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Electrochemistry of metal-CO_2 batteries: Opportunities and challenges

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ABSTRACT

As a greenhouse gas and common pollutant, atmospheric CO_2 is a pressing concern toward climate change caused by increased CO_2 emissions driven by fossil fuel-based energy production. There is an urgent need for a solution to capture and convert CO_2 as part of the effort to combat climate change. Metal-CO_2 batteries represent a promising technology to capture and recycle carbon dioxide while serving as an energy storage solution for a renewable energy network. Though metal-CO_2 research is very active, the technology is still in its very early stages. Therefore, more fundamental mechanisms need to be understood before a practical metal-CO_2 battery configuration is realized. Metal-CO_2 battery research delves into a large variety of materials and chemistries depending on the anode material, which can be lithium, sodium, zinc, aluminum, magnesium, or potassium. This review summarizes the fundamental electrochemistry and mechanisms of different metal-CO_2 batteries. The material selection, design considerations, mechanisms of electrochemical charge and discharge, and catalyzed behaviors of metal-CO_2 batteries are also comprehensively examined. We hope understanding the underlying electrochemistry of metal-CO_2 batteries will promise the development of the battery technologies that are applicable to a broad range of both carbon capture and energy storage applications.

1. Introduction

There is a strong consensus that the release of greenhouse gasses during fossil fuel-based energy production is a significant contributor towards global warming induced climate change. [1–4] This problem has led to significant research and development of renewable energy sources to replace fossil fuel energy in order to reduce the energy sector's carbon footprint. Due to the less predictable generation of common renewable energy sources such as solar and wind, a renewable energy network requires high-capacity, reliable, and safe energy storage to bank energy during peak production times and release energy during low production times. The lithium-ion battery, common across many energy storage applications, has several challenges preventing its widespread adoption for storing energy in a renewable energy network. [5] Several issues ranging across safety concerns, performance, price, and abundance have shown the need for an improved alternative battery technology.

Alongside renewable energy generation, carbon capture and conversion or sequestration has also emerged as an urgent method to combat climate change. The biggest challenge for carbon capture and sequestration (CCS) implementation is the initial method for the capture and isolation of CO_2, which is usually both expensive to build and energy intensive to operate. [6] Once the CO_2 has been captured and isolated, it can be stored or converted into carbon products used in chemical processing and fabrication. [6, 7]

Metal-CO_2 batteries have emerged as a distinctive economical and efficient CO_2 utilization technique, which provides a mechanism that combines CO_2 capture with electricity generation instead of electricity input. During the discharging mode, the metal anode is oxidized to give out electrons, which pass through the external circuit to reach the other electrode - the cathode, for instance activated carbon nanofibers with ruthenium nanoparticles. [8] With a proper electrochemistry, the cathode is able to use the incoming electrons to capture and reduce CO_2 to other chemicals. In a Li-CO_2 cell for example, the complete reaction is $4Li^+ + 3CO_2 + 4e^- \rightarrow 2Li_2CO_3 + C$. [9] During the charging mode, the system needs to enable the reverse charge process to release and concentrate CO_2. Compared to the Li-ion battery, the metal-CO_2 battery technology has the potential to be safer and more energy dense, allowing cost effective energy storage systems for a renewable energy network. Compared to traditional CCS methods which require energy input when capturing carbon, this technology generates electrical energy when in use and only requires energy when recharging the battery to release the concentrated CO_2. The dual purpose is appealing to solve both energy and climate issues, however metal-CO_2 batteries still face several challenges before the technology can be widely adopted in practical

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applications. Current metal-CO_2 batteries still suffer from short cycle life compared with Li-ion batteries and show parasitic side reactions in ambient gas environments.

This review considers the current understanding and challenges of metal-CO_2 batteries. As the origin of metal-CO_2 batteries from earlier work is necessary to contextualize current research, the history and context of metal-CO_2 battery research is discussed at first. We then review the design considerations of metal-CO_2 batteries, divided by the components of the battery. A metal-CO_2 battery typically contains a cathode, an electrolyte, and an anode as the active components. The cathode structure is well shared across different battery configurations and is discussed first, while the anode material changes the battery behavior quite significantly. Once the design of metal-CO_2 batteries is well understood, the fundamental electrochemical understanding of various battery configurations is discussed. It is known that the electrochemical characteristics of the battery are some of the most important aspects of a new battery technology that needs further investigation. Finally, we review the influence of catalyst additives on the electrochemical behavior of the battery. We hope this review can provide comprehensive information to the research field and also to those unfamiliar with all aspects of battery research, helping further understand and develop metal-CO_2 batteries.

1.1. The development of metal-CO_2 batteries

Metal-CO_2 research stems from the investigation of metal-air or metal-O_2 battery research. In the metal-O_2 battery structure, the cathodic half reaction is the reduction of dissolved oxygen absorbed from the air into the electrolyte on the cathode. By doing so, a smaller, lighter battery can provide higher energy by replacing the active cathode material in the battery with oxygen gas. By removing the solid cathode, some metal-oxygen battery configurations reach a theoretical specific energy comparable to the practical energy density of gasoline. [10] A real metal-air battery close to the capacity of the metal-O_2 battery with a long cycle life would improve current electric alternatives to gas-fed engines. Most recent cell structures of metal-O_2/air batteries must be provided with pure oxygen to achieve an acceptable cycle life, with a long-term goal of acceptable battery performance in ambient atmosphere. Oxygen and carbon dioxide are the most active gasses in ambient air. Along with water, these active gasses are the electrochemically active participants to be considered when designing metal-air battery configurations. The current challenge in designing a metal-O_2 battery for atmospheric applications is the removal of CO_2 and water to avoid parasitic side reactions. [11] A battery could instead use carbon dioxide as the active material of the cathode, but oxygen is both more abundant and more reactive than carbon dioxide. Therefore, initial research in metal-gas batteries focused on the structure of metal-O_2 batteries, due to the higher theoretical energy density than metal-CO_2 batteries. [12]

Several challenges caused by the interactions of other active species keep metal-O_2 batteries from direct atmospheric use. Water can be removed from a metal-O_2 battery's gas source with a hydrophobic membrane, but carbon dioxide cannot be easily separated from O_2. [13] Additionally, carbon dioxide is significantly more soluble than oxygen in the organic solvents typically used in metal-air batteries as electrolyte solvents, in fact counteracting the lower abundance of CO_2. [14] By replacing oxygen with carbon dioxide as the active cathode material in a metal-air battery, these challenges of removing CO_2 become advantageous. Likewise, metal-CO_2 batteries need to deal with the higher reactivity of O_2. [15] Even though the metal-CO_2 configuration is expected to be less energy dense than its oxygen counterpart, it still can maintain the high specific capacity that a metal-gas structure provides. These advantages, in addition to the appealing prospects of carbon capture, drive research into metal-CO_2 batteries.

Neither the metal-O_2 or metal-CO_2 electrochemistry is fully understood. The intense investigation into the electrocatalytic reduction of CO_2 gives the metal-CO_2 electrochemistry another distinct advantage. A cheap and effective catalyst to drive CO_2 reduction into useful feedstocks for capture and reduction is quite important to reduce atmospheric greenhouse gasses, which has its own body of research to study catalytic CO_2 reduction reaction (CDR). While much of the CDR research studies aqueous electrolytes with the water as a proton source, most metal-CO_2 research does not. The catalysts and materials investigation for CO_2 reduction activity can provide a useful stepping off point for metal-CO_2 battery optimization. [16] Therefore, the insights on the mechanism of CDR research can be applied to the rational design of catalysts for metal-CO_2 batteries. [17]

Due to its promises, research on metal-CO_2 batteries is quickly growing, with several reviews being published in the field. A review in 2019 by Xie et al. summarized the electrochemical understanding of Li-, Na-, Zn-, and Al-CO_2 batteries, alongside a summary of results in cathode design for Li-, Na-, and Zn-CO_2 batteries. [15] It is common for reviews to focus on one or two battery chemistries, typically lithium and sodium because these two metal-CO_2 batteries have been mostly investigated. Examples include: the review by Xie et al. in 2017 which excellently covered Li- and Na-CO_2 and O_2/CO_2 electrochemistry; the review by Xie et al. in 2019 focused on the electrochemical understandings of Li-CO_2 batteries and Zn-CO_2 batteries in aqueous electrolytes; a review by Mu et al. in 2019 which summarized Li- and Na-CO_2 and CO_2/O_2 electrochemistry as well as the applications of Li-CO_2 catalysts; and a work from Yanan et al. in 2021 which covered all facets of Li-CO_2 battery research. [13, 18-20] In some cases, reviews of just Li-CO_2 research can be quite important. The recent review by Yu et al. in 2021 covered Li-CO_2 electrochemistry, battery design, and the details of Li-CO_2 catalysis. [20, 21] The review by Sun et al. covered Li-CO_2 electrochemistry and a comprehensive review covers the catalytic methods and design for lithium-based batteries. [22] This review aims to distinguish itself by considering all metal-CO_2 battery configurations, with a focus on the electrochemistry of each configuration such that common elements between different battery chemistries can be clearly shown.

