Review

Exploring the Frontiers of Cathode Catalysts in Lithium–Carbon Dioxide Batteries: A Mini Review

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Abstract: To mitigate the greenhouse effect and environmental pollution caused by the consumption of fossil fuels, recent research has focused on developing renewable energy sources and new high-efficiency, environmentally friendly energy storage technologies. Among these, $Li–CO_2$ batteries have shown great potential due to their high energy density, long discharge plateau, and environmental friendliness, offering a promising solution for achieving carbon neutrality while advancing energy storage devices. However, the slow kinetics of the CO_2 reduction reaction and the accumulation of Li_2CO_3 discharge on the cathode surface lead to a significant reduction in space and active sites. This in turn results in high discharge overpotential, low energy efficiency, and low power density. This study elucidates the charge–discharge reaction mechanisms of lithium–carbon dioxide batteries and systematically analyzes their reaction products. It also summarizes the latest research advancements in cathode materials for these batteries. Furthermore, it proposes future directions and efforts for the development of $Li–CO_2$ batteries.

Keywords: lithium–carbon dioxide battery; electrode material; catalyst; first principles; electrochemical performance

1. Introduction

Among the various energy sources available to humanity, fossil fuels such as oil, natural gas, and coal still dominate. However, these resources are limited in supply, and their use results in significant carbon emissions and environmental pollution [1–3]. In the context of profound changes in the global landscape, addressing these issues has become particularly urgent. As a responsible major country, China put up a proposal in 2020 to reach carbon neutrality by 2060 and to peak carbon emissions by 2030 [4–6].

To address these issues, two main measures need to be taken. First, carbon emissions must be drastically reduced, which means minimizing reliance on carbon-based energy and promoting renewable energy alternatives across various industries [7,8]. Second, traditional technologies such as chemical conversion, photocatalytic reduction, electrochemical reduction, and biotransformation should be employed to process existing carbon dioxide [9,10]. The conversion efficiency of these methods still needs improvement, with the major bottleneck being that the carbon in carbon dioxide is in its highest oxidation state, requiring additional energy for direct conversion, thereby leading to more carbon emissions [11]. These methods can generate products such as CO, CH_4, $HCOOH$, and CH_3OH. Before these gaseous or liquid products can be used as energy storage materials, they need to undergo processes such as compression, packaging, storage, and transportation, which undoubtedly result in further energy loss. Therefore, traditional carbon dioxide conversion methods are inherently high-carbon processes [12].

Among the currently researched secondary batteries, lithium–carbon dioxide batteries have garnered researchers' interest because of their exceptional theoretical energy density and eco-friendliness. Li–CO_2 batteries utilize CO_2 as a carrier, offering both CO_2 conversion and energy storage capabilities. Based on reaction 1-1, the energy density of Li–CO_2 batteries is as high as 1876 Wh kg^{-1}, which is significantly larger than that of conventional lithium-ion batteries (100–120 Wh kg^{-1}). These batteries can convert carbon dioxide from the atmosphere into chemical energy, making them a promising choice for next-generation energy storage and conversion [13–16]. However, lithium–carbon dioxide batteries still face several key issues in practical applications, as follows. (1) Slow reaction kinetics. The chemical properties of carbon dioxide are extremely stable, resulting in slow electrochemical reaction kinetics in the battery, exacerbating carbon deposition on electrode materials and further affecting battery cycle life and performance stability [17–19]. (2) Poor electrolyte stability. Current electrolyte systems tend to decompose during charge and discharge, generating by-products that deposit on the electrode surface, forming a solid electrolyte interphase (SEI) film, the instability and non-uniformity of which lead to shortened battery cycle life and reduced safety [20,21]. (3) Carbon deposition issues. During the operation of lithium–carbon dioxide batteries, the reduction in carbon dioxide easily generates solid carbon deposits [22,23]. These carbon deposits cover the electrode surface, reducing the number of active sites and severely affecting battery reaction efficiency and capacity retention. Carbon deposition not only leads to electrode surface passivation but also causes structural changes in electrode materials, resulting in decreased mechanical properties and increased internal resistance of the battery [24].

To clearly elucidate the latest progress in the field of lithium–carbon dioxide electrochemistry, this paper discusses in detail the electrochemical reaction mechanism of lithium–carbon dioxide batteries and provides an in-depth analysis of the products. Additionally, the latest research progress on cathode catalyst materials is highlighted, and the challenges and future development trends of lithium–carbon dioxide batteries are summarized (Figure 1). It is believed that this paper will help deepen the understanding of lithium–carbon dioxide battery systems, thereby providing a reference for the future design of practical batteries.
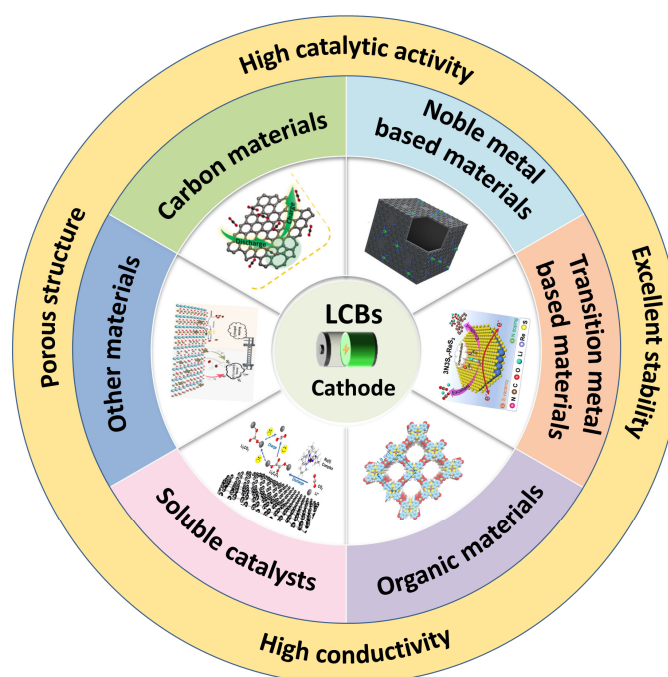

Figure 1. Schematic illustration of catalysts in Li–CO_2 batteries.

2. Overview of Lithium–Carbon Dioxide Batteries

2.1. Mechanism of Lithium–Carbon Dioxide Batteries

Lithium–carbon dioxide batteries primarily consist of a porous cathode with catalytic properties, a conductive electrolyte, a separator to isolate the anode and cathode, and a lithium metal sheet as the anode (Figure 2). During the discharge process, metallic lithium undergoes oxidation to form lithium ions. Driven by the voltage difference, these lithium ions migrate through the conductive electrolyte towards the cathode. As they move, the cathode loses electrons, allowing carbon dioxide molecules to combine with the lithium ions. This reaction produces lithium carbonate and carbon, which are the main discharge products of the lithium–carbon dioxide battery. During the charging process, Li_2CO_3 decomposes, releasing lithium ions and CO_2. However, solid Li_2CO_3 is a non-conductive substance, and its accumulation can block the catalytic pathways in the cathode, cover active sites, and hinder internal reactions within the battery. This leads to reduced capacity and affects the battery's stability. Therefore, studies on materials with stable electrochemical performance and high conductivity are ideal avenues of pursuit for researchers.
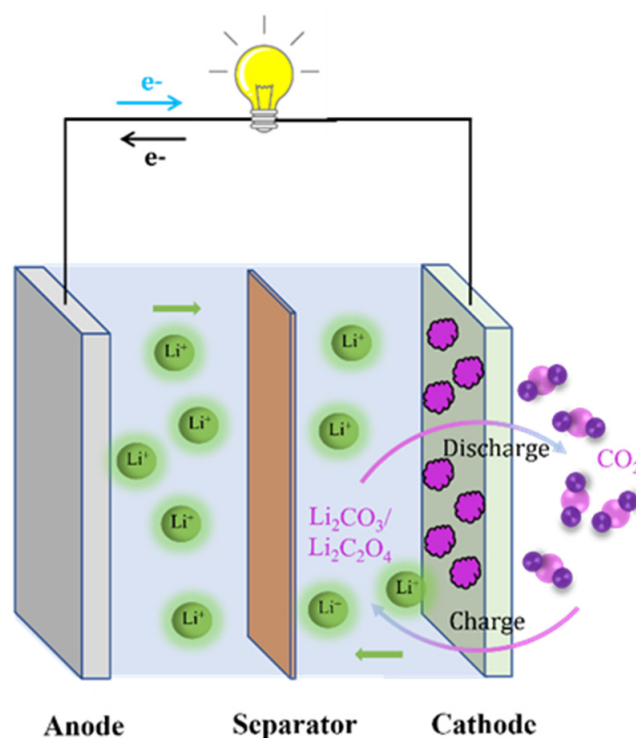

Figure 2. Lithium–carbon dioxide battery structure.

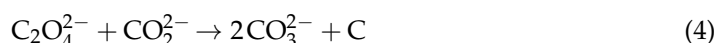### 2.2. Product Analysis of Lithium–Carbon Dioxide Batteries

It is well known that lithium–carbon dioxide batteries involve various complex reactions and multiple interfacial interactions among the reaction products. To understand these reaction mechanisms, researchers have conducted extensive experiments and analyses. Lithium carbonate requires a high charging voltage for its decomposition. This high voltage can lead to the decomposition of the electrolyte, triggering a series of side reactions.

In 2013, Archer et al. [25] used pure carbon dioxide as the reactant gas to develop a lithium–air battery with a lithium metal anode. During the discharge process, this battery achieved a discharge specific capacity of 2500 mA h g^{-1}. Li_2CO_3 was confirmed as the discharge product, and a feasible reaction formula was proposed:

$$4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C \tag{1}$$

In the same year, Kim and Kang et al. [26] investigated a lithium–air battery using dimethyl ether (DME) and dimethyl sulfoxide (DMSO) as electrolytes, with a 1:1 volume ratio of oxygen to carbon dioxide. Their research demonstrated that different electrolytes significantly influence the reaction pathways of discharge products. Lower-order electrolytes tend to form lithium peroxide, while higher-order electrolytes primarily facilitate the conversion of carbon dioxide to lithium carbonate, which exhibits reversibility over multiple cycles.

The reversibility of lithium carbonate has been confirmed, but its discharge reaction pathways remain unclear. Chen and colleagues [27] reasonably hypothesized that certain disproportionate reactions must occur in Li–CO_2 batteries, involving reaction Equations (2)–(5).

$$2CO_2 + 2e^- \rightarrow C_2O_4^{2-} \tag{2}$$

$$C_2O_4^{2-} \rightarrow CO_2^{2-} + CO_2 \tag{3}$$

$$C_2O_4^{2-} + CO_2^{2-} \rightarrow 2CO_3^{2-} + C \tag{4}$$

$$CO_3^{2-} + 2Li^+ \rightarrow Li_2CO_3 \tag{5}$$

Equation (2) describes the single-electron reduction of CO_2 to $C_2O_4^{2-}$ on the surface of carbon materials. Equations (3) and (4) illustrate the two-step decomposition of the unstable $C_2O_4^{2-}$ into CO_3^{2-} and carbon. In Equation (5), Li_2CO_3 forms as a crystalline product.

