrolytes in an open cathode structure experience poor thermal stability. As reported by Xu *et al.*^[25], failing to replenish the electrolyte in time would greatly affect the cycle performance of the battery. This can be solved to some extent by adopting a flow cell-type battery structure to limit electrolyte evaporation, but this may inevitably reduce the weight energy density of the battery. In addition, the narrow ESW of aqueous electrolytes (approximately 1.23 V) makes them prone to decomposition during battery operation, thereby affecting the battery's electrochemical performance. These features can be effectively addressed by designing more stable aqueous electrolytes to improve battery performance.

Water-in-salt electrolytes

Unlike aqueous electrolytes, water-in-salt electrolytes use water as a solvent and high-concentration salt as a solute, with the volume and weight of the solute salt significantly exceeding that of the solvent water^[42,43]. Compared to traditional low-concentration aqueous electrolytes, the high salt concentration strongly influences ion interactions in the system, with the solvation shell of metal ions mainly composed of contact ion pairs^[44]. Such a unique solvation structure enables contact between ion pairs containing specific anions to construct a stable solid electrolyte interface (SEI) layer *in-situ* on the cathode surface, significantly widening the ESW of the electrolyte^[45,46]. This also allows matching high-voltage cathode with low-voltage anode materials, effectively improving the energy density of the resulting batteries. Moreover, water-in-salt electrolytes exhibit excellent thermal stability in addition to inheriting the advantages of aqueous electrolytes, such as high safety and environmental friendliness. More importantly, the water-in-salt electrolytes tend to form a glassy state rather than a crystalline state at low-temperatures, suitable for maintaining continuous ion transport channels and ensuring stable battery operation under low-temperature conditions^[47,48]. Overall, water-in-salt electrolytes possess high safety, good ionic conductivity, elevated chemical compatibility, relevant thermal stability, and controllable solvation structure, providing an important foundation for the design and optimization of high-performance batteries. In fact, water-in-salt electrolyte systems have been widely used in various energy storage devices, such as metal-ion batteries^[49,50], metal-gas batteries^[51,52], and supercapacitors^[53,54]. In metal-gas batteries with open cathode structures, their high chemical and thermal stability provides key support for improving electrochemical performance^[55,56]. These attributes of water-in-salt electrolytes as the catholytes might also apply to hybrid Na-CO₂ batteries, deserving further research and development in this direction.

The first constructed hybrid Na-CO₂ battery based on the water-in-salt electrolyte was reported by Im *et al.*^[30]. As shown in Figure 5A, a 17 m NaClO₄ solution was used as the catholyte, and increasing the catholyte concentration effectively suppressed HER in the electrolyte, as shown by linear scanning voltammetry (LSV) and corresponding differential electrochemical mass spectrometry (DEMS) measurements. The rise in the electrolyte concentration from 1 m to 17 m also significantly broadened the ESW to 3.45 V and enhanced stability, as illustrated in Figure 5B. Benefiting from the excellent physicochemical properties of the electrolyte, the constructed hybrid Na-CO₂ battery exhibited excellent cycle stability, with a stable cycle time of over 1,200 h, as can be observed in Figure 5C. However, the high insulation and thermodynamic stability of the discharge product Na₂CO₃ still limited the battery in terms of the large overpotential (1.65 V) and the low round-trip efficiency (56.58%)^[30]. Additionally, a relatively low concentration of the water-in-salt electrolyte (17 m) formed an ionic structure in which each cation interacted with ~3 water molecules, resulting in relatively poor inhibition of water-molecule activity and leading to electrolyte decomposition during battery operation, affecting the battery's electrochemical performance.

As displayed in Figure 5D, we previously developed a dual-salt water-in-salt electrolyte featuring a wide ESW, and systematically evaluated its application as the catholyte of a hybrid Na-CO₂ battery^[28]. Our results