1.2. Battery structure

The previous work on CO_2 reduction, and earlier research on metal-O_2 batteries has influenced the initial design and structure of metal-CO_2 batteries. **Fig. 1** shows the general structure of a metal-CO_2 battery: the anode is generally a reactive metal foil, the electrolyte is typically an ion carrying liquid, and the cathode is usually carbon-based and has a high surface area. The choice of anode changes the battery's electrochemistry most significantly, which in part determines the available electrolyte selection. In contrast, the cathode structure, primarily a high surface area carbon, does not alter fundamentally between different metal-CO_2 configurations. As such, the cathode will be discussed first among the battery components in this review.

2. The cathode

Dissolved carbon dioxide gas is the electrochemically active cathodic material in metal-CO_2 batteries, but the battery discharge still requires a current collector to transfer electrons for the reaction to occur. Similar to cathode design in other types of battery configurations, the cathodic current collector (frequently called the cathode) needs to be electrically conductive, stable within the battery's working potentials, and unreactive with other components in the battery. [23] A practical battery cathode also needs to be inexpensive and producible in large scale. Finally, a battery cathode (as with all battery components) should have a minimal amount of non-active material in order to maximize volumetric specific energy density.

In metal-CO_2 batteries the cathode acts both as a current collector and reaction surface. By creating a cathode with a high surface area, the localized current density on the surface during charge and discharge is lowered, which has been shown to reduce the electrochemical overpotentials. [24] Because of these considerations, the most common cath-

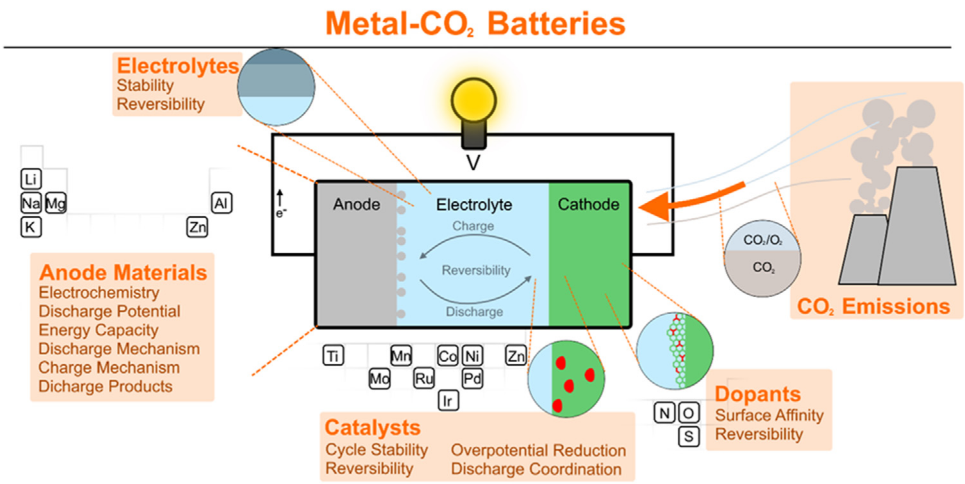

Fig. 1. The facets of metal-CO_2 battery research. Most investigated are different anode materials such as lithium, sodium, and more; electrolyte materials, such as organic-based (e.g., tetraethylene glycol, TEGDME), water-based, ionic liquids (1-ethyl-3-methylimidazolium chloride with aluminum chloride shown here), and water-in-salt electrolytes (WiSE); and cathode materials, typically carbon-based, and doped with elemental dopants or metal nanoparticles.

ode structures for metal-CO_2 batteries are the nanostructured conductive carbon materials held together by low weight percent binder additives. Carbon is highly conductive and stable at high voltages, whose nanostructures can provide a high surface area. [25, 26] This cathode structure in fact originated from earlier research on fuel cells using gas phase reactants, such as the alkaline fuel cell. [27]

Commercially available carbon materials are commonly used as cathode materials for metal-CO2 batteries that do not focus on the cathode structure. Researchers investigating cathode doping, electrolyte composition, catalyst behavior, or anode modification commonly use commercial conductive carbon black, carbon nanotubes (single- or multi-walled), or vapor grown carbon fiber as the carbon source in a cathode. [12, 28-31] More complex cathode structures include graphene, 3D carbon nanotube network, and dandelion-like carbon microspheres. [32–38] To create a high performance structure for a cathode, it is typically necessary to include a small weight percent of a binding agent to create a conductive carbon network. The binder is typically a thermoplastic polymer such as polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF), which allows the carbon materials to form a slurry by adding and mixing a nonreactive organic solvent. This mixture is then placed on a gas diffusion current collector and dried before assembling in a battery as a cathode. [12]

It is common for metal-CO_2 batteries to use various micro- or nanostructured carbon cathodes. A cathode structure with higher conductivity, good mechanical resilience, and high surface area will typically improve a battery's performance, which has been shown to be vital to the battery's function in some cases. [37] In addition, the source of carbon has been shown to improve reaction kinetics during charge and discharge by facilitating both ion and electron transport. [39] However, most recent investigation into complex cathode structures involves doping with catalytic materials such as nitrogen, gold, or manganese oxide. [29, 32, 40] The fabrication of new carbon structures with enhanced physical properties is a field of active research in metal-CO_2 batteries.

Though in metal-CO_2 batteries carbon cathodes are often referred to as catalysts to reversibly react with CO_2, using the term catalyst for a carbon cathode is not necessarily accurate. If a catalyst is defined as its effect on reaction rates, defining carbon cathodes as catalysts is true in the strictest sense, as it has been shown that the carbon reaction surface can have a very large influence on the reaction rate without changing the reaction electrochemistry. [41] However, this is typically explained as the ability of the carbon surface to stabilize the intermediate reaction products without any chemical reaction involving the surface. To some extent, this is an argument against defining carbon cathodes as the catalysts. In practice, the effect a novel carbon nanostructure can have on cell electrochemistry is very similar to the introduction of a directly catalytic material. Alongside the surface enhancement effect, this addition of catalytic materials to a cell has been commonly investigated. The most common methods of distributing catalysts are through doping of heterogeneous catalysts into the cathodes and the introduction of homogeneous catalysts into the electrolyte. Homogenous catalysts are clearly expected to be involved in the electrochemical reactions of charge and discharge; in contrast, heterogeneous catalysts can perform roles including improving electrochemistry, enhancing surface stabilization, and increasing affinity for reactive materials in the cell. The multiple purposes a heterogenous catalyst serves can obfuscate its actual role in the cell electrochemistry. In addition to doping catalysts in the cathode, it is common to dope with nitrogen. Nitrogen doping is often regarded as purely increasing surface affinity, in which the various common forms of nitrogen doping serve to stabilize carbon dioxide adsorption to the surface. [42] However, recent research has observed nitrogen acting as an electrochemically active species in the reduction of nitrogen gas to ammonia. [43] N-doped carbon cathodes have been applied with great success to Li and Zn batteries. [40, 44-47]

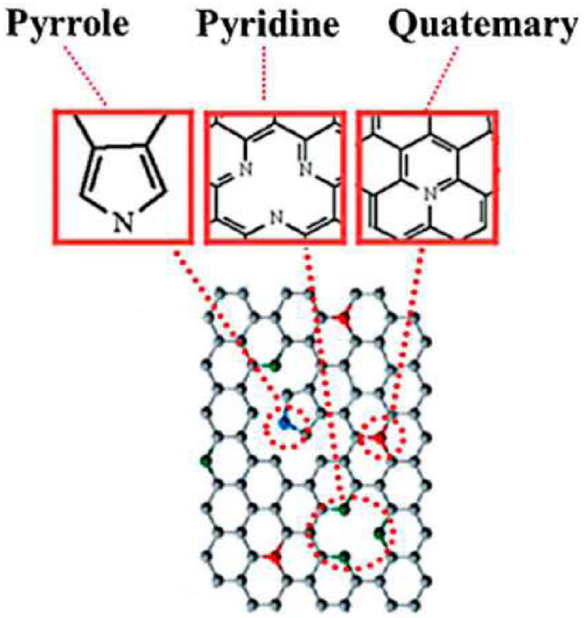

Fig. 2. Nitrogen configurations in N-doped carbon. Reprinted in part with permission from [42]. Copyright 2016 Elsevier.