Chen et al. [27] synthesized Mo_2C anchored on carbon nanotubes (Mo_2C–CNTs) via a carbothermal reduction method. Compared to pure carbon nanotubes, which exhibit a high charge voltage of up to 4.25 V, Mo_2C–CNTs demonstrated a significantly lower charge voltage of approximately 3.25 V. For the first time, $Li_2C_2O_4$ was identified as the sole formation product, as confirmed through Raman spectroscopy and X-ray photoelectron spectroscopy. These analyses showed that amorphous $Li_2C_2O_4$–Mo_2C, which decomposes more easily than Li_2CO_3, forms only when Mo_2C–CNTs are used as the cathode. $Li_2C_2O_4$–Mo_2C accelerates reaction kinetics and lowers the voltage plateau, facilitating the reaction. The chemical steps can be succinctly described by Equations (6) and (7).

$$2CO_2 + 2e^- \rightarrow C_2O_4^{2-} \tag{6}$$

$$C_2O_4^{2-} + 2Li^+ + Mo_2C \rightarrow Li_2C_2O_4 - Mo_2C \tag{7}$$
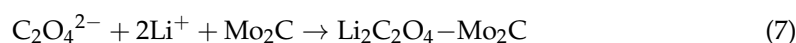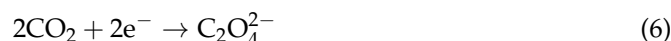
3. Lithium–Carbon Dioxide Battery Catalysts

Notably, there has been substantial advancement in the domain of cathode materials for lithium–carbon dioxide batteries in recent years, particularly in research on cathode catalysts [28,29]: (1) possessing a high inherent ability to catalyze electrochemical reactions by reducing the barriers to these reactions; (2) a significant surface area that allows for the efficient diffusion of reactants and the deposition of solid products [30]; (3) good conductivity to ensure rapid electron transfer; (4) chemical and electrochemical stability [31]; and (5) cost-effectiveness and eco-friendliness. To achieve high-performance lithium–carbon dioxide batteries, it is essential to develop catalysts with high catalytic activity and high conductivity. This section provides a comprehensive analysis of the most recent advancements in research and design approaches for these catalysts, providing valuable references for future research [32].

3.1. Carbon-Based Catalysts

Carbon compounds have several benefits, including exceptional electrical conductivity, a substantial specific surface area, and controllable pore structure, making them widely used in various electrochemical energy storage devices. In the early development of lithium–carbon dioxide batteries, commercial activated carbon was first introduced, but it had drawbacks such as poor catalytic activity and a limited structural system [33]. As research progressed, researchers began to investigate functional carbon nanomaterials with

unique quantum-size effects and surface chemical states (e.g., carbon nanotubes, graphene), which are currently the most widely used carbon materials in the field of Li–CO$_2$ batteries.

In 2015, a team led by Zhou initially utilized graphene as a cathode material in lithium–carbon dioxide batteries [34]. Although the battery exhibited large overpotential and poor reversibility during full charge–discharge experiments, this high-capacity rechargeable lithium–carbon dioxide battery still attracted widespread attention (Figure 3a–c). In the same year, Zhang et al. further explored carbon nanotubes as cathode catalysts for lithium–carbon dioxide batteries [35]. They designed cathode catalyst materials with a highly active three-dimensional porous structure, which facilitated the transport of electrons and carbon dioxide gas as well as the deposition of discharge products, thereby improving the battery's cycling stability. However, the electrocatalytic activity of pure carbon materials for the carbon dioxide reduction and emission reaction process is very low, which greatly limits their practicality in lithium–carbon dioxide batteries.
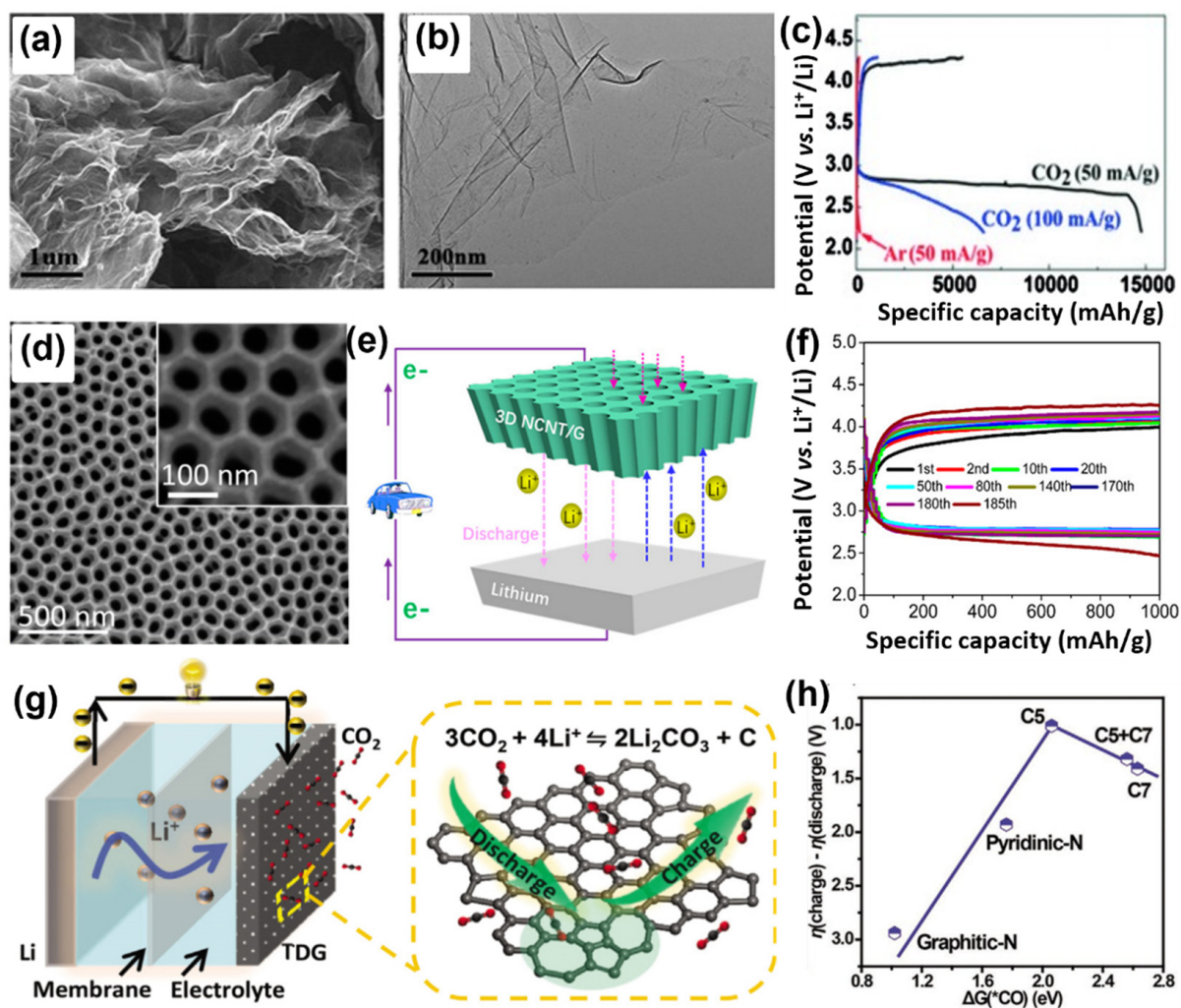

Figure 3. (**a**) SEM and (**b**) TEM images of graphene. (**c**) The initial discharge curves of the batteries with graphene cathodes at a current density of 50 mA g^{-1} and 100 mA g^{-1} in CO$_2$ atmosphere, as well as at 50 mA g^{-1} in Ar atmosphere. Copyright 2015, Wiley-VCH [34]. (**d**) Overhead view of the CNT–G interfaces (3D NCNT–G). The inset image is a magnified view. (**e**) Discharge–charge profiles and (**f**) cycling performance of the 3D NCNT–G-based Li–CO$_2$ battery tested at 100 mA g^{-1}. Copyright 2020, American Chemical Society [23]. (**g**) Schematic illustration of a Li–CO$_2$ battery assembly. (**h**) The overpotential of charge and discharge (ηcharge–ηdischarge) as a function of the adsorption energy of *CO (ΔG*CO intermediate). Copyright 2021, Wiley-VCH [32].

To address this issue, Dai et al. developed a self-supporting, binder-free N-doped bi-layer 3D carbon nanotube–graphene (CNT–G) cathode material. The 3D NCNT–G cathode material facilitated the spread of CO_2 gas and electrolyte by utilizing vertically aligned open carbon nanotube channels. Additionally, it achieved effective electron transport by utilizing a continuously connected 3D carbon framework. Its large surface area provided numerous active sites, facilitating CO_2 reduction and evolution reactions. The resulting lithium–carbon dioxide battery exhibited high specific capacity of 17,534.1 mAh g^{-1}, high coulombic efficiency of 98.3%, and low overpotential of 1.13 V (Figure 3d–f). However, during long-term cycling, the material still faced inevitable electrode structure degradation issues, requiring further verification of its long-term stability and reproducibility [23].

Doping heteroatoms (e.g., nitrogen atoms) can effectively modulate the electronic structure of carbon-based catalysts, significantly enhancing their catalytic activity voltage. Guided by theoretical simulations, Ding et al. designed and synthesized a self-supporting N-doped graphene carbon aerogel. The obtained graphene carbon aerogel with a three-dimensional hierarchical pore structure exhibited significantly enhanced initial energy efficiency (approximately 78.46%) and over 1500 h of cycling stability (at a current density of 20 μA cm^{-2}) in lithium–carbon dioxide batteries [36]. Additionally, topological defects (e.g., pentagonal and heptagonal structures replacing hexagonal structures) can introduce additional active sites in the carbon framework, thereby enhancing the catalytic activity of graphene materials. Based on this, researchers developed topological defect-rich graphene (TDG) as a metal-free cathode material for lithium–carbon dioxide batteries (Figure 3g,h). This exceptional performance was attributed to the introduction of sufficient active sites by topological defects in the carbon framework, promoting CO_2 reduction and Li_2CO_3 formation/decomposition. Density functional theory (DFT) calculations revealed the advantage of negatively charged C atoms in topological defects for CO_2 molecule adsorption and Li_2CO_3 decomposition, and the heterocyclic five-membered ring (C5) exhibited a lower theoretical voltage difference (1.01 V) during charge–discharge processes [32].

Despite the above progress, the catalytic activity of pure carbon materials is limited, and the aforementioned batteries still exhibit poor cycling stability and low coulombic efficiency in experiments. To effectively improve battery performance, researchers are continuously studying and designing more efficient cathode catalysts.

3.2. Noble Metal-Based Catalyst

Noble metals and their oxides are widely recognized for their unique electronic structures, which confer excellent chemical and electrochemical stability, making them highly esteemed cathode catalysts in the field of electrocatalysis [37–41]. These catalysts exhibit outstanding catalytic performance in lithium–carbon dioxide batteries, primarily because they can form optimal interactions with key intermediates during the reaction process, effectively lowering the energy barriers in the CO_2 reduction reaction (CO_2RR) and CO_2 evolution reaction (CO_2ER). Additionally, noble metal-based catalysts possess high electrical conductivity and excellent corrosion resistance, further enhancing their efficiency and stability in electrochemical reactions. Therefore, the application of noble metals and their oxides in lithium–carbon dioxide batteries holds great promise, providing important technical support for improving battery performance [30,42–45].