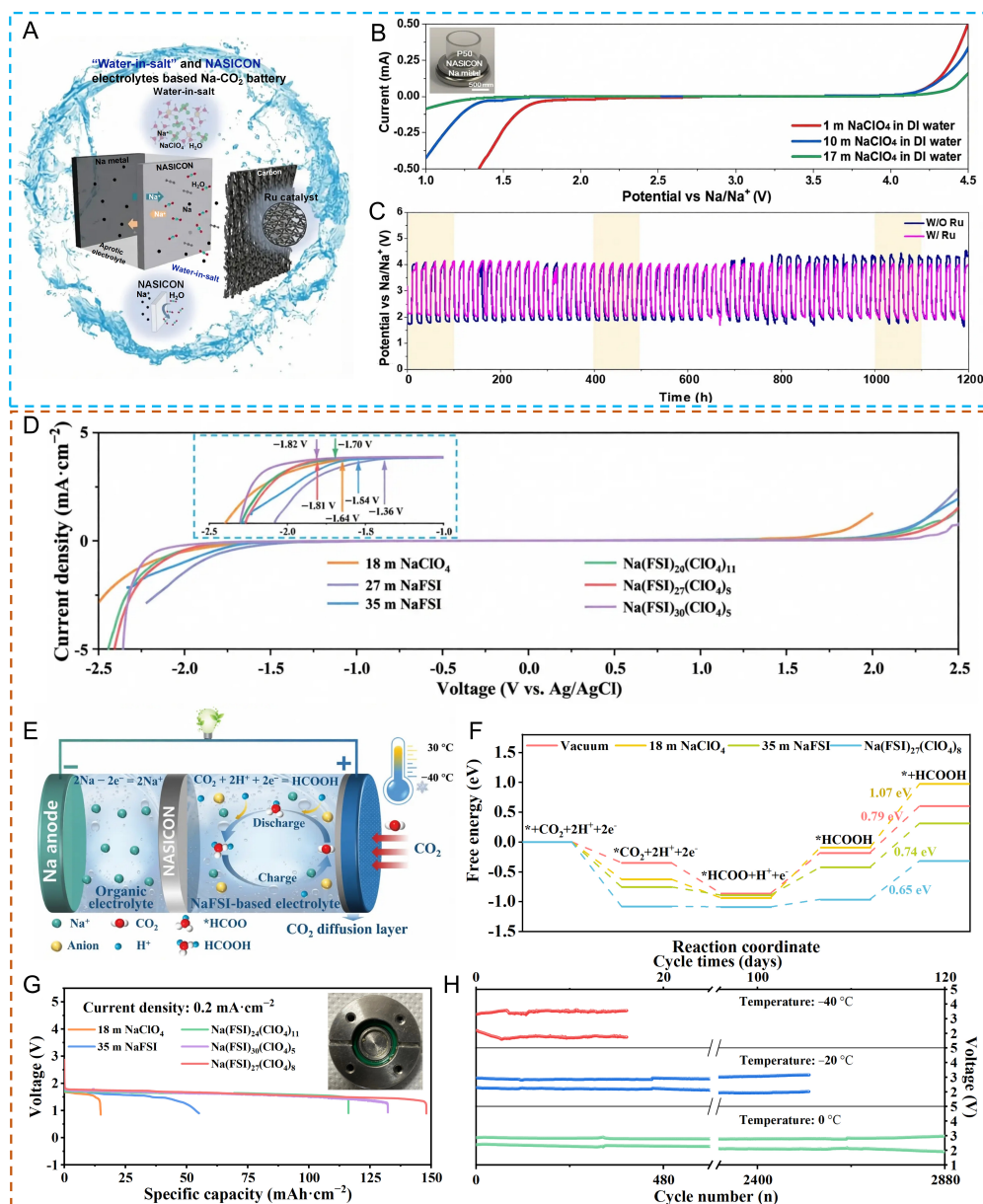


Figure 5. (A) Schematic representation of a hybrid Na-CO₂ battery with water-in-salt electrolyte, (B) ESW of different aqueous electrolytes (1, 10, and 17 m), and (C) cycle performance of the battery. (A-C) Reprinted with permission from Ref.^[30]. Copyright © 2021 Elsevier; (D) ESW of different water-in-salt electrolytes, (E) schematic diagram of hybrid Na-CO₂ battery with NaFSI-based electrolytes, (F) free energy profiles for CO₂ reduction to HCOOH in vacuum, 18 m NaClO₄, 35 m NaFSI, and Na(FSI)₂₇(ClO₄)₈. Electrochemical performance of hybrid Na-CO₂ battery: (G) discharge specific capacity curves, and (H) cycling curves of the battery at different temperatures. (D-H) Reprinted with permission from Ref.^[28]. Copyright © 2024 John Wiley & Sons. NASICON: Na₃Zr₂Si₂PO₁₂; ESW: electrochemical stability window.

revealed a successful transition of the discharge product from solid Na₂CO₃ to liquid HCOOH using this electrolyte [Figure 5E]. The obtained hybrid Na-CO₂ battery exhibited a low H/O atomic ratio at the catalyst/electrolyte interface, beneficial for forming a liquid product, HCOOH. Furthermore, the free energy calculations of CO₂ capture and its conversion to HCOOH in different water-in-salt electrolytes suggested a much lower generation of HCOOH in NaFSI-based water-in-salt electrolyte than in 17 m NaClO₄ electrolyte, as displayed in Figure 5F. IC and NMR characterization identified the discharge product of the hybrid Na-CO₂ battery using NaFSI-based water-in-salt electrolyte as liquid HCOOH. The high reversibility of HCOOH and the excellent thermal/chemical stability of the NaFSI-based water-in-salt electrolyte endowed

the hybrid Na-CO₂ battery with high electrochemical performance. In [Figure 5G](#), the hybrid Na-CO₂ battery based on a NaFSI-based water-in-salt electrolyte illustrated an ultra-high areal capacity of 148.1 mAh cm⁻², a value far exceeding those of alkali metal-CO₂ batteries at the time. The battery based on a NaFSI-based water-in-salt electrolyte also exhibited excellent cycle stability, especially in terms of low-temperature cycle stability [[Figure 5H](#)], with stable cycling for over 2,500 h at -20 °C, achieving the best low-temperature M-CO₂ cycle life.

The use of water-in-salt electrolytes not only endows hybrid Na-CO₂ batteries with excellent electrochemical performance at room temperature but also shows great potential for application in low-temperature environments. Additionally, water-in-salt electrolytes can expand the application of hybrid Na-CO₂ batteries to a wide temperature range and promote their development toward extreme operating conditions. However, water-in-salt electrolytes still suffer from several drawbacks. In fact, high concentration represents high costs, elevated viscosity, and low Na⁺ conductivity, restricting their practical large-scale application and further improvement of their electrochemical performance. Therefore, more research focus should be paid to optimizing electrolyte composition, improving transport performance, and promoting the practical application while taking into account both cost and efficiency.

Gel electrolytes

Gel electrolytes consist of confining a liquid electrolyte within a polymer or inorganic network. The use of this kind of electrolyte in battery systems is advantageous in terms of retaining the high ionic conductivity of liquids (typically reaching the order of 10⁻³ S cm⁻¹, higher than that of solid electrolytes) while endowing the system with leak-free properties, high safety, and excellent mechanical flexibility^[57-59]. Furthermore, gel electrolytes can effectively buffer changes in electrode volume and suppress dendrite growth, thereby combining the interfacial wettability of liquid batteries with the morphological stability of solid batteries. When applied to cathodes of hybrid Na-CO₂ batteries, gel electrolytes exhibit even more unique functions. First, the gel electrolyte induces a stable “solid-liquid-gas” three-phase reaction interface, ensuring not only the effective diffusion of CO₂ gas to the cathode catalyst layer, but also preventing the loss of liquid electrolyte due to gas scouring or airflow disturbance, thereby solving the drying problem of traditional liquid systems under gas flow conditions^[60,61]. Second, the moderate mechanical constraint in gel electrolytes can regulate the deposition morphology and spatial distribution of discharge products (such as Na₂CO₃), preventing dense accumulations of insulating products on the positive electrode surface and preventing premature termination of the reaction for significantly improved battery capacity and cycle stability^[62,63]. Moreover, the high viscoelasticity of the gel electrolyte can tightly adhere to the cathode catalyst layer and maintain good interfacial contact during cycling, crucial for hybrid Na-CO₂ batteries requiring to withstand large volume changes^[64,65].