Fig. 2 displays the three different structures of nitrogen in N-doped carbon. Quaternary carbon forms from a direct replacement of carbon with nitrogen without damaging the atomic structure. Pyrrolic and pyridinic carbon expose defects and rifts in the carbon crystal structure, which has been reported to further promote electrical conductivity and is therefore expected to promote electrochemical activity. [42] Alongside nitrogen, other elements such as boron, sulfur, and phosphorus can be used as carbon doping in order to enhance the surface affinity of CO_2 or its intermediates with the reaction surface. [33, 48, 49] Very recently, Hao et al. fabricated highly N-doped (5.38%) carbon nanostructures from wood biomass and showed the material's applicability as the cathode in Zn-CO_2 batteries. Using density functional theory (DFT) calculations, the authors concluded that the high pyridinic N content in the cathode lowers the free energy barrier of CO_2 reduction during discharge by facilitating the coordination and releasing of CO_2 during the electrochemical discharge and charge. The practical demonstration in an aqueous Zn-CO_2 battery was able to reduce CO_2 to carbon monoxide at a high Faradaic efficiency of 80% with a current density of 2.56 mA cm^{-2}. [44] X. Li et al. in 2019 demonstrated the use of highly N-doped (up to 8.93%) filamentous carbon nanotubes as the cathode material for flexible, fiber-shaped Li-CO_2 batteries. By promoting the reversible charge reaction which consumes all discharge products ($LiCO_2$ and C), the N-doped cathode containing dense active sites and high pyridinic N content can increase the cycle stability of their batteries from a previous 45 cycles (using a molybdenum catalyst) to 360 cycles (metal-free). [47, 50]

The improved performance of N-doped cathodes can be attributed to the increased affinity toward CO_2 on the carbon surface. This is again not necessarily catalytic, but its characteristics are comparable with catalysts. The doping can be intrinsic, where the dopant elements are present in the material precursors prior to synthesis; or extrinsic, where the dopant elements are introduced separately. Intrinsic doping is usually associated with the research of bio-derived carbon materials, where existing biomaterials such as wood, hair, or mycelium containing substantial amount of N, C, O and S are investigated for their application in energy related-research. [44, 48, 51, 52] The preexisting biomolecules like DNA and proteins serve as the dopant sources that can be introduced into a carbon matrix intrinsically. However, intrinsic doping using biomaterials struggles with controlling the precise amounts of various dopants, due to the natural variation of dopant elements in organic materials. Extrinsic doping by introducing additives to the synthesis process with additional treatment steps can achieve well controlled amounts of a given dopant, but it is typically more expensive.

Doping metal-based catalysts like ruthenium or manganese oxide in the carbon cathode is another research area of interest in metal-CO_2 batteries. [32, 53] The characteristics of the surface enhancement effects discussed here are understandable without a detailed knowledge of the electrochemistry involved, but the characterization of most catalysts requires a more in-depth investigation of the electrochemistry. Therefore, while most catalytic metal doping is based in the cathode, we will discuss the electrochemical characteristics of metal catalysts later in the section on catalysis.

It is common to examine the cathode morphology when researching the material characteristics of metal-CO_2 batteries. If a novel cathode material is developed, the comparison of the cathode morphologies by scanning electron microscopy (SEM) images at its pristine state and different stages of charge and discharge are an important characterization technique to understand the composition-structure-properties relationships of the cathode. [32] Other material characterization techniques including transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and focused ion beam (FIB) have also been adopted to study the spatial morphology of the cathode materials. [54] **Fig. 3** includes a range of cathode morphologies characterized by SEM, which allows the examination of cathode structures in submicroscale. Different morphologies including nano/microporous, needle, nanosheet, and dandelion-like have been adopted as the cathode materials for metal-CO_2 batteries due to the unique ionic and electronic properties each of the structures can provide.

The chemistry and composition of a battery cathode are the most important aspects to investigate in order to understand the underlying stability and electrochemistry of the metal-CO_2 batteries. A cathode after discharge can be removed from the cell and compared against the pristine cathode using Fourier-transform infrared spectroscopy (FTIR) or x-ray photoelectron spectroscopy (XPS) to identify discharge products. [57] The air-sensitive nature of most discharge products in metal-CO_2 batteries can complicate both experimental characterization and data interpretation. Raman spectroscopy can be applied similarly to FTIR to identify the discharge product. [37] As Raman spectroscopy has generally low signal, the cathode can be substituted for a rough gold surface, which provides surface enhancement effects. Batteries made this way show poor electrochemical performance, but the spectroscopic data can be quite valuable. This method is particularly applicable to battery discharge mechanisms that might produce carbon as a discharge product. Against a typical carbon-based cathode, this amorphous carbon discharge product is not visible.

Other means of analyzing a cathode include *in-situ* Raman, where a cell is specifically designed to allow Raman imaging during the cell's discharge and charge. [39] This can provide more detailed information about individual steps in a battery's mechanism, as opposed to the overall reaction. Electron dispersive spectroscopy (EDS) can be used alongside SEM or TEM images to identify the elemental composition of observed discharge products. [12] Selected area electron diffraction (SAD or SAED) or high-resolution TEM (HRTEM) can be then used to identify the crystal structure of the discharge products. [54]

3. The electrolyte

The electrolytes used in metal-CO_2 batteries are shared with lithium-ion batteries among other types of batteries. Compared to other applications, the electrolyte used in a metal-CO_2 battery needs to be able to dissolve CO_2. Carbon dioxide is soluble in most common aqueous and nonaqueous electrolytes used in non-CO_2 battery research, so there is significant overlap in terms of electrolyte selection in metal-CO_2 batteries. Metal-CO_2 battery technology has adapted electrolytes from previous and current research on electrolyte materials and additives.

There are several characteristics to determine a good electrolyte. The electrochemical stability window of an electrolyte is determined by its lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). Ideally, an electrolyte should be stable in the relevant voltage window, in which the electrolyte simply serves as a chemically inert medium to enable efficient ionic transport between the two electrodes, therefore it does not decompose during battery operation. [58, 59] It should readily dissolve the electrolyte salts and reaction products in the battery to avoid building up and clogging the electrodes. It should not be volatile or toxic in order to facilitate facile manufacturing. A volatile solvent can also evaporate during battery operation. [60, 61] It should not be viscous, so that ion transport across the cell is unimpeded. Last, it should be chemically stable against the other components of the cell to avoid unexpected side reactions and corrosions. [62] A common electrolyte will be a liquid solvent with a dissolved salt composed of a cation based on the anode materials and an inert anion to balance the charge in the electrolyte, which is still challenging to fulfill all the requirements mentioned above. None of the electrolytes used in metal-CO_2 batteries are ideal in all these aspects.

The conventional electrolytes in Li-ion batteries are a mixture of alkyl carbonates with a $LiPF_6$ salt. The most common alkyl carbonates are ethylene carbonate (EC), di-ethyl carbonate (DEC), di-methyl carbonate (DMC) and propylene carbonate (PC). Alkyl carbonate electrolytes have seen significant use in metal-O_2 batteries, but their instability against reactive oxygen species damages the stability of the batteries. [63] Other common electrolyte solvents in metal-CO_2 batteries include ethers, ionic liquids, water and polymers. [26, 64-66] Ethers share with alkyl carbonates the challenge of mediocre stability against the most reactive components of a battery at elevated potentials. Ionic

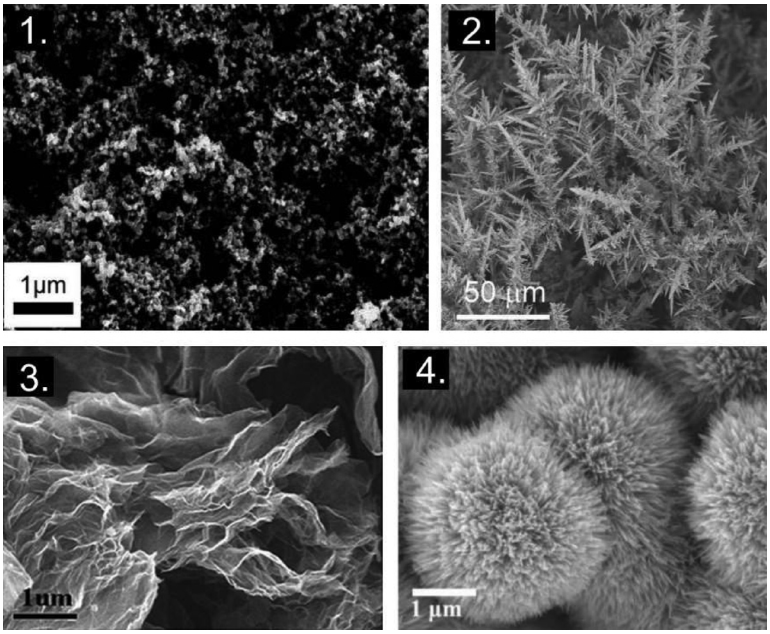

Fig. 3. SEM images of pristine metal-CO_2 cathodes. **1.** The porous carbon cathode of a Na-CO_2 battery. Reprinted in part with permission from [55]. Copyright 2014 Royal Society of Chemistry. **2.** The Ir@Au cathode of a Zn-CO_2 battery. Reprinted in part with permission from [56]. Copyright 2019 Wiley-VCH. **3.** Graphene used as a cathode in a Li-CO_2 cell. Reprinted in part with permission from [36]. Copyright 2015 Wiley-VCH. **4.** Hollow microspheres composed of $NiCO_2O_4$ used as a cathode in a Li-O_2/CO_2 cell. Reprinted in part with permission from [38]. Copyright 2019 Wiley-VCH.