In order to tackle the existing challenges related to low coulombic efficiency and high charging overpotential in lithium–carbon dioxide batteries, Zhou's team considered the excellent catalytic activity of ruthenium and applied ruthenium nanoparticles as cathode catalysts in lithium–carbon dioxide batteries. Experimental results showed that ruthenium nanoparticles significantly reduced the charging overpotential and enhanced the cycling performance of lithium–carbon dioxide batteries (Figure 4a–c).
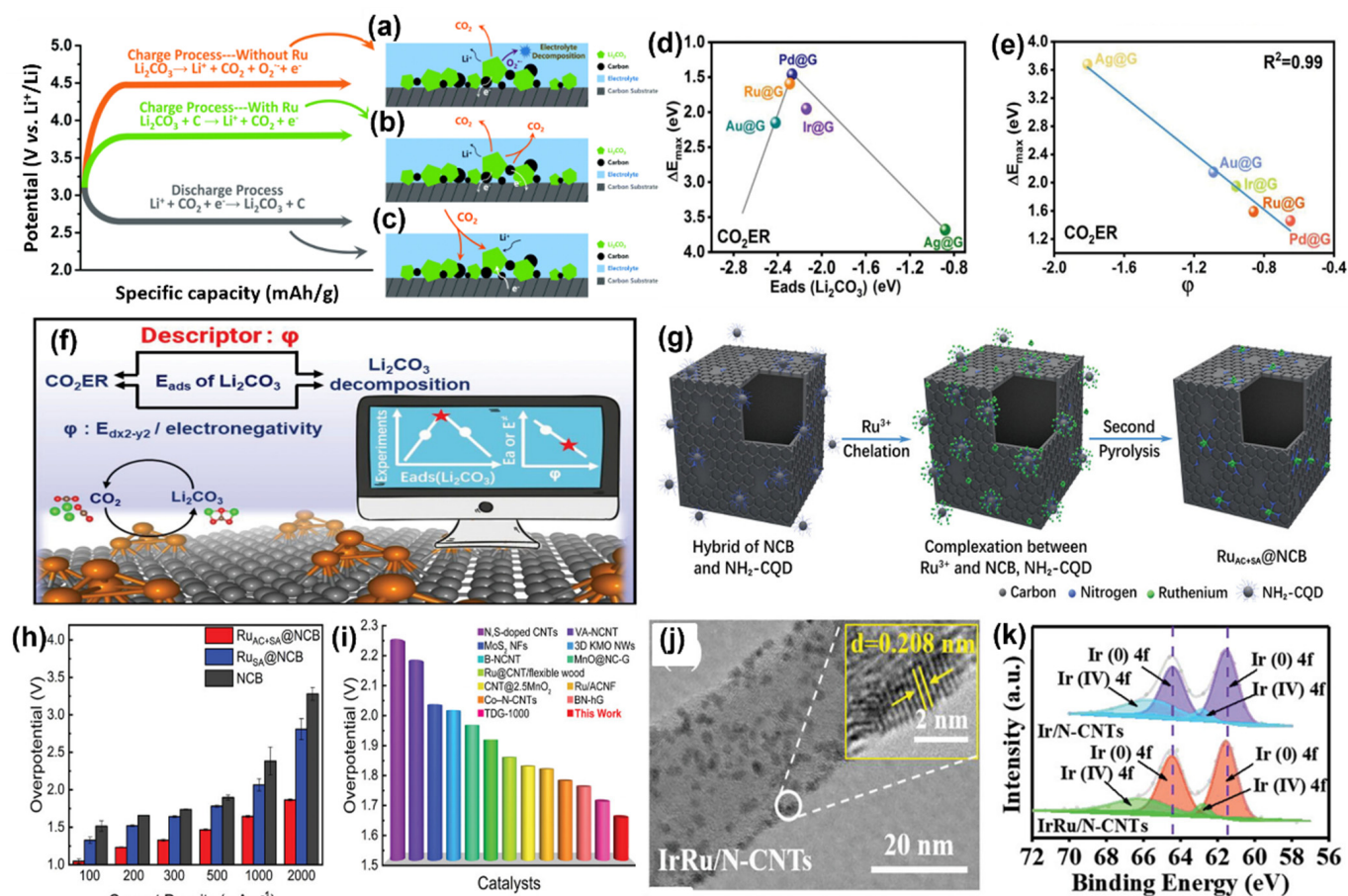
Figure 4. Schematic diagram of the (**a**) reaction mechanism of the charging process of the Li–CO$_2$ battery without the Ru catalyst, (**b**) possible charging mechanism of the Li–CO$_2$ battery with the Ru catalyst and (**c**) discharging process of the Li–CO$_2$ battery. Copyright 2017, Royal Society of Chemistry [33]. (**d**) Volcano-shaped relationship between the adsorption energy of Li$_2$CO$_3$ and the reaction energy of the rate-determining step of CO$_2$ER. (**e**) Linear relationship between the intrinsic descriptor and the reaction energy of the rate-determining step of CO$_2$ER. (**f**) Schematic diagram characterizing the catalytic performance of NM@G by the established thermodynamic reaction descriptor and intrinsic electronic descriptor. Copyright 2023, Wiley-VCH [46]. (**g**) Schematic illustrating the synthesis procedure for RuAC + SA@NCB. (**h**) Total overpotentials of RuAC + SA@NCB, RuSA@NCB, and NCB cells at different current densities. The overpotential refers to the voltage difference between the middle points of discharge and charge curves. (**i**) Comparison of overpotentials at 1 A g^{-1} for RuAC + SA@NCB with state-of-the-art catalysts in the literature. Copyright 2022, Wiley-VCH [45]. (**j**) TEM images of IrRu–N CNTs. (**k**) Ru 3d XPS spectra and Ir 4f XPS spectra of IrRu–N CNTs, respectively. Copyright 2023, Wiley-VCH [47].

To further explore the intrinsic properties of noble metals on the decomposition of Li$_2$CO$_3$, Xie et al. prepared a series of graphene-supported noble metal (NM@G, NM = Ag, Au, Pd, Ru, Ir) materials. Among them, the Pd@G cathode exhibited significantly reduced overpotential (0.41 V relative to Li$^+$/Li) and extremely low charging plateau (3.2 V) in lithium–carbon dioxide batteries (Figure 4d–f), which could be attributed to the excellent electron transport and ion and diffusion capabilities [46].

Furthermore, it was found that the charging process of lithium–carbon dioxide batteries often involves the self-decomposition reaction of Li$_2$CO$_3$. The application of ruthenium avoided this reaction and promoted a reversible reaction between Li$_2$CO$_3$ and carbon, thereby improving the reversibility of the battery [33]. Additionally, Han et al. designed and developed a novel catalyst comprising Ru atomic clusters (RuAC) and single-atom

Ru–N$_4$ (RuSA) composite sites. This composite catalyst structure optimized the interactions with key reaction intermediates, significantly lowering the energy barriers of the reactions and improving the reaction kinetics of the battery (Figure 4g–i). Specifically, the RuAC + SA@NCB catalyst exhibited extremely low overpotentials at ultrahigh current densities of 1 and 2 A g^{-1} (1.65 and 1.86 V, respectively), and its cycle life was twice that of the benchmark [45].

Research has found that constructing dual catalytic sites can significantly enhance the catalytic activity of batteries. Sun et al. prepared a synergistic catalyst composed of nitrogen-doped carbon nanotube composites modified with uniformly ultrafine iridium–ruthenium alloy nanoparticles (IrRu–N CNTs). This IrRu–N-CNT catalyst combined the synergistic effects of iridium–ruthenium dual catalytic sites, significantly enhancing the catalytic activity of the battery (Figure 4j,k). Experimental results showed that the lithium–carbon dioxide battery with this catalyst exhibited a discharge specific capacity of up to 6228 mAh g^{-1} and extended cycle life to 7660 h at a fixed specific capacity of 100 mA g^{-1} [47].

Although noble metals and their oxides exhibit excellent catalytic activity in lithium–carbon dioxide batteries, they have several notable drawbacks. Noble metals such as platinum, palladium, iridium, and ruthenium are expensive, significantly increasing the overall cost of the batteries, making large-scale applications difficult to achieve. Additionally, noble metals and their oxides may undergo morphological changes or corrosion in electrochemical environments, leading to catalyst deactivation, which affects the battery's lifespan and performance.

3.3. Transition Metal Compound-Based Catalysts

Although noble metals and their oxides have demonstrated excellent catalytic performance in batteries, their high cost and scarcity limit their widespread application in lithium–carbon dioxide batteries. In contrast, transition metals, due to their multivalence and lower cost, have become ideal substitutes for noble metals. In recent years, extensive study has been conducted on the utilization of transition metal-based materials in Li–CO$_2$ batteries and achieved significant results. By continuously optimizing and improving transition metal-based catalysts, scientists hope to further enhance battery efficiency and stability, thereby promoting their widespread adoption in practical applications.

Metal oxides and metal sulfides, as semiconductor catalysts, have received widespread attention in recent years due to their simple preparation methods and abundant raw materials. Through rational structural design, such as introducing element doping, creating vacancies, and constructing heterojunctions, these materials can significantly enhance the efficiency of the carbon dioxide reduction reaction (CO$_2$RR) and the carbon dioxide evolution reaction (CO$_2$ER). These engineering methods optimize the active sites of the catalysts, improve the transport performance of electrons and ions, and actively promote the electrochemical conversion process of CO$_2$ [17,29].