Xu et al.^[32] prepared a catholyte based on a gel electrolyte for a hybrid Na-CO₂ battery by dispersing 10 g of carbon nanotubes (CNTs) and 330 g of sodium(I)bis(trifluoromethanesulfonyl)imide (NaTFSI) in 1.5 mL of the ionic liquid 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide {[C₂C₁im][NTf₂]} via ultrasonication for 1 h. The resulting dispersion was then centrifuged to obtain the gel, as displayed in [Figure 6A](#). Compared with the original CNTs, transmission electron microscopy (TEM) imaging of the obtained gel electrolyte revealed the entangled CNT bundles forming a three-dimensional (3D) network due to the interaction between the organic cations of the imidazole ion groups and the π electrons of CNTs during the gelation process, suitable for improving the mechanical strength of the material, as shown in [Figure 6B](#). The gel electrolyte also illustrated high conductivity due to the presence of CNTs (10²-10³ S cm⁻¹), which served as electron conduction channels in the gel electrolytes. In [Figure 6C](#), the use of the gel electrolyte as catholyte in hybrid Na-CO₂ battery configurations stabilized the discharge product Na₂C₂O₄ by interacting with the organic cations in the gel electrolyte, thereby inhibiting its further conversion into Na₂CO₃. Also, the high

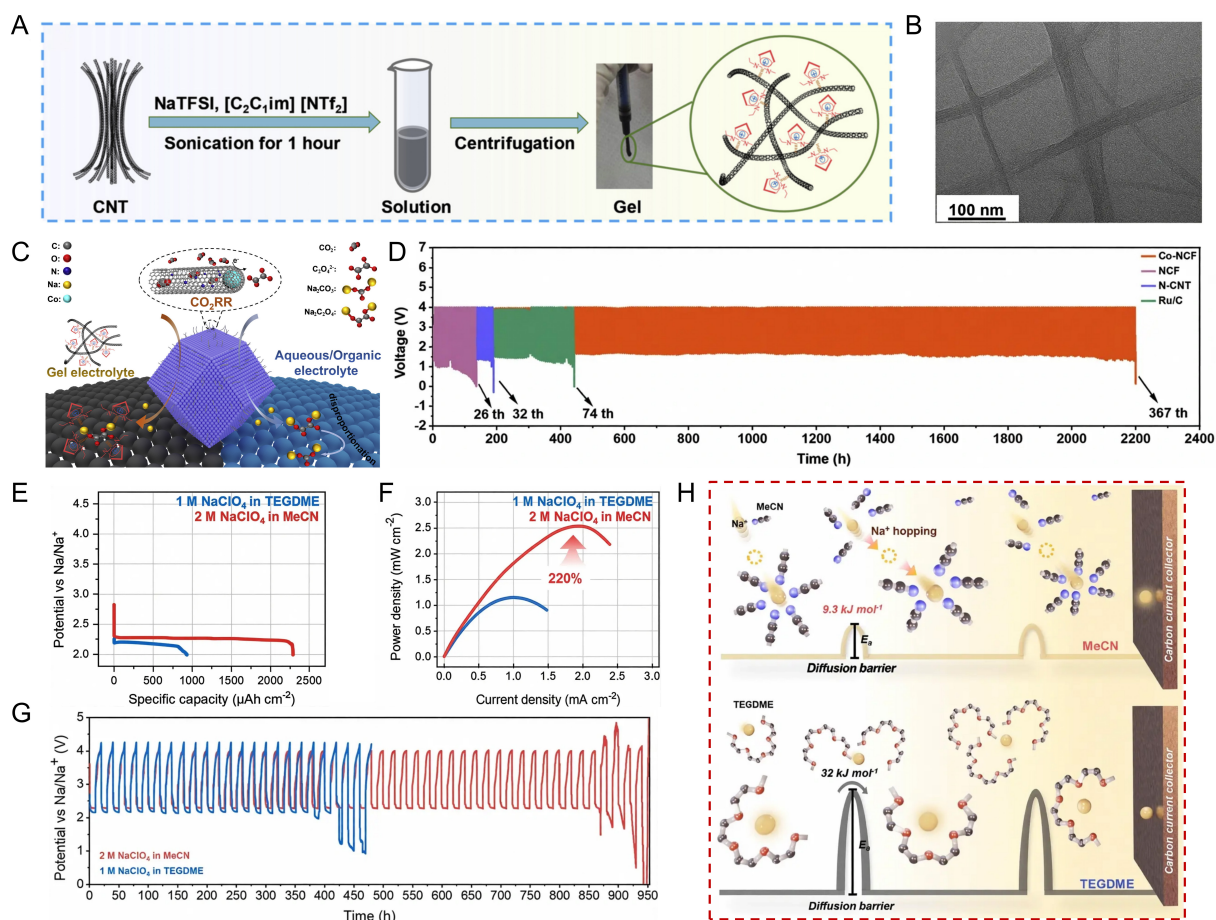


Figure 6. (A) Scheme of gel electrolyte synthesis process, (B) transmission electron microscopy (TEM) of gel electrolytes, (C) electrochemical reaction mechanism of the hybrid Na-CO₂ battery with gel electrolytes, and (D) cycling performance of the hybrid Na-CO₂ battery. (A-D) Reprinted with permission from Ref. [32]. Copyright © 2022 Elsevier; Plots of (E) specific capacities, (F) power densities, and (G) cycling performance of hybrid Na-CO₂ batteries, and (H) schematic illustration of the proposed Na⁺ diffusion in different electrolytes. (E-H) Reprinted with permission from Ref. [33]. Copyright © 2023 Elsevier. CNT: Carbon nanotube; TEGDME: tetraethylene glycol dimethyl ether; NCF: N-doped carbon framework.

reversibility of Na₂C₂O₄ as a discharge product endowed the hybrid Na-CO₂ battery with excellent cycle stability, achieving stable cycling for 367 cycles at a current density of 0.1 mA cm⁻², with a total cycle time exceeding 2,200 h [Figure 6D].

The electrochemical performance of gel electrolyte-based hybrid Na-CO₂ batteries can be further improved by using MeCN solvent, characterized by a wide ESW, a low viscosity, and high CO₂ solubility as the battery catholyte. In this view, Im *et al.* [33] applied MeCN to the catholyte of hybrid Na-CO₂ batteries and recorded improved battery performance, with a discharge specific capacity of approximately 2,200 μAh cm⁻² as shown in Figure 6E, a value 2.2-fold that of the conventional tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte. Such an improvement can be attributed to the low DN and high polarity of the MeCN solvent, which promote the generation of Na₂CO₃ discharge products. The hybrid Na-CO₂ battery based on MeCN cathode electrolyte also showed a power density of 2.59 mW cm⁻², a value about 220% higher than that of the TEGDME-based electrolyte, as displayed in Figure 6F. The cycle performance tests revealed better cycle performance of the MeCN-based catholyte battery when compared to that based on TEGDME, with severe polarization noticed only after 860 h in the former case versus 400 h in the latter [Figure 6G]. The reason for this might have to do with the large structure of the TEGDME solvent requiring Na⁺ to break free from its

five chelation sites to release Na^+ , while Na^+ in the MeCN solvent can easily jump to the adjacent solvation structure with a relatively small diffusion barrier, as reported by theoretical calculations [Figure 6H]^[33]. This aspect endowed the MeCN catholyte with a unique solvation structure and a lower diffusion barrier, leading to improved electrochemical performance of the hybrid Na- CO_2 battery.