liquids and polymers are usually more stable, but they have a high viscosity causing poor ion transport. Water-based electrolytes in the common case use the very flexible proton and electron transfer pathways in a protic solvent to tune CO_2 reduction chemistry. Water electrolytes are limited by the high reactivity of most metal anodes with water. Common salts include $LiN(SO_2CF_3)_2$ (LiTFSI) and $AlCl_3$. [32, 57] The salt is entirely dependent on the battery chemistry, while the choice of solvent is only partially influenced and different battery chemistries often share common solvents.

The aqueous electrolyte is a particularly interesting solvent in metal-CO_2 batteries. With few exceptions it is limited to the less reactive anode materials; those being zinc and magnesium. The main modification available is the pH of the solvent, compared to the much broader selection of characteristics that can be tuned in aprotic electrolytes. [65] The major benefit of an aqueous electrolyte is access to protic reaction mechanisms. The majority of CO_2 reduction research in the field of electrocatalysis is done with aqueous electrolytes due to the increased flexibility of reaction pathways when protons are present. [17] For this reason zinc-CO_2 batteries, the major battery technology that uses aqueous electrolytes, is the most promising initial prospect for carbon conversion among the metal-CO_2 battery technologies. [15]

Another interesting electrolyte classification is solid-state electrolytes. A solid-state electrolyte is a material that supports a high ionic conductivity despite being solid at operating temperatures. Solid-state electrolytes are more stable than liquid electrolytes, therefor they can suppress the ever-present issue of dendrite growth. In exchange, solid-state electrolytes have generally lower ionic conductivity than liquid phase electrolytes. [67] Solid-state electrolytes must overcome the challenge of strong interfacial contact between electrolyte and electrode. The majority of solid-state metal-CO_2 battery research is done in Na-CO_2 batteries, perhaps due to the comparable dendrite growth in sodium as in lithium without the benefits of a long history of research suppressing lithium dendrite formation. [61]

The “water-in-salt” electrolyte (WiSE) has been recently developed for metal-CO_2 batteries. Conceptually, a WiSE is an aqueous electrolyte with a very high concentration of salts, in effect sequestering the water molecules to solvation shells. WiSEs have been previously applied to Li-ion batteries, before an expansion of the electrolyte material to metal-CO_2 and metal-air configurations. [68] The major advantage that WiSE provides is being stable across a large potential window, alongside good conductivity and ion transport properties. Recent investigation into WiSEs has shown excellent preliminary results in Zn-air and Na-CO_2 batteries. [69, 70]

Apart from water-in-salt electrolytes, there has been little research on the electrolyte development for metal-CO_2 batteries after an electrolyte with acceptable physical properties is found. This is particularly true for Li-CO_2 batteries, where new electrolyte materials are usually taken from Li-O_2 research. Due to the high reactivity of reactive oxygen species, research into electrolyte composition in Li-O_2 batteries is quite active. [71] The most common electrolytes for a given metal-CO_2 battery chemistry will be discussed based on the anode materials.

4. The anode

The material used for the anode in a metal-CO_2 cell has the most significant influence on the cell’s electrochemistry. The operating voltage and practical capacity are dependent on the specific cell configuration, but the physical and chemical properties of the anode materials place an upper theoretical limit on both characteristics. This explains why Li-ion/lithium is the most used anode material, because lithium has the lowest standard hydrogen potential (−3.04 V) and highest theoretical capacity (3860 mAh/g). Aside from constraining the performance of a cell, the choice of anode material can change the discharge and charge process significantly. The exact chemical interactions between an anode material and the other electrochemically active components of the cell, like CO_2, are specific to the element in question and do not translate across anode materials. Even in cases such as lithium and sodium batteries where the anode electrochemistry is very similar, some differences in electrochemistry have been observed. To understand the differences between different anode materials, **Table 1** summarizes their electrochemical characteristics. This includes fundamental properties such as the half reaction, standard reduction potential, and theoretical specific capacity; and experimental properties such as the most common discharge product, its energy of formation, and the resulting standard reaction potential.

There are several challenges in anode design common across different battery chemistries and configurations. Most notably, dendrite growth is nearly universal across the different types of battery anode. The driving force for dendrite growth is the interaction between electrical fields and conductive materials during deposition, so it is intrinsic

Table 1
Electrochemical properties of anode materials and discharge products.

Material	Anodic Half Reaction [15]	Standard Reduction Potential [72]	Theoretical Specific Capacity	Typical Discharge Product	Gibbs Free Energy of Formation [72, 73]	Standard Reaction Potential
Li	$Li^{+}+e^{-}/Li$	−3.04 V	3860 mAh/g ([29])	2 Li_2CO_3 + C ([57])	−1132.12 kJ/mol	2.8 V ([74])
Zn	$Zn(OH)_4^{2-}+2e^{-}/Zn+4OH^{-}$	−1.285 V	820 mAh/g ([75])	$Zn(OH)_4^{2-}$ + CO ([56])	−553.5 kJ/mol [(a)]	1.2 V ([18])
Na	$Na^{+}+e^{-}/Na$	−2.713 V	1165 mAh/g ([29])	2 Na_2CO_3 + C ([39])	−1044.4 kJ/mol	2.35 V ([37])
Al	$Al^{3+}+3e^{-}/Al$	−1.676 V	2980 mAh/g ([76])	2 $Al_2(CO_3)_3$ + 3 C ([29])	–	–
Mg	$Mg^{2+}+2e^{-}/Mg$	−2.356 V	2205 mAh/g ([77])	$Mg(HCO_3)_2$ ([77])	–	–
K	$K^{+}+e^{-}/K$	−2.924 V	685.5 mAh/g [(b)]	K_2CO_3 + CO ([78])	−1063.5 kJ/mol	2.48 V ([37])

[(a)] An alkaline Zn-CO_2 cell will form $Zn(OH)_4^{2-}$ spontaneously from generated Zn^{2+} in solution. To allow comparison to other battery chemistries, the Gibbs free energy of formation of the precursor is listed.

[(b)] Specific capacity calculated following the Faraday equation.

to metal anodes. Dendrite growth during charge can puncture the separator and cause a battery to short. There is intensive research to mitigate the dendrite growth in metal-based battery anodes. As research on this subject is broadly applied to many different battery chemistries and widely investigated, a full exploration of the subject is outside the scope of this review. As well as dendrite growth, the formation of the interphase between the anode and electrolyte is innate to the use of reactive materials in electrochemical cells. [59] The mechanism of the interface forming, as well as its characteristics and behavior under typical battery operation is another field of research that goes beyond metal-CO_2 behaviors. In practice, research on metal-CO_2 batteries supplies an excess of anode material so the cathode behavior can be investigated, and the main aspect of the anode that is investigated is changing the material.

Lithium-CO_2 batteries are the most widely investigated because of the highest theoretical energy density of 1876 Wh/kg among all metal-CO2 batteries. [66] The other alkali metal anodes, sodium and potassium, are cheaper, but less energy dense than lithium. Batteries made with Na or K are less energy dense than batteries made with lithium, but a K-CO_2 battery could still outperform a Li-ion battery while being less expensive. All three anode materials, as alkali metals, have similar electrochemistry, and thus can share many advancements. The other metals (magnesium, aluminum, and zinc) involve multiple electron transfer processes that allow the anodes to have a higher theoretical capacity than their weight would imply. These anodes are also less reactive than the alkali metals. Their lower voltage windows could allow the applications of a broader range of electrolytes and cathodes. We separately discuss in the following section the characteristics of each type of metals that have been applied as the anode for metal-CO_2 batteries.