Cheng et al. systematically studied the synergistic effect of nucleophilic N-doping and electrophilic S vacancies in the ReS$_2$ plane, revealing their bifunctional catalytic performance in lithium–carbon dioxide (Li–CO$_2$) batteries. The study found that this dual-center design could effectively adjust the interaction with lithium atoms and carbon/oxygen atoms in intermediates, thereby reducing the energy barriers of the rate-determining steps and significantly enhancing catalytic efficiency (Figure 5a–c). The optimized catalyst achieved an ultrasmall voltage difference of 0.66 V and an ultrahigh energy efficiency of 81.1% at a current density of 20 μA cm^{-2} [31].
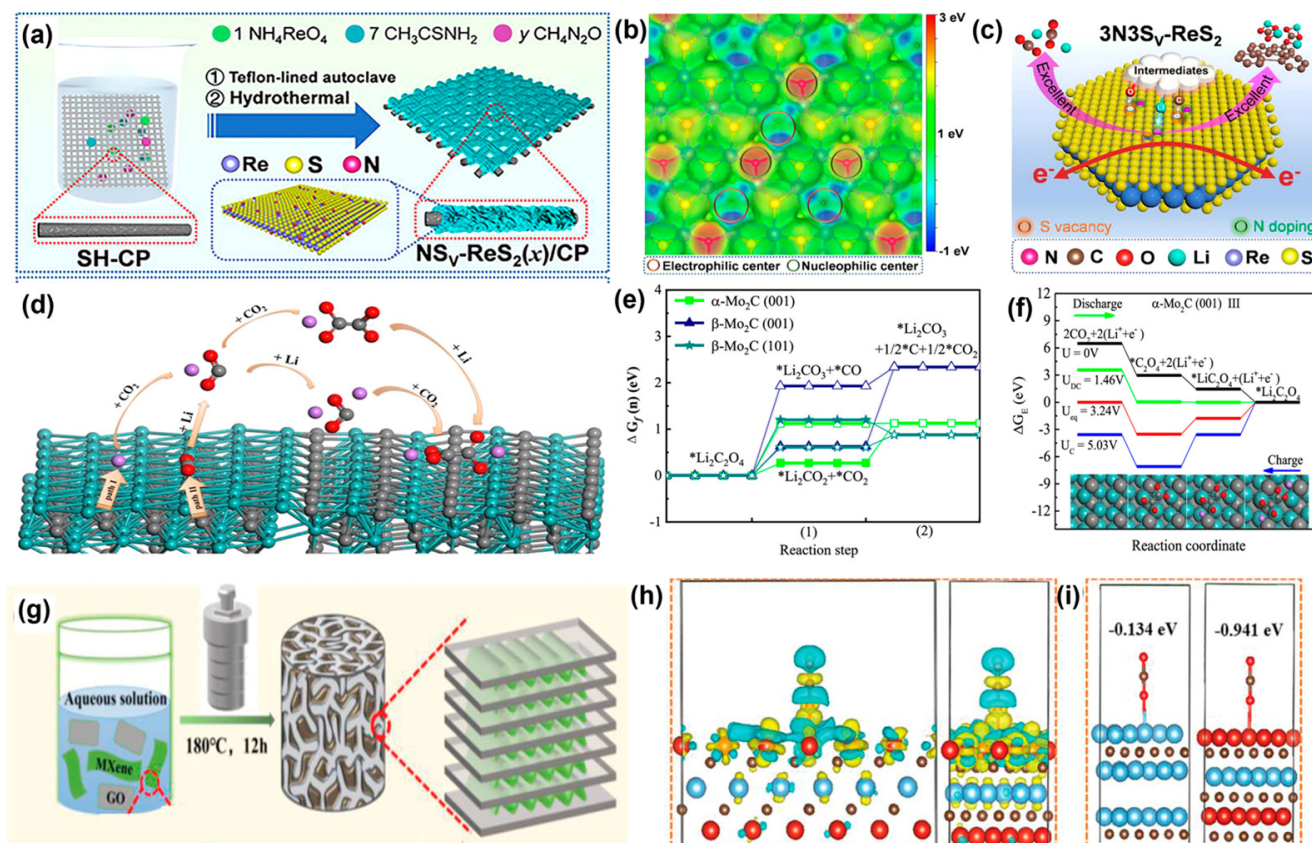
Figure 5. (**a**) Schematic of the synthesis process of NSV-ReS$_2$(x)/CP. (**b**) Surface electrostatic potential diagrams of 3N$_3$SV-ReS$_2$. (**c**) Illustration of the working mechanism of the nucleophilic N dopant and electrophilic S vacancy dual centers in the 3N$_3$SV-ReS$_2$ plane. Copyright 2022, American Chemical Society [31]. (**d**) Schematic illustration of Mo$_2$C as cathode catalyst in a Li–CO$_2$ battery. (**e**) Calculated energetic profiles for Li$_2$C$_2$O$_4$ splitting into Li$_2$CO$_3$ on three Mo$_2$C surfaces. Solid symbols indicate path 1; open symbols are path 2. (**f**) Electrochemical free energy changes in Li–CO$_2$ batteries with α-Mo$_2$C as cathode catalysts under different potentials. Insets show overhead views of the optimized adsorption systems. Copyright 2020, American Chemical Society [28]. (**g**) Synthesis of TVGA and schematic diagram of Li–CO$_2$ battery. (**h**) Charge density difference of TiVC (001) with surface-absorbed CO$_2$ molecules at different front and left views. (**i**) Adsorption energy of Ti$_3$C$_2$ (001) and TiVC (001) with surface-absorbed CO$_2$ molecules. Copyright 2023, Wiley-VCH [48].

MXene refers to a group of flat materials made up of transition metal carbides, nitrides, or carbonitrides. With its high conductivity and substantial specific surface area, this material offers an abundance of active sites. Consequently, it enhances the efficiency of charge transfer in batteries, facilitates the reduction reaction of CO$_2$, promotes the decomposition reaction of Li$_2$CO$_3$, and ultimately improves battery efficiency. By functionalizing the surface of MXene, its catalytic activity and selectivity can be further enhanced, improving the cycling stability and discharge capacity of the battery. Therefore, MXene materials have significant application potential as cathode materials in lithium–carbon dioxide batteries.

Yuan et al. systematically studied the reaction mechanism of molybdenum carbide (Mo$_2$C) for lithium–carbon dioxide (Li–CO$_2$) batteries. When Mo$_2$C–CNTs were used as the cathode catalyst, Li$_2$C$_2$O$_4$ was observed as the final discharge product. During the charging process, Li$_2$C$_2$O$_4$ could be decomposed below 3.5 V, the energy efficiency increased to 80%, and the reversible cycle life reached 40 cycles, with the overpotential decreasing from 1.8 V (CNTs) to 0.65 V (Mo$_2$C–CNTs) at an initial specific capacity of 100 Ah cm^{-2} (Figure 5d–f) [28].

Zhou et al. designed a bimetallic MXene solid solution. The results showed that the Li–CO_2 battery based on the bimetallic MXene solid solution TiVC cathode exhibited an excellent discharge specific capacity of 27,880 mAh g^{-1} at a current density of 100 mA g^{-1} and operated at a stable discharge plateau of 2.77 V and a low overpotential of 1.5 V (Figure 5g–i) [48].

3.4. Organic Catalysts

In the exploration of transition metal catalysts, researchers have discovered that designing catalysts with specific spatial structures can effectively improve battery performance. Metal–organic frameworks (MOFs) have uniform pore architectures, high porosity, significant specific surface areas, and adjustable pore diameters, and excellent structural stability, making them ideal choices for CO_2 capture and electrocatalysis [49–51]. Researchers have found that by designing MOF catalysts with specific spatial structures, battery performance can be significantly enhanced. These characteristics endow MOFs with significant advantages and broad prospects in the field of lithium–carbon dioxide battery cathode catalysts.

Wang et al. first explored the potential of MOFs as porous catalysts in CO_2 electrodes, utilizing their efficient CO_2 capture capability and monodispersed active metal sites to promote the decomposition of Li_2CO_3. The results showed that they could exhibit a low charging voltage, with a charging voltage of 4.46 V at a current density of 50 mA g^{-1}, and remained relatively stable up to the 10th cycle (Figure 6a,b). The study revealed the great potential of MOFs in improving the reversibility and energy efficiency of lithium–carbon dioxide batteries. However, despite their excellent performance, the long-term stability and cost-effectiveness of MOFs in practical applications still need further research and validation [52].

In order to achieve additional cost reductions, researchers have increased their emphasis on catalysts that are based on transition metals. He et al. used Cu–TCPP as a cathode catalyst in lithium–carbon dioxide batteries, achieving a high discharge specific capacity of 20,393 mAh g^{-1} at a current density of 100 mA g^{-1}, a long cycle life of 123 cycles at a current density of 500 mA g^{-1}, and a low overpotential of 1.8 V at a current density of 2000 mA g^{-1} (Figure 6c). The DFT simulations demonstrated that the porphyrin ligand possessed a remarkable ability to capture CO_2, and the presence of Cu atoms enhanced the thermodynamics and kinetics of the CO_2 reduction and evolution reactions through a synergistic catalytic effect [53].

Lan et al. successfully prepared a metal–organic framework (MOF) nanosheet based on phthalocyanine (CoPc–Mn–O) and applied it to light-assisted lithium–carbon dioxide batteries. The prepared CoPc–Mn–O exhibited nanosheet morphology (approximately 1 nm thick), dual active metal sites (Co–N_4 and Mn–O_4), high conductivity, and excellent photosensitivity. The battery with CoPc–Mn–O as the photocathode catalyst displayed an ultralow overpotential (0.05 V) and high energy efficiency (up to 98.5%) under full-spectrum conditions, and showed excellent cycling stability with rapid charge and discharge for 60 h at a current density of 0.02 mA cm^{-2} (Figure 6d,e) [54].

Covalent organic frameworks (COFs) are an emerging class of porous crystalline materials with highly ordered pore structures and extremely high specific surface areas, enabling them to provide numerous active sites, effectively capture and fix CO_2, and improve the CO_2 utilization efficiency in lithium–carbon dioxide batteries [55–57]. Xie et al. first used COF materials as high-efficiency cathodes for lithium–carbon dioxide batteries. The 1D channels in the COF served as diffusion channels for CO_2 and Li^+, improving the kinetics of the electrochemical reactions. The COF-based lithium–carbon dioxide battery exhibited an ultrahigh specific capacity of 27,348 mAh g^{-1} at a current density of 200 mA g^{-1} and a low overpotential of 1.24 V at a limited specific capacity of 1000 mAh g^{-1}. The battery showed slow discharge voltage decay over a current density range of 0.1 to 4 A g^{-1}, significantly improving the rate performance. The COF-based battery could stably operate for 200 cycles at a high current density of 1 A g^{-1} (Figure 6f,g) [58].
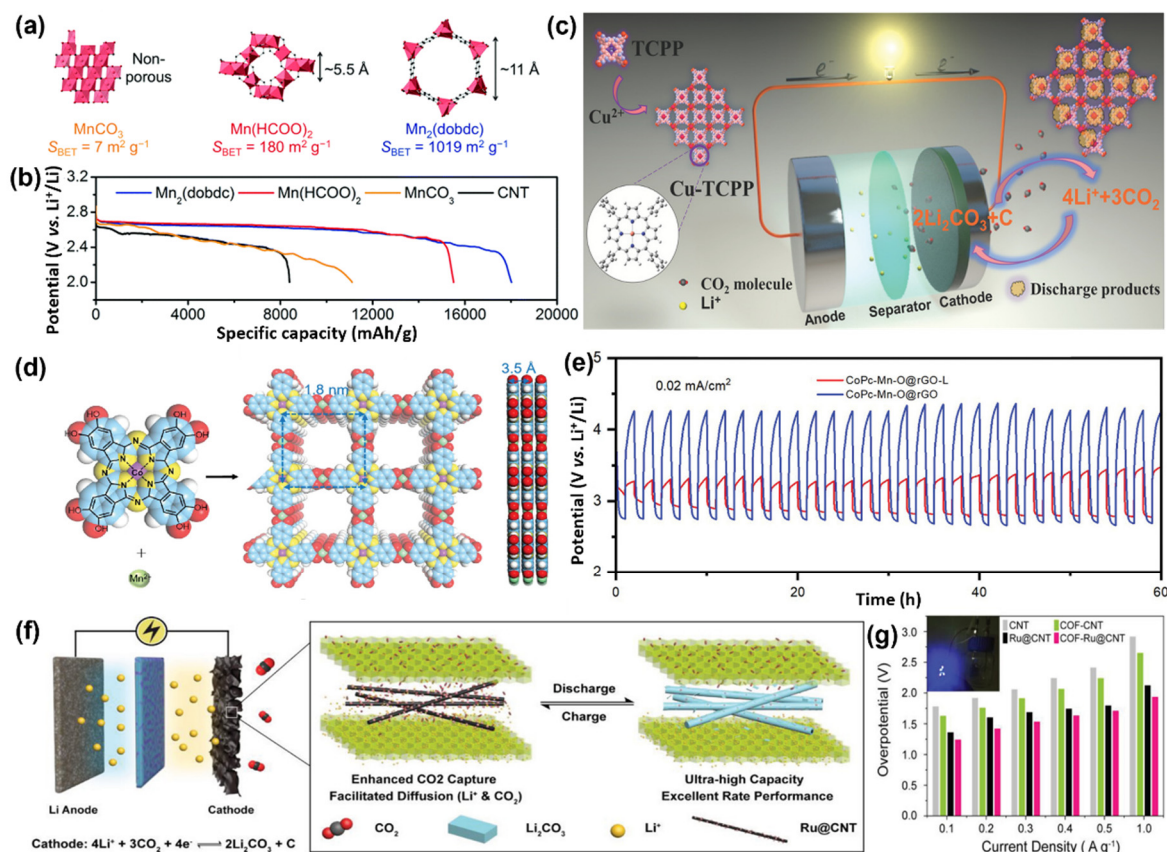
Figure 6. (**a**) Crystal structures of $MnCO_3$, $Mn(HCOO)_2$ and $Mn_2(dobdc)$ along certain directions. (**b**) Discharge voltage curves of $Mn_2(dobdc)$, $Mn(HCOO)_2$, $MnCO_3$ and CNTs at 50 mA g^{-1} with a cut-off voltage of 2.0 V. Copyright 2018, Royal Society of Chemistry [52]. (**c**) Structural model of Cu–TCPP and the schematic diagram of Li–CO_2 battery. Copyright 2022, Wiley-VCH [53]. (**d**) Design and synthetic scheme for CoPc–Mn–O, (**e**) Voltage profiles of typical Li–CO_2 battery cycled with 0.01 mAh cm^{-2} cut-off capacity with and without illumination for CoPc–Mn–O@rGO–L and CoPc–Mn–O@rGO. Copyright 2022, Wiley-VCH [54]. (**f**) Schematic illustration of COF working as the CO_2 collector and the gas-ion diffusion channels for Li–CO_2 battery cathode. (**g**) Battery overpotentials at various current densities (inset: four blue LEDs in parallel were lit brightly by the Li–CO_2 battery with COF–Ru@CNT cathode). Copyright 2019, Wiley-VCH [58].