The application of gel electrolytes in hybrid Na- CO_2 batteries can effectively suppress the leakage of liquid electrolytes and endows the system with higher safety, yet their practical applications still face several challenges. First, the high viscosity, low ionic conductivity, and poor CO_2 diffusion of gel electrolytes limit the kinetics of the CO_2 reduction reaction when compared to traditional aqueous electrolytes. This, in turn, affects the power density and rate performance of hybrid Na- CO_2 batteries. Second, gel electrolytes subjected to high-current-density cycling are prone to oxidative decomposition, affecting the cycle stability of the battery. Furthermore, the poor temperature adaptability of gel electrolytes renders the application of hybrid Na- CO_2 batteries for extreme environments more difficult. These drawbacks can be solved by optimizing the structure, conductivity, and temperature adaptability of the gel electrolyte to improve the overall performance of gel-based hybrid Na- CO_2 batteries.

Molten-salt electrolytes

Another category of materials that can be used as battery catholytes is molten-salt electrolytes, usually composed of one or more metal cations and anions^[66,67]. These ions exhibit excellent conductivity and chemical stability under high temperature conditions, making them useful for a wide range of electrochemical applications. As catholytes for hybrid Na- CO_2 batteries, molten-salt electrolytes have several advantages. First, their non-flammable and non-volatile properties are particularly important for use in open systems, such as metal-gas batteries^[68,69]. Second, the comparable ionic conductivity and electrochemical window of molten-salts to those of traditional organic electrolytes make them good alternative materials^[70]. Importantly, the higher operating temperature of molten-salts further accelerates reaction kinetics for improved battery performance^[71,72].

Based on the above characteristics, Zhong *et al.*^[36] designed a NaNO_3 - KNO_3 - CsNO_3 ternary molten-salt electrolyte by melting NaNO_3 (26.4 wt%), KNO_3 (27.3 wt%), and CsNO_3 (46.3 wt%) to 200 °C. Afterward, a glass fiber membrane with a diameter of 12 mm was immersed in the melt to adsorb the molten-salt, and a molten-salt electrolyte membrane was obtained after cooling down. As shown in Figure 7A, the electrochemical impedance spectroscopy (EIS) characterization of the electrolyte revealed an ionic conductivity of the molten-salt electrolyte reaching up to 96 mS cm^{-1} , a value 50-fold higher than that of the traditional organic electrolyte (1.78 mS cm^{-1} for 1 M $\text{NaClO}_4/\text{TEGDME}$)^[17]. The electrochemical stability of the molten-salt catholyte at 170 °C revealed an ESW of 1.6–4.2 V, a value comparable to that of organic electrolytes [Figure 7B]. The chemical stability of the catholyte evaluated at high temperature using the *in-situ* DEMS technique showed no decomposition of NaNO_3 - KNO_3 - CsNO_3 molten-salt at 170 °C to produce nitrogen oxides, such as NO, NO_2 , and N_2O . This confirmed the good stability of the nitrate system, without undergoing volatile decomposition under operating conditions [Figure 7C].

Subsequently, the hybrid Na- CO_2 battery was assembled according to the structure shown in Figure 7D to yield an Na- CO_2 battery composed of molten-salt electrolyte and 1 M $\text{NaClO}_4/\text{TEGDME}$ electrolyte, followed by electrochemical performance evaluation under an argon and CO_2 environment. Compared to the limited discharge specific capacity ($2,345 \text{ mAh g}^{-1}$) and poor Coulombic efficiency (43.1%) of traditional organic electrolytes, the respective discharge and charge capacities of the molten-salt-based hybrid Na- CO_2 battery significantly improved to $4,852 \text{ mAh g}^{-1}$ and $4,815 \text{ mAh g}^{-1}$ [Figure 7E]. Also, the Coulombic efficiency of the molten-salt-based hybrid Na- CO_2 battery reached 99.2%, a value close to 100%, with a charging platform voltage in the molten-salt system of only 3.2 V. Rate performance testing of the battery