4.1. *Li anode*

Lithium-CO_2 batteries are the most studied type of metal-CO_2 batteries due to the intrinsic benefits of the lithium metal. The common discharge products of both Li-CO_2 and Li-CO_2/O_2 batteries are lithium carbonate and carbon. Lithium carbonate (Li_2CO_3) is generally considered to be stable and an insulator from the previous research on Li-O_2 batteries. Due to the stability of Li_2CO_3, the initial research on Li-CO_2 batteries considered them primary batteries, because Li_2CO_3 is very difficult to decompose to initiate the reverse reaction. [57]

The anode for a lithium cell is typically lithium foil, and the cathode is usually nanostructured carbon. The initial Li-CO_2 cell was designed with an ionic liquid electrolyte of 1 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide. [57] The first reversible Li-CO_2 cell was developed by using a tetraethylene glycol (TEGDME) solvent with dissolved lithium triflate ($LiCF_3SO_3$) salt, as inspired by previous research on the degradation of Li_2CO_3 in Li-CO_2/O_2 batteries. [79, 80] The authors identified the electrolyte as the key difference compared to previous, primary-only, Li-CO_2 batteries. [79] This electrolyte has seen further use as a 'standard' electrolyte in Li-CO_2 research. [9, 81] Other research has used TEGDME with LiTFSI salt instead. [32, 35, 36, 82-84] LiTFSI is proposed to be more stable, particularly against water, but many lithium salts are common. [85, 86]

Lithium is an appealing choice for battery technology due to its reactivity and very high theoretical energy density. In addition, the prominence of Li-ion batteries means that there is broad technical knowledge for any practical design that can take advantage of the already established supply chains for mass manufacturing. For these reasons, the largest body of research of metal-CO_2 batteries concerns Li-CO_2 and Li-CO_2/O_2 electrochemistry. A recent review of Li-CO_2 battery technology by Yu and Manthiram very successfully covers the history and progress of research in Li-CO_2 batteries. [21]

4.2. *Zn anode*

Following lithium, zinc-CO_2 batteries have had the most investigation. Zinc-oxygen batteries were identified as an early possibility for high specific capacity primary energy storage technology. There are a number of technologies being developed to optimize Zn-O_2 batteries and in fact the primary cell has been broadly commercialized for hearing aids and other small, long-lifetime applications. [87, 88] The developments in separator design, electrolyte additives, and cathode structures have been to some extent coopted for Zn-CO_2 electrochemistry. [89]

Zinc-CO_2 batteries are frequently made with a zinc metal foil, a nanostructured carbon cathode, and an aqueous electrolyte. Aqueous electrolytes are uncommon in rechargeable batteries, but the low discharge potential of zinc means that the hydrogen evolution reaction (HER) can be minimized unless an included catalyst promotes it. To promote the solubility of zinc ions the anodic electrolyte is usually alkaline. To avoid parasitic reactions involving CO_2 in basic conditions, the cathodic electrolyte is separated from the anodic electrolyte and kept neutral. Common anodic additives include KOH and KCl, and common cathodic additives include NaCl, $KHCO_3$, and zinc acetate. [34, 56, 90]

4.3. *Na anode*

Sodium metal anode is the most direct alternative for lithium anode in metal-CO_2 batteries. Its standard reduction potential (−2.713 V) is comparable to lithium (−3.04 V), but its theoretical specific capacity (1165 mAh/g) is significantly less. The electrochemistry of sodium metal anode is quite like lithium and has been researched on both Na-CO_2 and Na-CO_2/O_2 batteries. Preliminary research suggests that the recharge reaction of sodium-CO_2 batteries has less kinetic barriers than its lithium analogue. [39]

The anode for a sodium cell is mostly a piece of sodium foil, and the cathode is usually nanostructured carbon material. The electrolyte in initial Na-CO_2 batteries was TEGDME with sodium perchlorate ($NaClO_4$) salt. [39] Further research has typically used TEGDME, although the additive has in some cases been replaced with NaTFSI salt. [30, 91]

4.4. Al anode

Al-CO_2 batteries offer a promising alternative to lithium-CO_2 batteries for energy storage. The Al metal is abundant and is relatively light for its three-electron transfer anodic mechanism, enabling a high specific capacity. The observed discharge product, aluminum carbonate, is not well characterized but is expected to be stable and an insulator. [29] Aluminum oxalate has also been observed in a primary Al-CO_2 battery. [12] The anode is typically aluminum foil, and the cathode is typically nanostructured carbon. The electrolyte is typically an imidazolium-based ionic liquid that is melted alongside $AlCl_3$. [12, 29]

4.5. Mg anode

Mg-CO_2 and Mg-CO_2/O_2 batteries have been demonstrated alongside aluminum and lithium CO_2 or CO_2/O_2 batteries, with very little primary research into the material. Mg is an attractive anode material for its high reduction potential (−2.356 V), high specific capacity (2205 mAh/g), and high abundance. Like Al-CO_2 batteries, the observed discharge product of magnesium bicarbonate is poorly characterized. A primary cell using a Mg metal anode, nanostructured carbon cathode, and propylene carbonate electrolyte with magnesium perchlorate salt has been demonstrated. Additionally, an aqueous, membrane-free rechargeable Mg-CO_2 battery with KOH and NaCl salts has been recently demonstrated. [57, 77] This secondary Mg-CO_2 battery is most inspired by aqueous Zn-CO_2 batteries, however, it does not require a pH difference between the anodic and cathodic electrolytes.

4.6. K anode

Potassium-CO_2 batteries would be another alternative for lithium-CO2 batteries because potassium is also a more abundant element on earth. A K-CO_2 battery has a significantly lower specific capacity (685.5 mAh/g vs 3860 mAh/g) than a lithium counterpart, but a comparable reduction potential (−2.924 V vs −3.04 V). A rechargeable K-CO_2 was recently demonstrated using a potassium metal anode, a nanostructured carbon cathode, and a TEGDME-based electrolyte with KTFSI salt additive. [37]

Of these anode materials used for metal-CO_2 batteries, the electrochemical characteristics of lithium, zinc, and sodium are thoroughly investigated. Potassium-CO_2 batteries, though only been recently developed, can benefit from the research of metal-CO_2 batteries by comparing its similarities with lithium-CO_2 and sodium-CO_2 batteries. In contrast, magnesium-CO_2 and aluminum-CO_2 battery chemistries have been less investigated, because of a lack of understanding of the discharge mechanisms and products. Nevertheless, a review of all these anode chemistries for metal-CO_2 batteries is beneficial.

5. The electrochemistry

An understanding of the electrochemistry of metal-CO_2 batteries is necessary for the rational design of practical metal-CO_2 batteries. The performance of the current benchmark metal-CO_2 batteries is promising, but still not good enough to compete with current Li-ion alternatives for practical applications. Further advancement is still needed for metal-CO_2 batteries to increase the cell level performance. One of the most direct pathways to advance metal-CO_2 batteries is the addition of a catalyst, which can alter the electrochemical reaction to a more favorable pathway. A homogeneous catalyst can be introduced into the electrolyte. Alternatively, a heterogeneous catalyst can be added to the cathode. As battery electrochemistry is so closely defined by electrode-electrolyte surface reactions, heterogenous catalysts are typically investigated. There has been some success in applying commonly useful catalysts such as ruthenium and palladium to metal-CO_2 batteries, which are shown to improve the performance regardless of the specific anode electrochemistry. However, the high price of these noble metal catalysts keeps this approach from commercial application. A practical electrocatalyst should be low cost as well as effective. Designing such a catalyst will require a fundamental understanding of the electrochemistry of the metal-CO_2 batteries. Therefore, this review will comprehensively cover the current understanding of electrochemical processes in metal-CO_2 batteries.

The electrochemistry of a metal-CO_2 battery is heavily influenced by the anode material, but almost all the charge/discharge reactions that involve CO_2 happen on the cathode. For this reason, understanding the battery cathodes at different stages of electrochemical testing is of importance to understanding the electrochemistry of a metal-CO_2 battery. In some cases, the electrolyte will be examined through similar methods as the cathode to trace reactive species produced during parasitic reactions or electrochemical cycling. Alongside methods such as FTIR, SEM, X-ray diffraction (XRD), and *in-situ* Raman spectroscopy, a powerful technique in investigating battery electrochemistry is differential electrochemical mass spectrometry (DEMS). In DEMS the gasses produced and consumed by a metal-CO_2 battery are measured using gas chromatography while the battery charges and discharges. The ratio of gas evolution to electricity production can inform the discharge and charge mechanism.

The overwhelming focus of electrochemical understanding of metal-CO_2 batteries is on the cathode, but the anode material has the most significant influence on the electrochemistry of metal-CO_2 batteries. Therefore, the exploration of the current understanding of metal-CO_2 electrochemistry will be divided by different anode materials. The review of the anode electrochemistry is roughly chronological and covers all significant findings relevant to the metal-CO_2 batteries. The reviewed materials are lithium, zinc, sodium, aluminum, magnesium, and potassium, and are in order of most to least understood. Alongside the electrochemistry of the pure Li-CO_2 and Na-CO_2 batteries, mixed CO_2/O_2 battery chemistries are also investigated for these anode materials.