Although COF materials have many advantages, their intrinsic conductivity is relatively low, requiring them to be combined with conductive materials (such as carbon nanotubes or graphene) to improve overall conductivity. Additionally, the synthesis and functionalization processes of COF materials are relatively complex, which may increase manufacturing costs and process difficulty. In practical applications, the large-scale production and consistency control of COF materials remain challenges that require further research and optimization.

3.5. Soluble Catalysts

Traditional Li–CO_2 batteries, based on common reaction pathways such as reducing CO_2 to CO, oxalates, or carbon, often exhibit low output voltage (<2.5 V) and low energy efficiency due to the formation of Li_2CO_3 as a discharge product. As a consequence, there is a decrease in energy efficiency and the occurrence of significant parasitic reactions in lithium–carbon dioxide batteries. Liquid catalysts can avoid the issue of active sites being covered by insulating products like Li_2CO_3 during use, thereby extending the battery's cycle life. By introducing liquid catalysts, lithium–carbon dioxide batteries can achieve higher

output voltage and larger discharge capacity, demonstrating superior electrochemical performance and practical application prospects.

Bhattacharyya et al. demonstrated a simple liquid electrolyte-soluble Cu compound, copper chloride ($CuCl_2$), as an alternative electrocatalyst for non-aqueous lithium–carbon dioxide (Li–CO_2) batteries. The key to choosing $CuCl_2$ was that the theoretical potential of the Li–CO_2 battery (about 2.8 V; Li^+/Li) fell within the potential range of the Cu^{1+} | Cu^0 redox couple (2.3–3.3 V; Li^+/Li). By adding $CuCl_2$ to the liquid electrolyte, efficient CO_2 electrocatalysis and excellent Li–CO_2 battery performance were achieved near the porous CO_2 cathode loaded with multiwalled carbon nanotubes (MWCNTs). With the addition of $CuCl_2$, the battery's overpotential was reduced to 0.65 V, less than half of that without the addition (about 1.7 V) [59].

Wang et al. used $Ru(bpy)_3Cl_2$ as a solution-phase catalyst for Li–CO_2 batteries, demonstrating it as one of the most effective catalysts to date (Figure 7a,b). Spectroscopic and electrochemical analyses showed that the RuII center could interact with dissolved CO_2 molecules, promoting the formation of oxalate intermediates. The interaction with the RuII center stabilized the generated oxalate intermediates, delaying their conversion to carbonates. During charging, the overpotential required to decompose the oxalate species was significantly reduced (about 3.86 V), thereby improving energy efficiency and reducing side reactions. At a current density of 300 mA g^{-1}, the Li–CO_2 battery with $Ru(bpy)_3Cl_2$ as the catalyst achieved over 60 charge–discharge cycles at a fixed specific capacity of 1000 mAh g^{-1} [60].
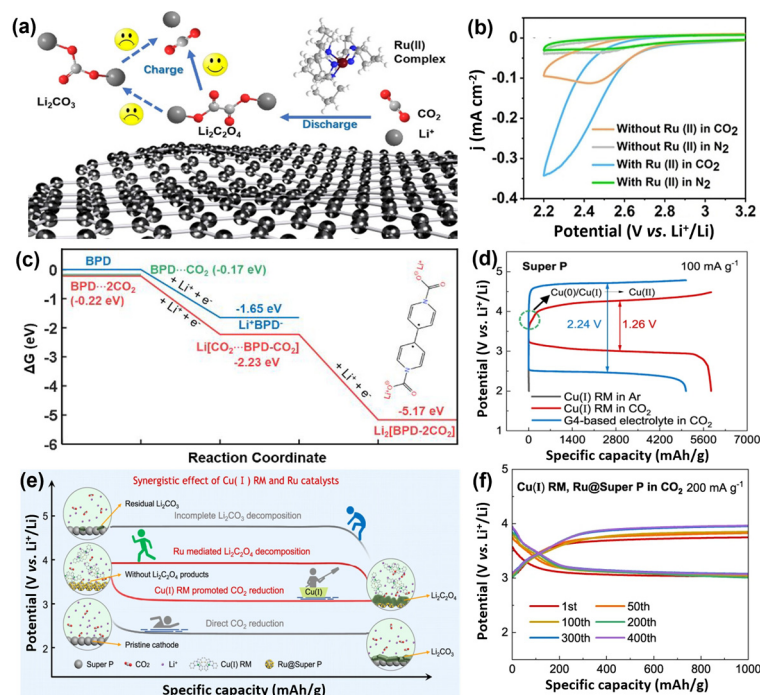

Figure 7. (**a**) Illustration of the function of the RuII catalyst in Li–CO_2 electrochemistry. (**b**) CO_2RR potential range CV at steady states of 1.0 M LiTFSI/TEGDME with or without RuII in N_2 or CO_2 atmosphere. Copyright 2021, Wiley-VCH [60]. (**c**) Calculated energetic profiles of BPD-assisted Li–CO_2 electrochemistry. Copyright 2023, American Chemical Society [61]. (**d**) Galvanostatic discharge–charge curves for Super P carbon cathodes in various electrolytes and atmospheres: 0.5 mM Cu(I) RM in 0.1 M LiClO$_4$–MeCN under Ar (dark gray), 0.5 mM Cu(I) RM in 0.1 M LiClO$_4$–MeCN under CO_2 (red), and 1 M LiTFSI–G$_4$ under CO_2 (blue). Current density is 100 mA g^{-1}. (**e**) Schematic of the synergetic effect of Cu(I) RM and Ru catalysts for the Li–CO_2 battery system. (**f**) Cyclic performance of the Li–CO_2 battery with a Cu(I) RM-based electrolyte and a Ru@Super P cathode under a fixed specific capacity of 1000 mAh g^{-1} at a current density of 200 mA g^{-1}. Copyright 2023, Springer Nature [62].

Peng et al. proposed a new concept of Li–CO$_2$ batteries based on the redox cycle of 4,4′-bipyridine (BPD), achieving reversible CO$_2$ capture/release and efficient energy storage. Direct evidence from spectroscopic and theoretical calculations showed that BPD first coordinated with CO$_2$ to form a [BPD$\cdots$2CO$_2$] complex, which was further reduced to Li$_2$[BPD-2CO$_2$] via a two-electron pathway during discharge. During charging, the reaction reversed, regenerating BPD and CO$_2$. The battery exhibited high discharge specific capacity (>1000 mAh g^{-1}), low discharge–charge voltage difference (about 0.3 V), and almost no side reactions (Figure 7c). The BPD-assisted Li–CO$_2$ battery minimized the overpotential required to drive the discharge/charge reactions, eliminated adverse side reactions associated with traditional Li–CO$_2$ batteries, and provided high discharge specific capacity [61].

To address these issues, Zhou et al. presented a soluble binuclear copper(I) complex as a liquid catalyst for the production of Li$_2$C$_2$O$_4$ in Li–CO$_2$ batteries. Spectroscopic and electrochemical analyses revealed that the copper(I) complex could easily capture CO$_2$ to form bridged Cu(II)–oxalate adducts, which were reduced during discharge. The Li–CO$_2$ battery using the copper(I) complex exhibited an electromotive force of up to 3.38 V, an output voltage of 3.04 V, and a discharge specific capacity of 5846 mAh g^{-1}. Additionally, with the assistance of a Ru catalyst, the battery showed strong cycling stability over 400 cycles. The study indicated that liquid catalysts (or redox mediators, RMs) could reduce the number of phases involved in the CO$_2$ reduction process, effectively lowering the discharge overpotential (Figure 7d–f). The copper(I) complex, as a liquid catalyst, fully contacted CO$_2$, improving reaction kinetics and avoiding the drawbacks of solid catalysts [62].

While liquid catalysts in lithium–carbon dioxide batteries have shown many advantages, they also have some drawbacks and limitations. The stability of liquid catalysts may be poor, and they may degrade or fail during long-term cycling, affecting the overall performance of the battery. Additionally, the solubility and uniform distribution of liquid catalysts in the electrolyte may affect their catalytic effectiveness, leading to inconsistent battery performance.

3.6. Others

Perovskites, known for their high electronic conductivity and excellent catalytic activity, are considered affordable and highly potential electrode catalysts. Chi et al. prepared Cu–LSCM (La$_{0.96}$Sr$_{0.04}$Cu$_{0.3}$Mn$_{0.7}$O$_{3-\delta}$) heterostructures [63]. The Cu–LSCM heterostructure catalyst in Li–CO$_2$ batteries exhibited an ultrahigh discharge specific capacity of 11,350 mAh g^{-1}, a low voltage gap of 1.35 V, and a prolonged cycle lifespan of 107 cycles without significant degradation (Figure 8a–c).

Amin et al. developed a novel medium-entropy cathode catalyst (NbTa)$_{0.5}$BiS$_3$ that offers abundant oxygen vacancies and strong intercalation, significantly enhancing the catalytic activity, durability, and conductivity of the battery [64]. Combined with an ionic liquid-based electrolyte blend, the Li–CO$_2$ battery operated at high current densities (5000 mA g^{-1}) and high capacities (5000 mAh g^{-1}), achieving a cycle life of 125 cycles, far exceeding the performance reported in the literature (Figure 8d–f).