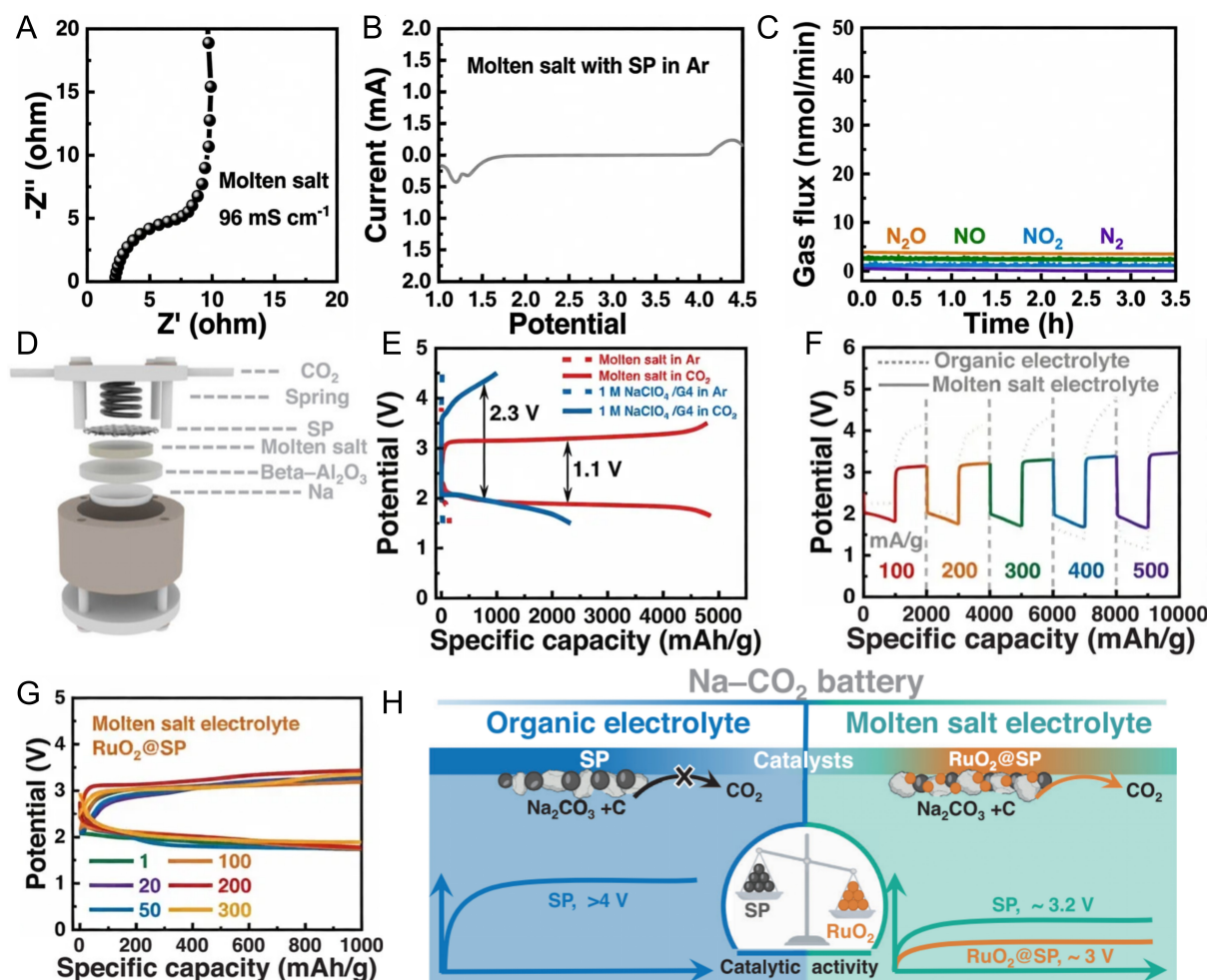


Figure 7. (A) Electrochemical impedance spectroscopy (EIS) and (B) ESW profiles of the molten-salt electrolyte, (C) *in-situ* DEMS curves during hybrid Na-CO₂ battery operation at 170 °C, and (D) schematic structure of a hybrid Na-CO₂ battery with molten-salt electrolyte; Electrochemical performance of hybrid Na-CO₂ battery with molten-salt electrolyte: (E) charge-discharge curves, (F) rate performance, and (G) cycling performance. (H) Schematic of a hybrid Na-CO₂ battery with a cathode. (A-H) Reprinted with permission from Ref.^[36]. Copyright © 2026 John Wiley & Sons. ESW: Electrochemical stability window; DEMS: differential electrochemical mass spectrometry; SP: super P.

revealed the molten-salt battery maintaining a low charging plateau of approximately 3.4 V even at a high current density of 500 mA g⁻¹, as shown by Figure 7F. By comparison, the batteries assembled with organic electrolytes exhibited severe polarization, with charging voltages exceeding 4.8 V at the same current density, rendering cycling impossible. Furthermore, the cycle performance characterization of the hybrid Na-CO₂ battery revealed stable cycling for over 300 cycles at a cutoff discharge specific capacity of 1,000 mAh g⁻¹, with a charging potential consistently below 3.5 V [Figure 7G]. By contrast, Na-CO₂ batteries based on organic electrolytes typically require charging voltages exceeding 4.0 V and fail within 150 cycles. The fundamental mechanism behind this performance difference can be explained by the scheme illustrated in Figure 7H. In organic electrolytes, the insulating properties of Na₂CO₃ induce its continuous accumulation on the cathode, resulting in severe electrode passivation, parasitic side reactions, and gradual electrolyte decomposition, leading to rapid battery failure. Conversely, nitrate-based molten-salt electrolytes promote rapid Na⁺ transport and facilitate the efficient decomposition of Na₂CO₃, thereby minimizing side reactions and enabling stable and continuous battery cycling.

Therefore, the use of molten-salt electrolytes as the catholyte in hybrid Na-CO₂ batteries can significantly improve the Coulombic efficiency and reduce the battery charging potential. However, the requirement for high temperatures to achieve high conductivity increases the complexity and cost of the battery system, limiting their application in room-temperature or low-temperature environments and challenging battery thermal management. Some electrode materials may also be unstable or undergo side reactions in a high-temperature molten-salt environment, affecting battery performance and lifespan. These drawbacks can be overcome to some extent by adopting specific strategies to reduce the operating temperature of molten-salt electrolytes and enhance their practical applications.

Solid-state electrolytes

The solid-state technology brings several advantages to the development of hybrid Na-CO₂ batteries^[73,74]. The first is a significant improvement in safety^[22], since solid electrolytes are non-flammable and non-volatile, fundamentally eliminating the risks of flammability and leakage inherent in traditional liquid electrolytes with open cathode structures. Even under extreme conditions (such as high temperatures), solid electrolytes can effectively prevent thermal runaway and fire/explosion, significantly reducing battery safety risks. The second advantage is the significantly increased energy density of solid electrolytes^[75,76]. As a result, solid-state hybrid Na-CO₂ battery structures allow for more compact electrode designs and more efficient ion transport pathways. The wider ESW of solid electrolytes also allows battery operation under high voltage platforms to achieve higher energy densities. The third advantage is extended cycle life^[77,78]. The use of solid electrolytes effectively prevents the volatilization problem of traditional liquid electrolytes under airflow disturbances, as well as avoiding the occurrence of side reactions, effectively improving the cycle life of the battery.

An ideal solid-state hybrid Na-CO₂ battery cathode electrolyte should facilitate the conduction of electrons, Na⁺ and CO₂ gas molecules to realize the so-called “tri-conductive” electrolytes. In this regard, Tong *et al.*^[31] and Liu *et al.*^[35] first melted a mixture of 92.5 wt% succinonitrile (SN) and 7.5 wt% NaClO₄ to obtain a homogeneous SN-based solution [Figure 8A], and then drop-coated this mixture onto a prepared cathode at 50 °C to ensure full wetting onto the solid electrolyte membrane to form a solid-state cathode. As illustrated in Figure 8B, the use of this solid-state cathode switched the traditional “point-to-point” contact to “face-to-face” contact, effectively improving the interfacial contact between the cathode catalyst and the solid electrolyte. The XRD characterization of the SN-based electrolyte revealed almost vanished characteristic peaks of SN at 20° and 28° after mixing with NaClO₄, effectively reducing the long-range order of SN [Figure 8C]. Subsequent assembly of the prepared solid-state cathode into a full cell resulted in a small semicircle in the high-frequency region of the EIS for the hybrid Na-CO₂ battery without SN-based electrolyte, as displayed in Figure 8D, while capacitance and resistance were observed in the low-frequency region. In the presence of SN electrolyte, the EIS profile displayed a double semi-circular characteristic, indicative of the importance of the SN additive in significantly improving the rate of interfacial charge transfer. Evaluation of the battery electrochemical reactions using cyclic voltammetry revealed the presence of a significant redox peak for the battery containing an SN-based solid-state cathode, which accelerated the reaction rate and improved sodium ion diffusion [Figure 8E]. Stability tests on the all-solid-state hybrid Na-CO₂ battery suggested a battery capable of stably cycling for 100 cycles at a current density of 50 mA g⁻¹, with a stable cycle time of over 2,400 h [Figure 8F]. Furthermore, a comprehensive comparison with previously reported Na-CO₂ batteries highlighted the superiority of batteries associated with SN-based solid-state cathodes in providing the best electrochemical performance [Figure 8G]. Together, these results show that the development of high-performance all-solid-state hybrid Na-CO₂ batteries can not only provide a foundation for CO₂ fixation and resource utilization but also provide a reliable energy supplement for outer space exploration [Figure 8H].