5.1. Li electrochemistry

As the most studied metal-CO_2 battery electrochemistry, the characteristics of lithium-CO_2 batteries are relatively well understood. Though some mechanisms of more complex Li-CO_2 battery systems still require further investigation, Li-CO_2 electrochemistry can be used in many ways as a template for other metal anode materials in metal-CO_2 batteries. While the specific electrochemistry will be different based on different anode materials, the exploration of Li-air electrochemistry can be used to predict what factors can influence other metal-CO_2 batteries. In addition, some of the most informative techniques have been first applied to the Li-CO_2 battery to understand its electrochemical characteristics. The understanding of the Li-CO_2 cell is the most complete among metal-CO_2 batteries, and this level of understanding is required for the other metal-CO_2 battery types. As catalyst design is still a challenge in Li-CO_2 batteries, other metal-CO_2 battery chemistries are likely to require at least the same degree of understanding before rational catalyst design is possible in those batteries.

5.1.1. Li-CO_2 electrochemistry

Xu et al. in 2013 demonstrated a primary Li-CO_2 cell. The cell was constructed with a porous carbon black cathode on an aluminum mesh, a Li foil anode, and an ionic liquid electrolyte 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([*bmim*][Tf2N]) with 1 M LiTFSI salt. The primary Li-CO_2 battery was developed by taking from previous research design on Li-O_2 batteries and Li-O_2/CO_2 batteries, which were in turn inspired by aqueous Zn- and Al-air batteries. [92] The ionic liquid electrolyte was also commonly used in Li-air batteries due to its stability and hydrophobicity. [64] The cell reached a discharge capacity nearing 4000 mAh/g at 100 °C, with a strong dependence on temperature. The discharge capacity in this primary Li-CO_2 cell is comparable to the discharge capacity of initial Li-O_2 batteries and initial Li-O_2/CO_2 batteries. [93, 94] As shown in

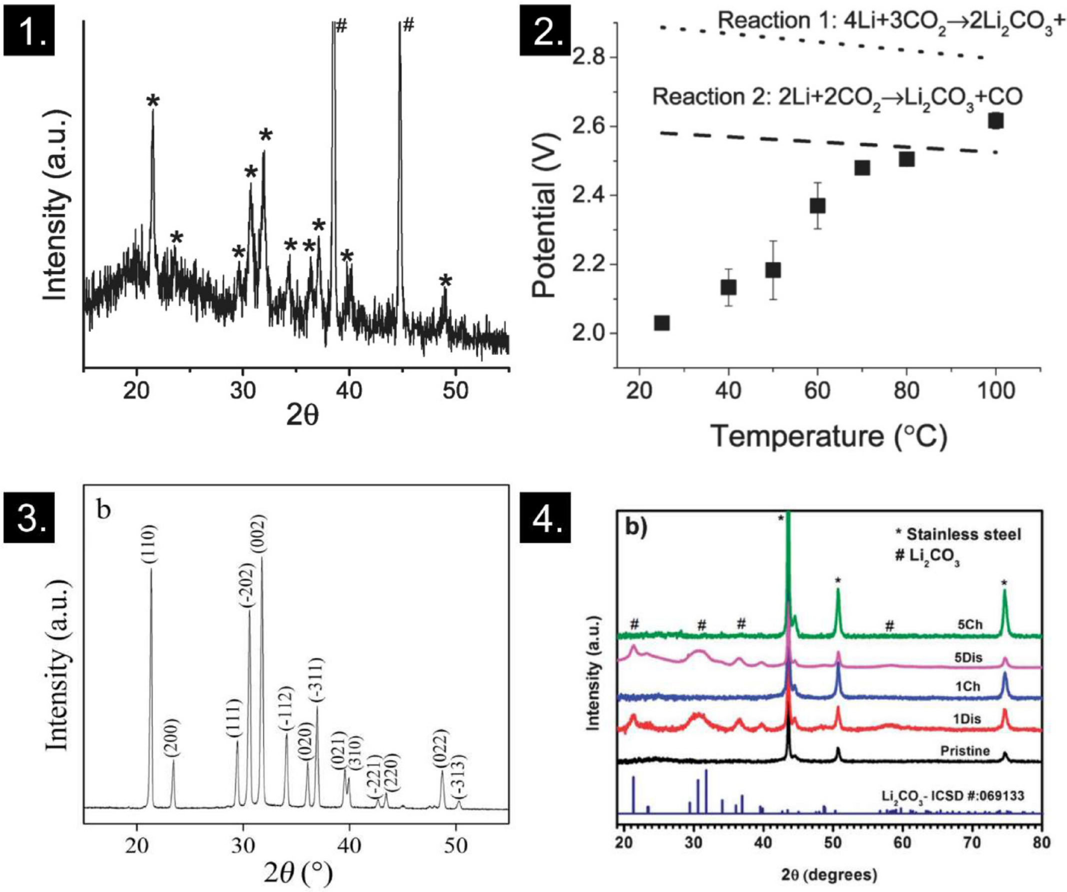

Fig. 4. Identification of Li_2CO_3 discharge product. **1.** XRD spectrum of discharged Li-CO_2 cathode. Peaks labeled with a * are assigned to Li_2CO_3, while peaks labeled # are assigned to the Al substrate. Reprinted in part with permission from [57]. Copyright 2013 RSC Publishing. **2.** Discharge potential growth as a function of discharge temperature alongside theoretical discharge potentials of theorized discharge reactions. Reprinted in part with permission from [57]. Copyright 2013 RSC Publishing. **3.** XRD spectrum of raw Li_2CO_3. Reprinted in part with permission from [95]. Copyright 2017 Elsevier. **4.** XRD patterns of pristine, discharged, and charged cathode of the Li-CO_2 batteries. Peaks labeled with a # are assigned to Li_2CO_3, while peaks labeled * are assigned to the stainless-steel substrate. Reprinted in part with permission from [79]. Copyright 2013 Royal Society of Chemistry.

Fig. 4, the authors observed lithium carbonate as a discharge product by using XRD to characterize the cathode after discharge. Xu et al. proposed Eq. (1) as the electrochemical reaction for this cell, in which Li metal reacts directly with CO_2 to form lithium carbonate (Li_2CO_3) and carbon. This reaction was selected from several known reactions by comparing theoretical equilibrium potentials of each reaction with the observed discharge potential of the cell. The authors in addition briefly explored Mg-CO_2 and Al-CO_2 primary batteries. [57]

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

In the proposed reaction, lithium and carbon dioxide directly form lithium carbonate and carbon. The reaction has a standard reaction potential of −4.98 V, which is driven by the high reactivity of lithium metal and the high stability of lithium carbonate.

Further research has validated that Li_2CO_3 is the primary discharge product in most Li-CO_2 battery configurations. Inspired by research on Li-O_2 batteries where Li_2CO_3 degradation was explored due to the parasitic reactions with the electrolyte, Liu et al. designed the first secondary Li-CO_2 cell with a ($LiCF_3SO_3$)– TEGDME electrolyte, which was able to reversibly degrade Li_2CO_3. The authors identified the presence of Li_2CO_3 after discharge and its absence after charge by using XRD, as shown in Figure 4.4. [79] Subsequent research continues to support Li_2CO_3 as the primary discharge product in most cell configurations. [36, 82] However, it is uncommon to observe the presence of amorphous carbon or another discharge product, as most batteries use a carbon-based cathode against which this discharge product is not visible. Zhang et al. in 2018 observed the growth of dispersed lithium carbonate particles across a Ni-doped graphene cathode alongside the formation of thin films of amorphous material identified as carbon using SEM and selected area electron diffraction (SAED). [96] The reversible consumption and generation of CO_2 was also observed using differential electrochemical mass spectrometry (DEMS).

Qiao et al. in 2017 performed a systematic analysis of Li-CO_2 discharge and charge mechanisms in aprotic environments. Using *in-situ* Raman spectroscopy enhanced by a gold-sputtered cathode, the authors were able to observe Li_2CO_3 and C formation during discharge of a cell using a DMSO electrolyte with 0.5 M lithium perchlorate additive. The cell was observed to produce Li_2O as an additional discharge product when deeply discharging the cell to 1.80 V in a fixed CO_2 concentration. The authors proposed that Li_2O was formed by an additional direct reaction of lithium metal and carbon dioxide, shown in Eq. (2).

$$4\ Li +\ CO_2\ \rightarrow 2\ Li_2O + C \tag{2}$$

Qiao et al. were able to detect the presence of an oxalate ($C_2O_4{}^{2-}$) as an early intermediate of the discharge process. [97] The work of Xu et al., Liu et al., and Qiao et al. has led to a widely supported discharge mechanism, described in Eqs. (3) to (6). [9, 57, 79, 97] According to this mechanism carbon dioxide is reduced to form $C_2O_4{}^{2-}$ in a two-molecule and two-electron process. $C_2O_4{}^{2-}$ disproportionation and subsequent reactions produces carbon and $CO_3{}^{2-}$, which can react with Li^+ ions to form the stable Li_2CO_3.