Additionally, structurally engineered polymers as cathode catalysts for Li–CO$_2$ batteries have shown great potential. Li et al. prepared conjugated cobalt polyphthalocyanine (CoPPc) [65]. Electrochemical measurements indicate that CoPPc enhances the reversible production and breakdown of Li$_2$CO$_3$, allowing for high-performance Li–CO$_2$ batteries with a significant areal capacity and remarkable cycle performance. Moreover, as a result of its interconnected structure, the polymer possesses inherent elasticity and exhibits enhanced chemical, physical, and mechanical stability. The elasticity and reprocessability of the polymeric catalyst make the fabrication of flexible batteries possible (Figure 8g,h).
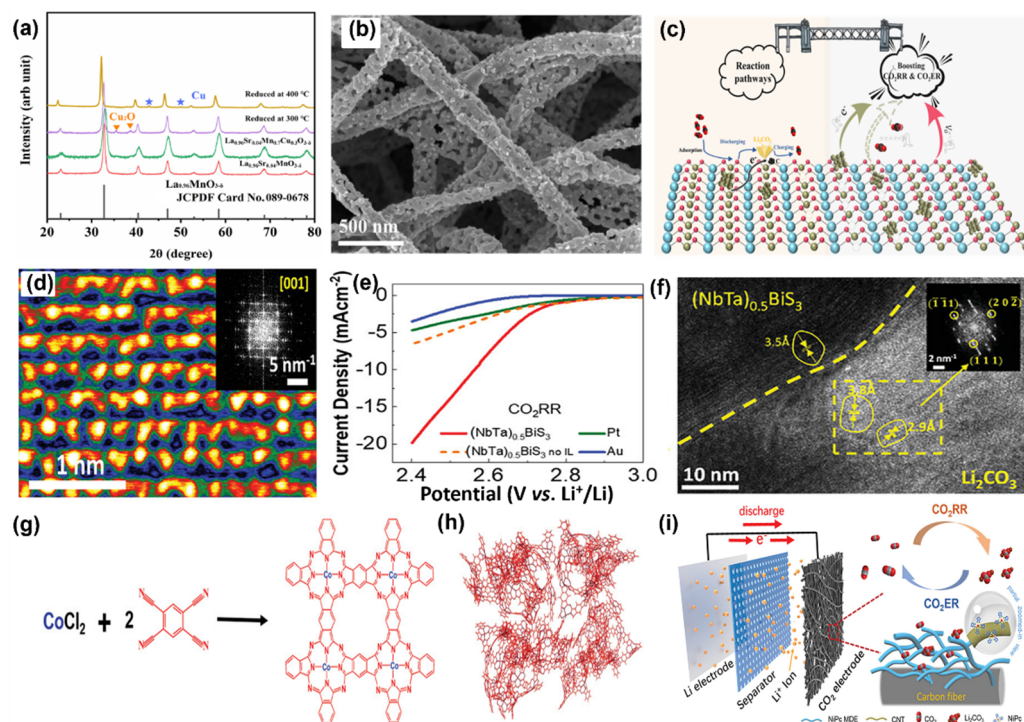
Figure 8. (**a**) XRD spectra of LSCM reduced at different temperatures in 5% H_2/Ar. (**b**) SEM images of Cu–LSCM catalysts. (**c**) Illustration of the CO_2RR and CO_2ER mechanisms of Cu–LSCM heterostructure. Copyright 2021, Elsevier [63]. (**d**) HR-STEM image along the [001] direction. The inset figure includes a Fourier transform of the STEM image. (**e**) Linear sweep voltammetry results of $(NbTa)_{0.5}BiS_3$ NFs, Au, and Pt nanoparticle (NP)-coated cathode electrodes under CO_2RR. (**f**) Low- and high-resolution TEM images of discharged cathode showing Li_2CO_3, and C deposited on $(NbTa)_{0.5}BiS_3$ cathode. Copyright 2023, Wiley-VCH [64]. (**g**) Schematic synthetic process of 2D CoPPc; (**h**) proposed 3D cross-linked network of CoPPc in practice. Copyright 2019, Wiley-VCH [65]. (**i**) Structures of the battery with NiPc MDE cathode. Copyright 2023, Wiley-VCH [66].

Li et al. developed molecularly dispersed electrocatalysts (MDEs), specifically nickel phthalocyanine (NiPc) anchored on carbon nanotubes (CNTs), as cathode catalysts for Li–CO_2 batteries [66]. By anchoring NiPc on multiwalled CNTs, the intrinsic activity of NiPc in CO_2 reduction reactions is fully displayed, while CNTs possess a large surface area and a porous structure, which aids in the breakdown of Li_2CO_3. The Li–CO_2 battery, utilizing a NiPc–CN MDE cathode, demonstrated a notable discharge voltage of 2.72 V and a minimal overpotential gap of 1.4 V between discharging and charging. Furthermore, it exhibited stable operation for more than 120 cycles (Figure 8i).

4. Conclusions and Outlook

Li–CO_2 batteries are very promising and provide a fresh and innovative method for capturing and using CO_2. Nevertheless, advancement in Li–CO_2 batteries is currently in a nascent phase and encounters obstacles such as elevated overpotential, subpar cycle efficiency, limited rate capability, and diminished discharge capacity. The main cause of these problems can be linked to the slow reaction kinetics of CO_2 gas. Hence, the imperative objective is to advance the development of cathode catalysts that are both highly efficient and stable in order to facilitate CO_2 electrochemical processes. This work presents a comprehensive examination of the electrochemical reaction mechanisms involved in Li–CO_2 batteries, as well as the most recent advancements in cathode catalysts and their design techniques. Despite certain advancements in prior research, there remains a significant distance to go in order to fulfill all the necessary criteria for the practical implementation of

Li–CO$_2$ batteries. In light of the most recent study findings, we will clarify some significant benefits and drawbacks of Li–CO$_2$ batteries, along with potential prospects for the future.

Li–CO$_2$ batteries have shown promising advancements as an emerging energy storage technology. However, significant challenges remain before they can be scaled up and commercialized. While noble metal catalysts demonstrate exceptional electrochemical performance, their high cost and scarcity limit widespread application. Therefore, developing cost-effective and stable non-noble metal catalysts is crucial for commercialization. The stability and cycle life of cathode materials are critical factors for the long-term application of these batteries. In practical applications, the battery must maintain excellent performance under various complex environmental conditions, which demands higher chemical stability and mechanical durability of the cathode materials. Currently, many materials still experience performance degradation during extended cycling, a challenge that must be addressed through material design and optimization. Research on and development of cathode materials for Li–CO$_2$ batteries must focus on enhancing performance while also considering cost control, stability improvement, and environmental sustainability. Future research should prioritize these challenges to advance the scalability and commercialization of the technology.

(1)	Unstable intermediates and discharge products have been identified in lithium–carbon dioxide batteries, and successfully detected and characterized using in situ characterization methods. The complexity of the electrochemical reaction mechanisms in Li–CO$_2$ batteries arises from the involvement of intricate electrochemical and chemical processes and multiple interfacial reactions. Currently, the correlation between the inherent composition of catalysts and the efficiency of batteries remains inadequately comprehended. Research highlights the necessity for enhanced in situ spectroscopic techniques and distinctive probe technologies to provide real-time and precise qualitative and quantitative analysis. A deeper investigation from kinetic and thermodynamic perspectives is necessary to fully elucidate the electrochemical reaction mechanisms in Li–CO$_2$ batteries. Future research should develop advanced methods such as in situ analysis, isotope calibration, and theoretical calculations to facilitate real-time detection of unstable intermediates and confirm specific reaction pathways involving CO$_2$ electrochemistry.

(2)	Future research on solid catalysts should explore more novel materials and elucidate their working mechanisms in CO$_2$ reduction reaction (CO$_2$RR) and CO$_2$ oxidation reaction (CO$_2$ER) kinetics. The impact of soluble catalysts on Li–CO$_2$ battery performance has not received sufficient attention. The design and selection of catalytic materials are crucial for improving the slow kinetics of CO$_2$RR and CO$_2$ER in Li–CO$_2$ batteries. Nevertheless, the precise operational methods of catalysts in electrochemical reactions remain incompletely comprehended, necessitating additional investigation. Enhancing the inherent activity of catalysts through methods such as heteroatom doping, defect control, and strain engineering can improve their activity and conductivity. Additionally, designing electrodes with hierarchical pore structures and high specific surface areas helps increase the utilization efficiency of active sites. Despite some progress in catalysts, the relationship between catalyst structure and battery performance remains unclear and requires further investigation through theoretical calculations and advanced in situ characterization tools. Future research should combine molecular structure simulation, free energy calculations, and electron transfer rates to design efficient catalysts for Li–CO$_2$ batteries.

(3)	Research on photoelectric effects and plasmonic interactions is expected to become a focal point in the application of catalytic systems. The photoelectric effect has been widely applied in photocatalytic water splitting and nitrogen fixation, accelerating electrochemical reactions through the formation of photo-generated electrons and holes. In Li–CO$_2$ batteries, photo-generated carriers participate in CO$_2$ electroreduction and redox reactions, improving battery performance. Numerous novel catalyst materials, such as MOFs, show great potential in photo-assisted Li–CO$_2$ batteries.

Future research should focus on improving the light transmission of photocatalysts, the effective separation of holes and electrons, and the high photocatalytic activity for CO_2 reduction and evolution reactions to advance photo-assisted Li–CO_2 battery technology.

(4) From the perspective of future development of flexible Li–CO_2 battery catalysts, research should focus on developing flexible cathode materials that can maintain high efficiency and stability under bending and deformation conditions. To achieve this, new material morphologies need to be explored, and their working mechanisms in CO_2 reduction reaction (CO$_2$RR) and CO_2 oxidation reaction (CO$_2$ER) should be elucidated. The impact of electrolytes and solvents on battery performance also needs in-depth study, especially when applying certain RMs or additives. Future research directions should focus on improving the performance of flexible cathode materials, reducing preparation costs, and developing environmentally friendly catalysts to promote the further development and commercialization of flexible Li–CO_2 battery technology. By addressing these key issues, flexible Li–CO_2 batteries are expected to become an ideal energy storage solution for future wearable devices.

As global climate change and environmental pollution become increasingly severe, Li–CO_2 batteries hold significant market potential. Their application prospects are particularly promising in fields such as electric vehicles, aerospace, electronics, and rail transportation. However, before considering them as a feasible replacement for lithium-ion batteries, several key technical challenges must first be addressed, including high overpotential, low reversibility, and poor rate capability. Given the current state of technology, Li–CO_2 batteries may be more suited as a complementary technology rather than a direct replacement for lithium-ion or lithium–sulfur batteries. However, considering their potential advantages, and with increasing research investment, Li–CO_2 batteries are poised to play a significant role in the future of electrochemical energy storage and could see widespread application.

Li–CO_2 battery systems with enhanced stability are paving the way for a range of innovative applications. In deep space exploration and extreme environment research, these batteries provide crucial energy security. Medical implant devices and remote sensor networks will also benefit from their enduring power supply, significantly reducing maintenance requirements. Additionally, drones and smart grid energy storage systems will leverage their high energy density and long cycle life to optimize performance. Applications such as emergency backup power, deep-sea mining operations, and long-life satellites will further benefit from reduced maintenance frequency and costs. These fields demand exceptional stability and environmental adaptability, making high-stability Li–CO_2 battery systems well suited to meet these needs and poised to play a pivotal role in future technological advancements.