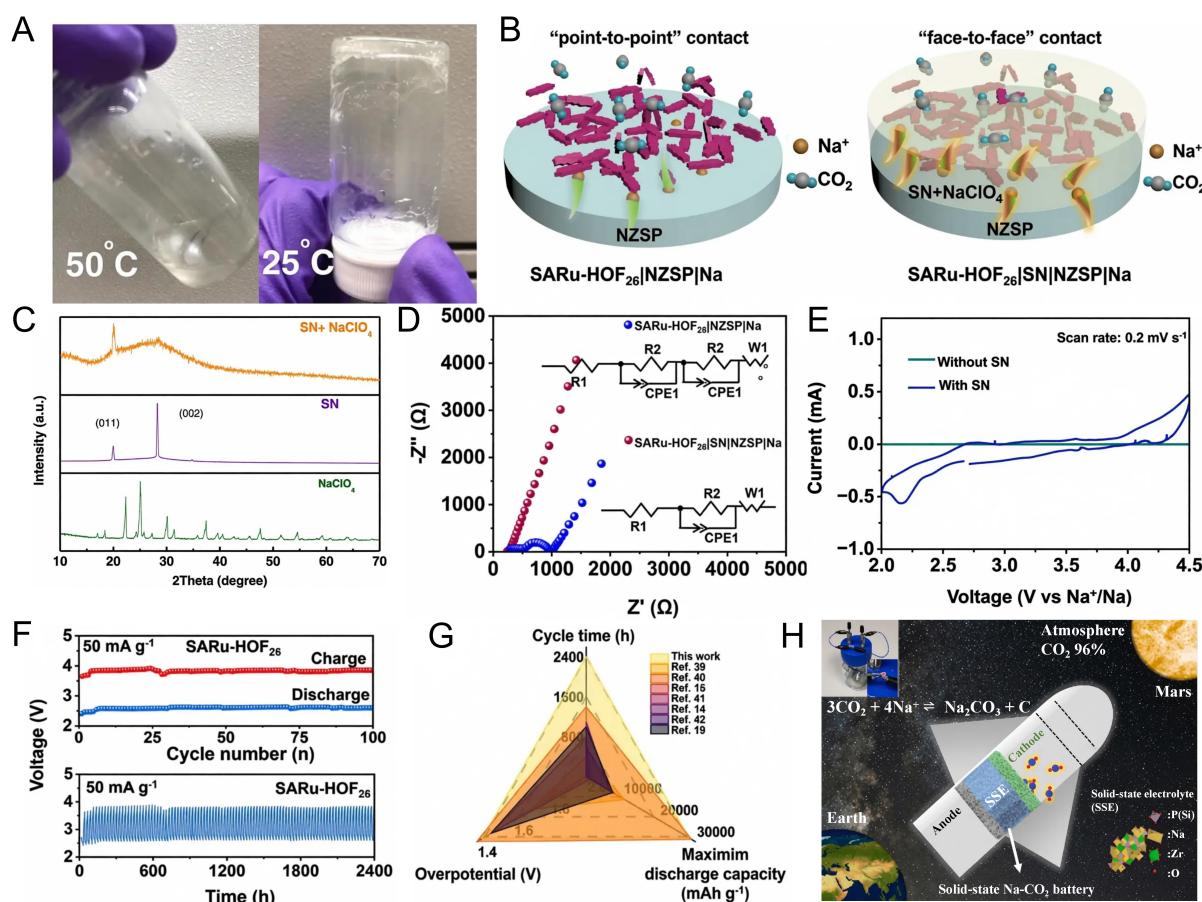


Figure 8. (A) Photos of succinonitrile (SN) with NaClO₄. (A) Reprinted with permission from Ref.^[31]. Copyright © 2021 Elsevier; (B) Illustration of "point-to-point" and "face-to-face" contact between the cathode and NASICON. (B) Reprinted with permission from Ref.^[35]. Copyright © 2025 Elsevier; (C) XRD patterns of SN with NaClO₄. (C) Reprinted with permission from Ref.^[31]. Copyright © 2021 Elsevier; The electrochemical performance of hybrid Na-CO₂ battery: (D) EIS curves, (E) CV curves, and (F) cycling curves. (G) Compared the key properties of Na-CO₂ battery. (D-G) Reprinted with permission from Ref.^[35]. Copyright © 2025 Elsevier; (H) Future application scenarios of solid-state hybrid Na-CO₂ batteries. (H) Reprinted with permission from Ref.^[31]. Copyright © 2021 Elsevier. NASICON: Na₃Zr₂Si₂PO₁₂; XRD: X-ray diffraction; CV: cyclic voltammetry; EIS: electrochemical impedance spectroscopy; NZSP: Na₃Zr₂Si₂PO₁₂.

Despite the significant advantages of solid-state hybrid Na-CO₂ batteries, their development is still in its early stages of exploration and faces several key challenges. First, the solid-solid contact between the solid electrolyte and the cathode results in a much higher interfacial impedance than that of liquid-solid contact. This might be problematic during charging and discharging processes, where volume changes in the cathode catalyst layer and the metal anode can lead to failure of interfacial contact. Second, the construction and maintenance of the three-phase reaction interface of electrons, ions, and gases in these cells poses problems since solid electrolytes cannot wet porous cathodes as liquids can, resulting in a scarcity of effective reaction sites. Solid products can also dynamically block the three-phase channels. More importantly, the decomposition kinetics of discharge products (such as Na₂CO₃) are slow, and all-solid configurations lack a flowable medium to assist their operation^[31]. Once the solid products isolate the catalyst from the electrolyte, the charging process is terminated prematurely. Therefore, future research should focus on solid-solid interface optimization and efficient three-phase cathode structural design.