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

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

$$CO_2^{2-} + C_2O_4^{2-} \rightarrow 2\,CO_3^{2-} + C \tag{5}$$

$$2\,Li^+ + CO_3^{2-} \rightarrow Li_2CO_3 \tag{6}$$

Feng et al. in 2021 proposed a modified mechanism of the Li-CO_2 battery discharge process. [98] Following Eq. (3), the oxalate intermediate reacts with lithium ions immediately to form lithium oxalate ($Li_2C_2O_4$). Since lithium oxalate is not stabilized, it then degrades into lithium carbonate and carbon before precipitating onto the cathode. By introducing a heterogeneous catalyst to stabilize the proposed lithium oxalate intermediate, the authors were able to generate $Li_2C_2O_4$ as the primary discharge product in the Li-CO_2 battery.

The charge mechanism of Li-CO_2 batteries has also been studied in some detail. Yang et al. in 2016 identified three possible charge mechanisms from thermodynamic calculations, given as equations (7) through (9). The authors proposed three possible mechanisms: 1) direct degradation of Li_2CO_3 to form carbon dioxide, oxygen, and lithium ions; 2) degradation of Li_2CO_3 alongside carbon to form carbon dioxide and lithium ions; and 3) the degradation of Li_2CO_3 to form carbon dioxide, superoxide, and lithium ions. The first and third mechanisms are similar, but the superoxide product in Eq. (9) is significantly more reactive than the oxygen product in Eq. (7).

$$2\,Li_2CO_3 \rightarrow 2\,CO_2 + O_2 + 4\,Li^+ + 4e^- \tag{7}$$

$$2\,Li_2CO_3 + C \rightarrow 4\,Li^+ + 3\,CO_2 + 4\,e^- \tag{8}$$

$$2\,Li_2CO_3 \rightarrow 2\,CO_2 + O_2^{\bullet -} + 4\,Li^+ + 3\,e^- \tag{9}$$

Yang et al. fabricated ‘discharged’ cathodes by adding lithium carbonate to Al mesh working electrodes in a TEGDME-LiTFSI electrolyte. By increasing the applied potential, the electrochemistry of charging was investigated while maintaining the initial composition of the electrode. Yang et al. were able to rule out Eq. (7), as no oxygen was detected when ‘charging’ their artificial Li_2CO_3 cathodes. The authors in addition were able to rule out Eq. (8) by comparing artificial Li_2CO_3 cathodes with added ^{12}C or ^{13}C. The authors observed comparable evolution of $^{12}CO_2$ as identified by in situ gas chromatography-mass spectrometry measurements (GC–MS) from the artificial Li_2CO_3 cathodes, shown in **Fig. 5**. The comparable presence of CO_2 evolution and presence of fragment-45 indicate that fragment-45 is not $^{13}CO_2$, and thus the charge mechanism does not involve the added amorphous ^{13}C. The authors found support for the third reaction by fabricating an Al mesh cathode with artificially introduced superoxide, which during ‘charge’ to 5.2 V produced similar fragments as the Li_2CO_3 charge reaction under GC–MS measurements. The authors proposed that this supports the theory that the detected mass fragments are the result of electrolyte degradation caused by superoxide ions at high potential. Though no oxygen was observed during charge, this was attributed to the high reactivity of the superoxide species. The authors showed that the observed electrolyte degradation is changed by the presence of Li_2CO_3, which in turn was not just the previously reported degradation of TEGDME at a high potential. [99]

Qiao et al. were the first to observe the gradual accumulation of carbon in a Li-CO_2 cell by using Raman spectroscopy on a rough gold cathode, allowing them to distinguish their battery as being rechargeable, but not reversible. [97] In a rechargeable cell the application of a negative potential or current is enough to recharge the battery to a similar capacity as its initial state. In a reversible cell, this recharge process returns the battery to its initial state chemically, not just electrically. This distinction is less important for Li-ion battery electrochemistry, as a chemical return to the original state is required for the electrical return. However, due to the addition of a gaseous cathode in metal-CO_2 batteries, carbon accumulation does not chemically hinder the charge/discharge process. Instead, carbon buildup is expected to electrochemically hinder charge/discharge by interfering with charge and ion transport processes, which is difficult to observe before a cell is repeatedly cycled many times. The accumulation of carbon by production during discharge without consumption during charge is therefore an issue that damages Li-CO_2 cycle life.

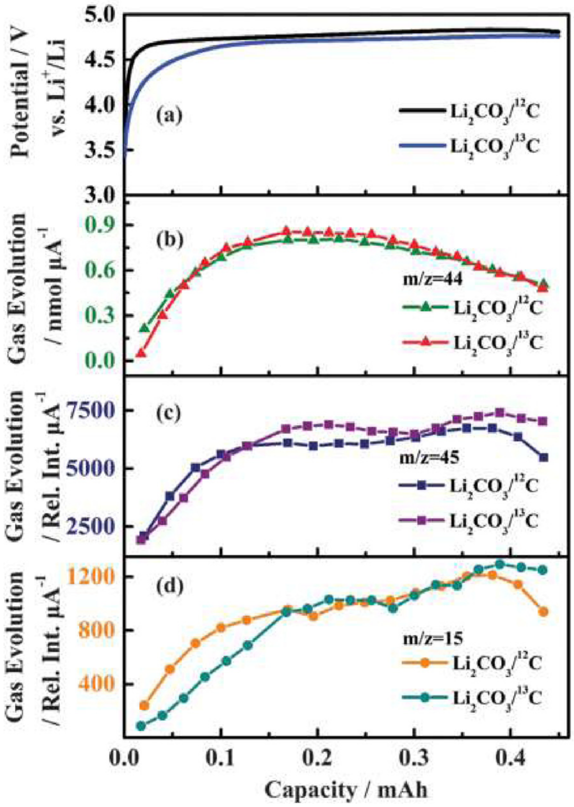

Fig. 5. Comparison between Li_2CO_3 cathodes with added ^{12}C and ^{13}C of a) CO_2 evolution and b), c), d) identified GC–MS fragments. Reprinted with permission from [99]. Copyright 2016 Royal Society of Chemistry.

Additionally, the authors detected buildup of dimethyl sulfone ($DMSO_2$) after several charge/discharge cycles. The authors attributed its presence to a nucleophilic attack on their dimethyl sulfoxide (DMSO)-based electrolyte by a reduced oxygen species, which had been observed in metal-O_2 batteries previously and hypothesized to be caused by superoxide. The authors then constructed a cell using a more typical porous carbon cathode and observed the same behaviors as the gold-based cell. Using DEMS, Qiao et al. observed the ratio of gas evolution to the controlled charging current density. At 500 mA g^{-1} nearly three electrons were observed per two CO_2, supporting Eq. (10) as the charge reaction.

$$2\,Li_2CO_3 \rightarrow 2\,CO_2 + O_2^{\bullet -} + 4\,Li^+ + 3\,e^- \tag{10}$$

However, at an increased current density of 2000 mA g^{-1}, oxygen was detected. Eq. (11) was proposed as the charge reaction based on the molar ratio of CO_2, O_2, and electrons. The researchers charged a cathode following Eq. (11), discharged the cathode, and recharged it following Eq. (10). The first charge used a 2000 mA g^{-1} charge rate, while the second used a 500 mA g^{-1} charge rate. The authors propose that at a higher current rate, superoxide ions are oxidized by the charge current directly, and form gaseous oxygen instead of other parasitic products.

$$2\,Li_2CO_3 \rightarrow 2\,CO_2 + O_2 + 4\,Li^+ + 4\,e^- \tag{11}$$

Qiao et al. also showed that the charge mechanism can be altered catalytically. Using a cell constructed with a ruthenium-based catalyst, the authors demonstrated that the amorphous carbon discharge product can be consumed during charge, creating a reversible charge/discharge cycle. [97] The introduction of catalysts to improve the performance of Li-CO2 batteries is highly investigated. Many of the catalytic materials and methods investigated show applications in other metal-CO_2 battery chemistries, therefore these catalytic methods will be considered in detail in a later section after other metal-CO_2 battery chemistries have all been discussed.