References

1. Wu, X.; Liu, Y.; Wang, J.; Tan, Y.; Liang, Z.; Zhou, G. Toward Circular Energy: Exploring Direct Regeneration for Lithium-Ion Battery Sustainability. *Adv. Mater.* **2024**, *36*, 2403818. [CrossRef] [PubMed]
2. Ning, Y.; Zhang, Y.; Zhu, B.; Wei, G.; Wang, Q.; Qu, J. Reducing the Environmental Impact of Lithium-Ion Battery Recycling through Co-Processing of NCM and LFP. *Process Saf. Environ. Prot.* **2024**, *187*, 810–819. [CrossRef]
3. Mao, J.; Ye, C.; Zhang, S.; Xie, F.; Zeng, R.; Davey, K.; Guo, Z.; Qiao, S. Toward Practical Lithium-Ion Battery Recycling: Adding Value, Tackling Circularity and Recycling-Oriented Design. *Energy Environ. Sci.* **2022**, *15*, 2732–2752. [CrossRef]
4. Chigbu, B.I. Advancing Sustainable Development through Circular Economy and Skill Development in EV Lithium-Ion Battery Recycling: A Comprehensive Review. *Front. Sustain.* **2024**, *5*, 1409498. [CrossRef]
5. Abu, S.M.; Hannan, M.A.; Hossain Lipu, M.S.; Mannan, M.; Ker, P.J.; Hossain, M.J.; Mahlia, T.M.I. State of the Art of Lithium-Ion Battery Material Potentials: An Analytical Evaluations, Issues and Future Research Directions. *J. Clean. Prod.* **2023**, *394*, 136246. [CrossRef]
6. Yang, X.; Wen, H.; Lin, Y.; Zhang, H.; Liu, Y.; Fu, J.; Liu, Q.; Jiang, G. Emerging Research Needs for Characterizing the Risks of Global Lithium Pollution under Carbon Neutrality Strategies. *Environ. Sci. Technol.* **2023**, *57*, 5103–5106. [CrossRef] [PubMed]
7. Wang, K.; Hua, W.; Huang, X.; Stenzel, D.; Wang, J.; Ding, Z.; Cui, Y.; Wang, Q.; Ehrenberg, H.; Breitung, B.; et al. Synergy of Cations in High Entropy Oxide Lithium Ion Battery Anode. *Nat. Commun.* **2023**, *14*, 1487. [CrossRef] [PubMed]
8. Gong, S.; Lee, Y.; Choi, J.; Lee, M.; Chung, K.Y.; Jung, H.; Jeong, S.; Kim, H. In Situ Mesopore Formation in SiO_x Nanoparticles by Chemically Reinforced Heterointerface and Use of Chemical Prelithiation for Highly Reversible Lithium-Ion Battery Anode. *Small* **2023**, *19*, 2206238. [CrossRef] [PubMed]
9. Lai, X.; Gu, H.; Chen, Q.; Tang, X.; Zhou, Y.; Gao, F.; Han, X.; Guo, Y.; Bhagat, R.; Zheng, Y. Investigating Greenhouse Gas Emissions and Environmental Impacts from the Production of Lithium-Ion Batteries in China. *J. Clean. Prod.* **2022**, *372*, 133756. [CrossRef]
10. Li, Q.; Liu, S.; Wang, L.; Chen, F.; Shao, J.; Hu, X. Efficient Nitrogen Doped Porous Carbonaceous CO_2 Adsorbents Based on Lotus Leaf. *J. Environ. Sci.* **2021**, *103*, 268–278. [CrossRef] [PubMed]
11. Kamkeng, A.D.N.; Wang, M.; Hu, J.; Du, W.; Qian, F. Transformation Technologies for CO_2 Utilisation: Current Status, Challenges and Future Prospects. *Chem. Eng. J.* **2021**, *409*, 128138. [CrossRef]
12. Valluri, S.; Claremboux, V.; Kawatra, S. Opportunities and Challenges in CO_2 Utilization. *J. Environ. Sci.* **2022**, *113*, 322–344. [CrossRef] [PubMed]
13. Yu, X.; Manthiram, A. Recent Advances in Lithium-Carbon Dioxide Batteries. *Small Struct.* **2020**, *1*, 2000027. [CrossRef]
14. Wang, F.; Li, Y.; Xia, X.; Cai, W.; Chen, Q.; Chen, M. Metal-CO_2 Electrochemistry: From CO_2 Recycling to Energy Storage. *Adv. Energy Mater.* **2021**, *11*, 2100667. [CrossRef]
15. Chen, B.; Wang, D.; Zhang, B.; Zhong, X.; Liu, Y.; Sheng, J.; Zhang, Q.; Zou, X.; Zhou, G.; Cheng, H.-M. Engineering the Active Sites of Graphene Catalyst: From CO_2 Activation to Activate Li-CO_2 Batteries. *ACS Nano* **2021**, *15*, 9841–9850. [CrossRef] [PubMed]
16. Xing, Y.; Wang, K.; Li, N.; Su, D.; Wong, W.-T.; Huang, B.; Guo, S. Ultrathin RuRh Alloy Nanosheets Enable High-Performance Lithium-CO_2 Battery. *Matter* **2020**, *2*, 1494–1508. [CrossRef]
17. Ezeigwe, E.R.; Dong, L.; Manjunatha, R.; Zuo, Y.; Deng, S.-Q.; Tan, M.; Yan, W.; Zhang, J.; Wilkinson, D.P. A Review of Lithium-O_2/CO_2 and Lithium-CO_2 Batteries: Advanced Electrodes/Materials/Electrolytes and Functional Mechanisms. *Nano Energy* **2022**, *95*, 106964. [CrossRef]
18. Xu, S.; Chen, C.; Kuang, Y.; Song, J.; Gan, W.; Liu, B.; Hitz, E.M.; Connell, J.W.; Lin, Y.; Hu, L. Flexible Lithium-CO_2 Battery with Ultrahigh Capacity and Stable Cycling. *Energy Environ. Sci.* **2018**, *11*, 3231–3237. [CrossRef]
19. Song, L.; Hu, C.; Xiao, Y.; He, J.; Lin, Y.; Connell, J.W.; Dai, L. An Ultra-Long Life, High-Performance, Flexible Li-CO_2 Battery Based on Multifunctional Carbon Electrocatalysts. *Nano Energy* **2020**, *71*, 104595. [CrossRef]
20. Chen, K.; Huang, G.; Ma, J.; Wang, J.; Yang, D.; Yang, X.; Yu, Y.; Zhang, X. The Stabilization Effect of CO_2 in Lithium-Oxygen/CO_2 Batteries. *Angew. Chem.-Int. Ed.* **2020**, *59*, 16661–16667. [CrossRef] [PubMed]
21. Qiu, F.; Ren, S.; Mu, X.; Liu, Y.; Zhang, X.; He, P.; Zhou, H. Towards a Stable Li-CO_2 Battery: The Effects of CO_2 to the Li Metal Anode. *Energy Storage Mater.* **2020**, *26*, 443–447. [CrossRef]
22. Ahmadiparidari, A.; Warburton, R.E.; Majidi, L.; Asadi, M.; Chamaani, A.; Jokisaari, J.R.; Rastegar, S.; Hemmat, Z.; Sayahpour, B.; Assary, R.S.; et al. A Long-Cycle-Life Lithium-CO_2 Battery with Carbon Neutrality. *Adv. Mater.* **2019**, *31*, 1902518. [CrossRef] [PubMed]
23. Xiao, Y.; Du, F.; Hu, C.; Ding, Y.; Wang, Z.L.; Roy, A.; Dai, L. High-Performance Li-CO_2 Batteries from Free-Standing, Binder-Free, Bifunctional Three-Dimensional Carbon Catalysts. *ACS Energy Lett.* **2020**, *5*, 916–921. [CrossRef]
24. Hu, Z.; Xie, Y.; Yu, D.; Liu, Q.; Zhou, L.; Zhang, K.; Li, P.; Hu, F.; Li, L.; Chou, S.; et al. Hierarchical $Ti_3C_2T_x$ MXene/Carbon Nanotubes for Low Overpotential and Long-Life Li-CO_2 Batteries. *ACS Nano* **2021**, *15*, 8407–8417. [CrossRef] [PubMed]
25. Xu, S.; Das, S.K.; Archer, L.A. The Li-CO_2 Battery: A Novel Method for CO_2 Capture and Utilization. *RSC Adv.* **2013**, *3*, 6656. [CrossRef]
26. Lim, H.-K.; Lim, H.-D.; Park, K.-Y.; Seo, D.-H.; Gwon, H.; Hong, J.; Goddard, W.A.; Kim, H.; Kang, K. Toward a Lithium-"Air" Battery: The Effect of CO_2 on the Chemistry of a Lithium-Oxygen Cell. *J. Am. Chem. Soc.* **2013**, *135*, 9733–9742. [CrossRef] [PubMed]

27. Hou, Y.; Wang, J.; Liu, L.; Liu, Y.; Chou, S.; Shi, D.; Liu, H.; Wu, Y.; Zhang, W.; Chen, J. Mo_2C/CNT: An Efficient Catalyst for Rechargeable Li-CO_2 Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1700564. [CrossRef]

28. Yang, C.; Guo, K.; Yuan, D.; Cheng, J.; Wang, B. Unraveling Reaction Mechanisms of Mo_2C as Cathode Catalyst in a Li-CO_2 Battery. *J. Am. Chem. Soc.* **2020**, *142*, 6983–6990. [CrossRef] [PubMed]

29. Jiao, Y.; Qin, J.; Sari, H.M.K.; Li, D.; Li, X.; Sun, X. Recent Progress and Prospects of Li-CO_2 Batteries: Mechanisms, Catalysts and Electrolytes. *Energy Storage Mater.* **2021**, *34*, 148–170. [CrossRef]

30. Qiao, Y.; Wu, J.; Zhao, J.; Li, Q.; Zhang, P.; Hao, C.; Liu, X.; Yang, S.; Liu, Y. Synergistic Effect of Bifunctional Catalytic Sites and Defect Engineering for High-Performance Li-CO_2 Batteries. *Energy Storage Mater.* **2020**, *27*, 133–139. [CrossRef]

31. Chen, B.; Wang, D.; Tan, J.; Liu, Y.; Jiao, M.; Liu, B.; Zhao, N.; Zou, X.; Zhou, G.; Cheng, H.-M. Designing Electrophilic and Nucleophilic Dual Centers in the ReS_2 Plane toward Efficient Bifunctional Catalysts for Li-CO_2 Batteries. *J. Am. Chem. Soc.* **2022**, *144*, 3106–3116. [CrossRef] [PubMed]

32. Ye, F.; Gong, L.; Long, Y.; Talapaneni, S.N.; Zhang, L.; Xiao, Y.; Liu, D.; Hu, C.; Dai, L. Topological Defect-Rich Carbon as a Metal-Free Cathode Catalyst for High-Performance Li-CO_2 Batteries. *Adv. Energy Mater.* **2021**, *11*, 2101390. [CrossRef]

33. Yang, S.; Qiao, Y.; He, P.; Liu, Y.; Cheng, Z.; Zhu, J.; Zhou, H. A Reversible Lithium-CO_2 Battery with Ru Nanoparticles as a Cathode Catalyst. *Energy Environ. Sci.* **2017**, *10*, 972–978. [CrossRef]

34. Zhang, Z.; Zhang, Q.; Chen, Y.; Bao, J.; Zhou, X.; Xie, Z.; Wei, J.; Zhou, Z. The First Introduction of Graphene to Rechargeable Li-CO_2 Batteries. *Angew. Chem.-Int. Ed.* **2015**, *54*, 6550–6553. [CrossRef] [PubMed]

35. Zhang, X.; Zhang, Q.; Zhang, Z.; Chen, Y.; Xie, Z.; Wei, J.; Zhou, Z. Rechargeable Li-CO_2 Batteries with Carbon Nanotubes as Air Cathodes. *Chem. Commun.* **2015**, *51*, 14636–14639. [CrossRef] [PubMed]

36. Yu, W.; Liu, L.; Yang, Y.; Li, N.; Chen, Y.; Yin, X.; Niu, J.; Wang, J.; Ding, S. N, O-Diatomic Dopants Activate Catalytic Activity of 3D Self-Standing Graphene Carbon Aerogel for Long-Cycle and High-Efficiency Li-CO_2 Batteries. *Chem. Eng. J.* **2023**, *465*, 142787. [CrossRef]