The electrochemical performances of the hybrid Na-CO₂ batteries utilizing various catholytes are summarized in Table 1. The analysis suggests that the catholyte plays a decisive role in determining the overall electrochemical performance of the battery. Diverse electrolyte systems possess distinct

Table 1. Comparative summary of the electrochemical performances of the hybrid Na-CO₂ batteries with different catholytes

Electrolyte types	Catholyte	Discharge products	Voltage gap, applied current	Capacity (mAh g ⁻¹ /mAh cm ⁻²)	Cyclability	Refs.
Traditional aqueous electrolyte	0.1 M NaOH and seawater	H ₂	≈1.4 V, 50 mA g ⁻¹	210,000 mAh g ⁻¹	700 h	[21]
	1 M NaOH	Formate	3 V, 5 mA cm ⁻²	-	25 h	
	0.5 M NaHCO ₃	CO	3 V, 4 mA cm ⁻²	-	24 h	[34]
	1 M NaOH	CO/C ₂ chemicals	2.8 V, 8 mA cm ⁻²	-	-	
	Saturated NaCl solution	Na ₂ CO ₃	0.49 V, 0.1 mA cm ⁻²	2,293 mAh g ⁻¹	300 cycles	[25]
Water-in-salt electrolyte	17 m NaClO ₄	Na ₂ CO ₃	1.65 V	-	1,200 h	[30]
	35 m NaFSI	HCOOH	0.92 V, 0.1 mA cm ⁻²	55.1 mAh cm ⁻²	452 cycles	
	Na(FSI) ₂₄ (ClO ₄) ₁₁	HCOOH	0.70 V, 0.1 mA cm ⁻²	116.2 mAh cm ⁻²	-	[28]
	Na(FSI) ₃₀ (ClO ₄) ₅	HCOOH	0.69 V, 0.1 mA cm ⁻²	132.3 mAh cm ⁻²	-	
	Na(FSI) ₂₇ (ClO ₄) ₈	HCOOH	0.64 V, 0.1 mA cm ⁻²	148.1 mAh cm ⁻²	1,218 cycles	
Gel electrolyte	CNT-based gel electrolyte	Na ₂ C ₂ O ₄	1.75 V, 0.1 mA cm ⁻²	1,777 mAh g ⁻¹	367 cycles	[32]
	MeCN	Na ₂ CO ₃	≈1.72 V, 50 μA cm ⁻²	≈2,200 μAh cm ⁻²	860 h	[33]
Molten-salt electrolyte	NaNO ₃ -KNO ₃ -CsNO ₃ eutectic electrolyte	Na ₂ CO ₃	≈1.2 V, 250 mA g ⁻¹	6,715 mAh g ⁻¹	300 cycles	[36]
Solid-state electrolyte	Succinonitrile	Na ₂ CO ₃	1.3 V, 50 mA g ⁻¹	28,830 mAh g ⁻¹	70 cycles	[31]
	Succinonitrile	Na ₂ CO ₃	1.43 V, 50 mA g ⁻¹	28,148.3 mAh g ⁻¹	2,400 h	[35]

physicochemical properties, each offering unique advantages in enhancing energy efficiency, prolonging cycle life, and improving battery safety. However, no single electrolyte could satisfy all ideal criteria simultaneously to deliver flawless electrochemical performance. Consequently, the development and optimization of catholytes require further advancement by optimally balancing ionic conduction, interfacial stability, and reaction kinetics to achieve a comprehensive breakthrough in the overall performance of hybrid Na-CO₂ batteries.

CONCLUSIONS AND OUTLOOK

Hybrid Na-CO₂ batteries are promising platforms that synergistically combine energy storage with CO₂ utilization. Compared to nonaqueous Na-CO₂ batteries, hybrid systems offer distinct advantages, including intrinsically safe operation, efficient reaction kinetics enabled by high CO₂ diffusion rate in water, prevented solid-product passivation through the formation of soluble discharge species, and the ability to steer the reduction pathway toward valuable chemicals (such as formate, CO, and C₂ products). The nature and characteristics of the catholyte play a decisive role in determining the reaction mechanism, discharge product speciation, and overall battery performance. In this review, the fundamentals and advances of hybrid Na-CO₂ batteries were discussed to gain a better understanding of the science and technology of hybrid Na-CO₂ batteries. The fundamental properties of hybrid Na-CO₂ electrochemistry were provided, with the challenges and optimization strategies associated with battery catholytes. Considering the problems allowing further development of hybrid Na-CO₂ batteries, some perspectives for high-performance hybrid Na-CO₂ batteries are summarized in Figure 9.

In-depth understanding of reaction mechanisms

The electrochemical reaction pathways in hybrid Na-CO₂ batteries highly depend on the catholyte composition, catalyst structure, and operating conditions, resulting in a complex interplay between CO₂ reduction mechanisms and product distributions. The range of discharge products may include solids (such as Na₂CO₃ and Na₂C₂O₄), liquids (such as HCOOH, C₂H₄, and C₂H₅OH), and gases (such as CO and H₂). The reaction mechanisms are often inferred from these final discharge products, yet the precise reaction

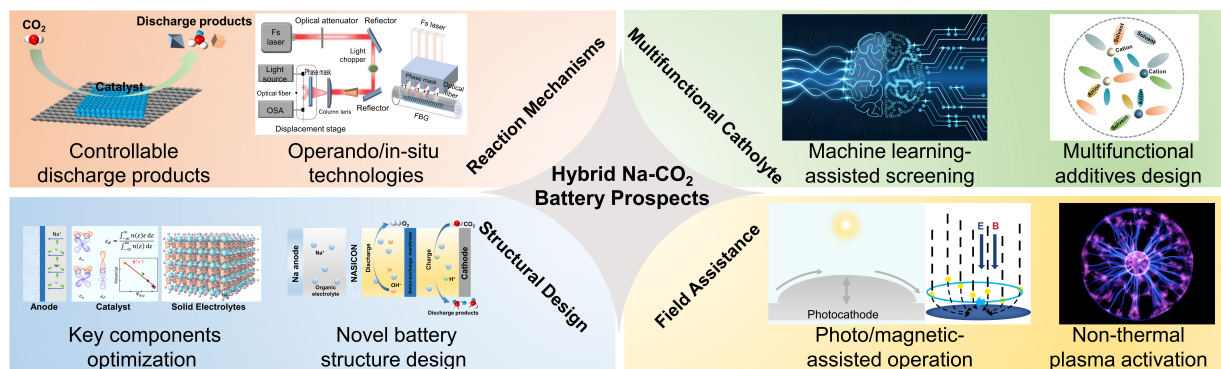


Figure 9. Schematic illustration of future research for high-performance hybrid Na-CO₂ batteries. NASICON: Na₃Zr₂Si₂PO₁₂; OSA: optical spectrum analyzer; FBG: fiber bragg grating.

intermediates and their dynamic evolution under operating conditions are still poorly understood. While Na₂CO₃ and C are widely recognized as the primary products in most studies, the nucleation and growth of Na₂CO₃ into different macroscopic structures remains poorly understood. Thus, the precise control over the type of discharge products in hybrid Na-CO₂ batteries is crucial since these directly affect key performance indicators of the battery, such as capacity, energy density, and cycle performance. Furthermore, the main sources and nature of the electrochemical side reactions in the hybrid Na-CO₂ batteries still require clarification. Current research on the cycling reaction mechanism of hybrid Na-CO₂ batteries mainly relies on *ex-situ* characterization [XRD, scanning electron microscope (SEM), Raman, TEM, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), *etc.*] of the cathode catalyst layer before and after discharge and charging processes. However, capturing crucial dynamic information during actual charging and discharging processes using these methods remains challenging. Furthermore, real-time monitoring of gas consumption and byproducts during a complete battery cycle is still lacking. Therefore, future research should focus on using advanced operando/*in-situ* characterization techniques [such as XRD, DEMS, TEM, atomic force microscope (AFM), XPS, SEM, and XAS], widely employed in other battery systems, in combination with theoretical calculations to identify key reaction intermediates, monitor the nucleation and growth processes of discharge products, and reveal the reaction mechanisms of hybrid Na-CO₂ batteries.

Design of multifunctional catholytes

The catholyte not only governs ion transport but also directly participates in the CO₂ reduction reaction through the modulation of the local proton activity, solvation structure, and electrode/electrolyte interfacial micro-reaction environment. Furthermore, the chemical and thermal stability of the catholyte is equally crucial to the electrochemical stability of batteries with open cathode structures. The properties of the catholyte can be significantly affected by the nature and properties of the salts, solvents, and additives. Optimal components can be effectively screened using machine learning and computational methods. For aqueous and water-in-salt systems, water offers a range of advantages as a solvent, including high ionic conductivity and high safety, but its unstable electrochemical activity presents challenges. As a consequence, optimizing salt concentration, anion chemistry, and introducing multifunctional additives can regulate the properties of solvent water and the interfacial micro-reaction environment to expand the ESW and regulate the selectivity of discharge product formation. For example, introducing hydrophilic organic or inert inorganic compounds may form strong H-bonds between water molecules and some highly polar aprotic solvents, which may inhibit HER and expand the ESW. Similarly, introducing solute salts with different

chemical properties may regulate the interfacial micro-reaction environment by forming different discharge products. For gel electrolytes, improving ionic conductivity, CO₂ diffusivity, and mechanical robustness while maintaining long-term stability under gas-flow conditions remains a key challenge. For molten-salt electrolytes, reducing the operating temperature through eutectic composition engineering and exploring new low-melting-point systems may enhance the practical viability of the batteries. For solid-state systems, establishing efficient triple-phase boundaries and maintaining stable solid-solid contacts during cycling is essential. These issues can be solved by constructing three-dimensional mixed-conducting cathode architectures, incorporating compliant interfacial layers, and designing “tri-conductive” (electron, ion, and gas) networks. Finally, given the potential demand for hybrid Na-CO₂ batteries in practical applications (such as Mars exploration), their low-temperature electrochemical performance is expected to hinder their applications under extreme conditions. This can be overcome by systematically exploring the influence mechanism of electrolyte components on ion transport behavior at low-temperatures, solvation structure stability, and desolvation kinetics at the electrode/electrolyte interface to optimize the catholyte. Specifically, the low-temperature electrochemical performance of batteries can be effectively improved by controlling the freezing point of the solvent system, adjusting the salt concentration to suppress low-temperature salt precipitation, or introducing functional additives to reduce interfacial charge transfer resistance. These electrolyte engineering strategies may result in high-performance hybrid Na-CO₂ batteries combining superior energy density and wide temperature range adaptability, thereby providing key technical support for energy systems under special scenarios like deep space exploration.

Integration of emerging concepts and multifunctional systems

Current hybrid Na-CO₂ batteries still suffer from issues, such as low round-trip efficiency, poor rate performance, and poor cycle stability. Improving catalyst performance should be addressed by solving the aforementioned issues of optimizing the cathode electrolyte, since both are linked by the mechanistic pathway at the interface. Integrating catholyte with emerging technologies offers a new way to overcome existing limitations. By introducing solvents or solutes with specific functions into the electrolyte, the electrochemical performance of the battery can be improved with the assistance of an external field. For instance, photo-assisted operation can leverage photogenerated carriers to reduce the overpotential and enhance reaction kinetics, potentially enabling more efficient CO₂ conversion under mild conditions. Similarly, adding a substance sensitive to magnetic fields to the electrolyte, coupled with the application of an external magnetic field, can accelerate the migration rate of charge carriers in the electrolyte and guide their directional transport, thereby improving the rate performance and energy conversion efficiency of the battery. In addition to the two external-field assistance methods mentioned above, using non-thermal plasma to pre-activate CO₂ or provide necessary active intermediates can effectively promote the CO₂ reduction reaction and further improve the electrochemical performance of the battery.

System-level engineering and scalability

Beyond materials development, the practical realization of hybrid Na-CO₂ batteries necessitates holistic system design. The open-cathode configuration raises challenges regarding electrolyte evaporation, CO₂ supply management, and long-term operation under fluctuating environmental conditions. Flow-cell architectures can mitigate evaporation issues but introduce additional complexity and reduce gravimetric energy density. Therefore, developing novel hybrid Na-CO₂ battery structures is vital to mitigate these issues. Examples of solutions include constructing Na-CO₂ battery configurations with dual-membrane structures to integrate functions such as high-efficiency energy storage, CO₂ recovery, value-added chemicals, and oxygen production, while effectively avoiding problems such as electrolyte volatilization. Sealing and gas management strategies must be carefully engineered to maintain a stable CO₂ atmosphere while preventing moisture and oxygen infiltration that may degrade the sodium anode. Furthermore, the cost and availability of key components, including NASICON membranes, electrocatalysts, and electrolyte salts, ultimately

determine the economic feasibility. Therefore, future efforts should focus on techno-economic assessments and life-cycle analyses to guide the selection of materials and architectures for balancing performance, durability, and cost.

In summary, current hybrid Na-CO₂ batteries stand at a critical juncture where fundamental understanding, materials innovation, and system engineering must progress in parallel. The unique ability of these batteries to simultaneously store electrical energy while converting CO₂ into value-added products makes them a compelling technology for carbon-neutral energy storage. However, achieving the required combination of high energy efficiency, long cycle life, and practical viability requires further sustainable research efforts across various disciplines, including electrochemistry, materials science, and chemical engineering. Continuous advances in catholyte design, mechanistic elucidation, and system integration would further improve hybrid Na-CO₂ batteries for future sustainable energy infrastructures, particularly in niche applications where safety, environmental adaptability, and CO₂ utilization are of paramount importance.

DECLARATIONS

Authors' contributions

Conceived the review and wrote the manuscript: Yang, X.; Guo, X.; Dong, J.; Li, Q.; Gu, P.; Gao, X.

Revised and polished the manuscript: Yang, X.; Liang, F.; Xia, S.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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