37. Huang, N.-Y.; He, H.; Liu, S.; Zhu, H.-L.; Li, Y.-J.; Xu, J.; Huang, J.-R.; Wang, X.; Liao, P.-Q.; Chen, X.-M. Electrostatic Attraction-Driven Assembly of a Metal-Organic Framework with a Photosensitizer Boosts Photocatalytic CO_2 Reduction to CO. *J. Am. Chem. Soc.* **2021**, *143*, 17424–17430. [CrossRef] [PubMed]

38. Wu, K.; Sun, K.; Liu, S.; Cheong, W.-C.; Chen, Z.; Zhang, C.; Pan, Y.; Cheng, Y.; Zhuang, Z.; Wei, X.; et al. Atomically Dispersed Ni-Ru-P Interface Sites for High-Efficiency pH-Universal Electrocatalysis of Hydrogen Evolution. *Nano Energy* **2021**, *80*, 105467. [CrossRef]

39. Li, F.; Tang, D.; Jian, Z.; Liu, D.; Golberg, D.; Yamada, A.; Zhou, H. Li-O_2 Battery Based on Highly Efficient Sb-Doped Tin Oxide Supported Ru Nanoparticles. *Adv. Mater.* **2014**, *26*, 4659–4664. [CrossRef] [PubMed]

40. Zhang, P.-F.; Lu, Y.-Q.; Wu, Y.-J.; Yin, Z.-W.; Li, J.-T.; Zhou, Y.; Hong, Y.-H.; Li, Y.-Y.; Huang, L.; Sun, S.-G. High-Performance Rechargeable Li-CO_2/O_2 Battery with Ru/N-Doped CNT Catalyst. *Chem. Eng. J.* **2019**, *363*, 224–233. [CrossRef]

41. Zhang, P.-F.; Zhang, J.-Y.; Sheng, T.; Lu, Y.-Q.; Yin, Z.-W.; Li, Y.-Y.; Peng, X.-X.; Zhou, Y.; Li, J.-T.; Wu, Y.-J.; et al. Synergetic Effect of Ru and NiO in the Electrocatalytic Decomposition of Li_2CO_3 to Enhance the Performance of a Li-CO_2/O_2 Battery. *ACS Catal.* **2020**, *10*, 1640–1651. [CrossRef]

42. Wu, G.; Li, X.; Zhang, Z.; Dong, P.; Xu, M.; Peng, H.; Zeng, X.; Zhang, Y.; Liao, S. Design of Ultralong-Life Li-CO_2 Batteries with IrO_2 Nanoparticles Highly Dispersed on Nitrogen-Doped Carbon Nanotubes. *J. Mater. Chem. A* **2020**, *8*, 3763–3770. [CrossRef]

43. Kang, Z.; Wu, C.; Dong, L.; Liu, W.; Mou, J.; Zhang, J.; Chang, Z.; Jiang, B.; Wang, G.; Kang, F.; et al. 3D Porous Copper Skeleton Supported Zinc Anode toward High Capacity and Long Cycle Life Zinc Ion Batteries. *ACS Sustain. Chem. Eng.* **2019**, *7*, 3364–3371. [CrossRef]

44. Chen, C.-J.; Yang, J.-J.; Chen, C.-H.; Wei, D.-H.; Hu, S.-F.; Liu, R.-S. Improvement of Lithium Anode Deterioration for Ameliorating Cyclabilities of Non-Aqueous Li-CO_2 Batteries. *Nanoscale* **2020**, *12*, 8385–8396. [CrossRef] [PubMed]

45. Lin, J.; Ding, J.; Wang, H.; Yang, X.; Zheng, X.; Huang, Z.; Song, W.; Ding, J.; Han, X.; Hu, W. Boosting Energy Efficiency and Stability of Li-CO_2 Batteries via Synergy between Ru Atom Clusters and Single-Atom Ru-N_4 Sites in the Electrocatalyst Cathode. *Adv. Mater.* **2022**, *34*, 2200559. [CrossRef] [PubMed]

46. Guo, C.; Zhang, F.; Han, X.; Zhang, L.; Hou, Q.; Gong, L.; Wang, J.; Xia, Z.; Hao, J.; Xie, K. Intrinsic Descriptor Guided Noble Metal Cathode Design for Li-CO_2 Battery. *Adv. Mater.* **2023**, *35*, 2302325. [CrossRef] [PubMed]

47. Wang, Z.; Liu, B.; Yang, X.; Zhao, C.; Dong, P.; Li, X.; Zhang, Y.; Doyle-Davis, K.; Zeng, X.; Zhang, Y.; et al. Dual Catalytic Sites of Alloying Effect Bloom CO_2 Catalytic Conversion for Highly Stable Li-CO_2 Battery. *Adv. Funct. Mater.* **2023**, *33*, 2213931. [CrossRef]

48. Zhao, W.; Yang, Y.; Deng, Q.; Dai, Q.; Fang, Z.; Fu, X.; Yan, W.; Wu, L.; Zhou, Y. Toward an Understanding of Bimetallic MXene Solid-Solution in Binder-Free Electrocatalyst Cathode for Advanced Li-CO_2 Batteries. *Adv. Funct. Mater.* **2023**, *33*, 2210037. [CrossRef]

49. Lamagni, P.; Miola, M.; Catalano, J.; Hvid, M.S.; Mamakhel, M.A.H.; Christensen, M.; Madsen, M.R.; Jeppesen, H.S.; Hu, X.; Daasbjerg, K.; et al. Restructuring Metal-Organic Frameworks to Nanoscale Bismuth Electrocatalysts for Highly Active and Selective CO_2 Reduction to Formate. *Adv. Funct. Mater.* **2020**, *30*, 1910408. [CrossRef]

50. Jiao, L.; Wang, Y.; Jiang, H.; Xu, Q. Metal-Organic Frameworks as Platforms for Catalytic Applications. *Adv. Mater.* **2018**, *30*, 1703663. [CrossRef] [PubMed]

51. Deng, H.; Grunder, S.; Cordova, K.E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gándara, F.; Whalley, A.C.; Liu, Z.; Asahina, S.; et al. Large-Pore Apertures in a Series of Metal-Organic Frameworks. *Science* **2012**, *336*, 1018–1023. [CrossRef] [PubMed]

52. Li, S.; Dong, Y.; Zhou, J.; Liu, Y.; Wang, J.; Gao, X.; Han, Y.; Qi, P.; Wang, B. Carbon Dioxide in the Cage: Manganese Metal-Organic Frameworks for High Performance CO_2 Electrodes in $Li-CO_2$ Batteries. *Energy Environ. Sci.* **2018**, *11*, 1318–1325. [CrossRef]

53. Xu, Y.; Gong, H.; Ren, H.; Fan, X.; Li, P.; Zhang, T.; Chang, K.; Wang, T.; He, J. Highly Efficient Cu-Porphyrin-Based Metal-Organic Framework Nanosheet as Cathode for High-Rate $Li-CO_2$ Battery. *Small* **2022**, *18*, 2203917. [CrossRef] [PubMed]

54. Wang, J.; Li, S.; Chen, Y.; Dong, L.; Liu, M.; Shi, J.; Li, S.; Lan, Y. Phthalocyanine Based Metal-Organic Framework Ultrathin Nanosheet for Efficient Photocathode toward Light-Assisted $Li-CO_2$ Battery. *Adv. Funct. Mater.* **2022**, *32*, 2210259. [CrossRef]

55. Huang, N.; Wang, P.; Jiang, D. Covalent Organic Frameworks: A Materials Platform for Structural and Functional Designs. *Nat. Rev. Mater.* **2016**, *1*, 16068. [CrossRef]

56. Diercks, C.S.; Yaghi, O.M. The Atom, the Molecule, and the Covalent Organic Framework. *Science* **2017**, *355*, eaal1585. [CrossRef] [PubMed]

57. Kandambeth, S.; Dey, K.; Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. *J. Am. Chem. Soc.* **2019**, *141*, 1807–1822. [CrossRef]

58. Li, X.; Wang, H.; Chen, Z.; Xu, H.; Yu, W.; Liu, C.; Wang, X.; Zhang, K.; Xie, K.; Loh, K.P. Covalent-Organic-Framework-Based $Li-CO_2$ Batteries. *Adv. Mater.* **2019**, *31*, 1905879. [CrossRef]

59. Bharti, A.; Achutharao, G.; Bhattacharyya, A.J. Efficient Rechargeable $Li-CO_2$ Battery with a Liquid Electrolyte-Soluble $CuCl_2$ Electrocatalyst. *ACS Appl. Mater. Interfaces* **2023**, *15*, 53342–53350. [CrossRef]

60. Zhang, Z.; Bai, W.; Cai, Z.; Cheng, J.; Kuang, H.; Dong, B.; Wang, Y.; Wang, K.; Chen, J. Enhanced Electrochemical Performance of Aprotic $Li-CO_2$ Batteries with a Ruthenium-Complex-Based Mobile Catalyst. *Angew. Chem.-Int. Ed.* **2021**, *60*, 16404–16408. [CrossRef] [PubMed]

61. Wu, Y.; Zhao, Z.; Peng, Z. Tailoring $Li-CO_2$ Electrochemistry Based on 4,4′-Bipyridine Redox Cycle. *ACS Energy Lett.* **2023**, *8*, 3430–3436. [CrossRef]

62. Sun, X.; Mu, X.; Zheng, W.; Wang, L.; Yang, S.; Sheng, C.; Pan, H.; Li, W.; Li, C.-H.; He, P.; et al. Binuclear Cu Complex Catalysis Enabling $Li-CO_2$ Battery with a High Discharge Voltage above 3.0V. *Nat. Commun.* **2023**, *14*, 536. [CrossRef] [PubMed]

63. Zou, L.; Li, R.; Wang, Z.; Yu, F.; Chi, B.; Pu, J. Synergistic Effect of $Cu-La_{0.96}Sr_{0.04}Cu_{0.3}Mn_{0.7}O_{3-\delta}$ Heterostructure and Oxygen Vacancy Engineering for High-Performance $Li-CO_2$ Batteries. *Electrochim. Acta* **2021**, *395*, 139209. [CrossRef]

64. Jaradat, A.; Zhang, C.; Shashikant Sutar, S.; Shan, N.; Wang, S.; Singh, S.K.; Yang, T.; Kumar, K.; Sharma, K.; Namvar, S.; et al. A High-Rate $Li-CO_2$ Battery Enabled by 2D Medium-Entropy Catalyst. *Adv. Funct. Mater.* **2023**, *33*, 2300814. [CrossRef]

65. Chen, J.; Zou, K.; Ding, P.; Deng, J.; Zha, C.; Hu, Y.; Zhao, X.; Wu, J.; Fan, J.; Li, Y. Conjugated Cobalt Polyphthalocyanine as the Elastic and Reprocessable Catalyst for Flexible $Li-CO_2$ Batteries. *Adv. Mater.* **2019**, *31*, 1805484. [CrossRef] [PubMed]

66. Zheng, H.; Li, H.; Zhang, Z.; Wang, X.; Jiang, Z.; Tang, Y.; Zhang, J.; Emley, B.; Zhang, Y.; Zhou, H.; et al. Dispersed Nickel Phthalocyanine Molecules on Carbon Nanotubes as Cathode Catalysts for $Li-CO_2$ Batteries. *Small* **2023**, *19*, 2302768. [CrossRef] [PubMed]