The most investigated aspect of this charge mechanism is the oxygen species. It is uncommon to detect oxygen evolution during the charge, even using real-time methods. [99] This makes it difficult to determine what form this oxygen species takes. The commonly accepted mechanism proposes superoxide ($O_2^{\bullet -}$) as the intermediate oxygen species, while some researchers propose singlet oxygen ($^1O_2$). Mahne et al. in 2018 investigated the introduction of a $^1O_2$ quencher, 9,10-dimethylanthracene (DMA) as the stabilizer against superoxide, which had also been shown to be stable beyond 4 V vs. Li/Li$^+$. [100] DMA will form DMA-O_2 in the presence of singlet oxygen, which is also stable to 4 V vs. Li/Li$^+$. The researchers observed the presence of DMA-O_2 in Li-CO_2 batteries charged above 3.8 V, suggesting that the reactive species may be singlet oxygen. However, the most common quenching method of singlet oxygen is vibrational quenching to form triplet oxygen, which has not been observed. [101]

Freiberg et al. in 2020 investigated this mechanism by fabricating carbon/Li_2CO_3 cathodes where the Li_2CO_3 is either in electrical contact or electrically isolated from the carbon cathode. [101] The authors observed Li_2CO_3 degradation even when it is electrically isolated, which is supported by isotope tracing and gas monitoring as a function of potential. The authors proposed that Li_2CO_3 degradation is instead an entirely chemical process, driven by the electrochemical formation of protons. The authors instead proposed an alternate charge mechanism in which anodic oxidation of an organic electrolyte produces protons. The protons produced react with the electrolyte salt $LiPF_6$ to form HF. HF can then decompose Li_2CO_3 to produce water. The water is then recycled to form more HF by reacting with $LiPF_6$, allowing even minor electrolyte degradation to fully decompose Li_2CO_3. The proposed reaction is given in Eqs. (12) to (16). In addition to electrolyte degradation, small impurities of alcohol or HF could also initiate Li_2CO_3 degradation. [101]

[H^+ *Production*]

$$R - CH_2OH \rightarrow R - HCO + 2\,H^+ + 2\,e^- \tag{12}$$

$$(Solvent) \rightarrow (Solvent\ **) + H^+ + e^- \tag{13}$$

[HF F*ormation*]

$$H^+ + PF_6^{\ -} \rightarrow HF + PF_5 \tag{14}$$

$$H_2O + LiPF_6 \rightarrow LiF + 2\,HF + POF_3 \tag{15}$$

[Li_2CO_3 *Decomposition*]

$$Li_2CO_3 + 2\,HF \rightarrow 2\,LiF + H_2O + CO_2 \tag{16}$$

The charge mechanism in Li-CO_2 batteries requires further investigation. It is important to understand the initial form of any oxygen species and what pathway it takes to reach steady-state before any novel elements can be introduced to the Li-CO_2 battery with the rational expectation of the cell being stable. The proposal of LiF forming as a charge product in organic $LiPF_6$ electrolytes is interesting, but the mechanism identified by Freiberg et al. is insufficient to completely explain lithium carbonate decomposition. Organic electrolytes are common in Li-CO_2 batteries, but many batteries use other lithium salts like LiTFSI which have not been shown to form HF when protons are present.

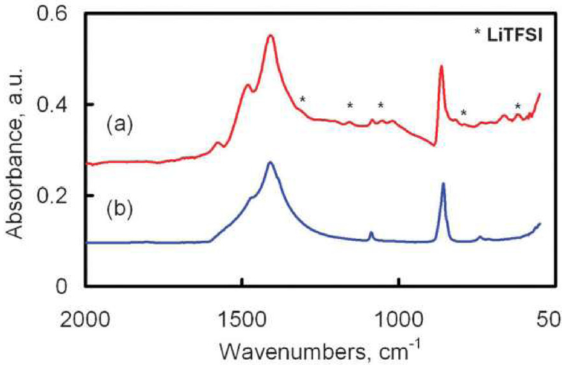

Fig. 6. IR spectra of (a) a discharged Li-O_2/CO_2 cell and (b) a Li_2CO_3 standard. Reprinted with permission from [94]. Copyright 2011 Royal Society of Chemistry.

5.1.2. *Li-CO_2/O_2 electrochemistry*

If the charge process produces reactive oxygen intermediate species, a high performing Li-CO_2 battery is likely to require quenching of this oxygen species to prevent degradation of the electrolyte. By quenching a reactive oxygen intermediate during charge, oxygen gas can be introduced even in pure Li-CO_2 batteries. Therefore, an understanding of how oxygen influences Li-CO_2 battery electrochemistry is important to the design of high-performance Li-CO_2 batteries. Fortunately, the study of Li-CO_2/O_2 batteries is an established research field due to the fact that Li-CO_2/O_2 batteries (sometimes called Li-air) have been shown to have a higher discharge capacity than either pure Li-CO_2 or Li-O_2 batteries in initial research. [79]

Initial research on Li-gas batteries primarily focused on Li-O_2 batteries following a 1996 paper by Abraham and Jiang who introduced a rechargeable Li-O_2 cell. [93] The authors treated CO_2 as a contaminant gas in the Li-O_2 batteries from the parasitic electrolyte decomposition. These researchers assumed that a membrane can be applied to separate oxygen from other atmospheric elements in real Li-O_2 battery applications. [11, 102] Li-air batteries with mixed CO_2/O_2 cathodes were introduced later because of the fact that Takechi et al. noted that the introduction of the presumed CO_2 contaminant can increase the battery capacity. [94] Li-CO_2 batteries came last, prompted by the fact that Xu *et al.* demonstrated that Na- and Mg-CO_2 batteries used as controls had capacity during examination of Na- and Mg-CO_2/O_2 batteries. [21, 57] While Li-CO_2/O_2 batteries have a longer history of research, the electrochemistry fundamental to the batteries is still less understood. This can be explained by the increased complexity of uncontrolled reactions by involving more reactive species. In order to fully understand the electrochemistry of pure metal-CO_2 batteries, a summary of research in Li-CO_2 batteries is necessary.

Takechi et al. proposed the first Li-CO_2/O_2 batteries in 2011 by studying the discharge mechanism. [94] This mechanism starts with the reduction of oxygen to form superoxide (Eq. (17)). The authors identified Li_2CO_3 as the primary discharge product by using FTIR to characterize the discharged cathodes, as shown in **Fig. 6**. Though the Li-CO_2/O_2 battery has a different electrochemistry compared with the Li-CO_2 battery, it is not surprising to see Li_2CO_3 as the primary discharge product in both systems due to its high stability. However, the mechanism study in this work was hampered by the chosen electrolyte, carbonate/diethyl carbonate, which was later found to form Li_2CO_3 through parasitic reactions of the electrolyte with the generated superoxide. [80]

It was proposed by Lim et al. that subsequent steps in the discharge reaction mechanism are dependent on the electrolyte. [80] In a high dielectric solvent, Li$^+$ ions are shielded. Thus, superoxide reacts initially with carbon dioxide. In a low dielectric solvent, the reaction of Li$^+$ ions with superoxide is thermodynamically favored. Further research by Yin et al. validated this concept, though the authors proposed that solvent donor number is the contributing factor instead. [103] This suggestion was supported by Zhao et al. in 2019, who utilized *in-situ* surface-enhanced Raman spectroscopy to observe electrochemical evolution of their cells. [104] The authors observed that in a high donor number electrolyte, oxygen acts as a "pseudo-catalyst", by first forming superoxide according to Eq. (17) and then recycling following Eqs. (18) and (19) while reducing carbon dioxide to form lithium carbonate.

$$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{17}$$

$$2\,O_2^{\bullet -} + 2\,CO_2 \rightarrow C_2O_6^{2-} + O_2 \tag{18}$$

$$C_2O_6^{2-} + 2\,O_2^{\bullet -} + 4\,Li^+ \rightarrow 2\,Li_2CO_3 + 2\,O_2 \tag{19}$$

In a low donor number solvent Zhao et al. observed initial formation of Li_2O_2 and no evolution of $C_2O_6^{2-}$. [104] Their study supports the mechanism initially suggested by Gowda et al. in 2012, who used oxygen isotope labeling and gas evolution/consumption data to demonstrate that Li_2O_2 is the source of oxygen evolution during charge of Li-O_2 batteries. [11] As shown in Eqs. (20) to (22), superoxide reacts first with lithium ions instead of carbon dioxide to form Li_2O_2. The lithium oxide will then spontaneously react with ambient carbon dioxide to form lithium carbonate.

$$O_2^{\bullet -} + Li^+ + e^- \rightarrow LiO_2^{--} \tag{20}$$

$$LiO_2^- + Li^+ \rightarrow Li_2O_2 \tag{21}$$

$$2\,Li_2O_2 + 2\,CO_2 \rightarrow 2\,Li_2CO_3 + O_2 \tag{22}$$

In the mechanism proposed by Zhao et al. carbon dioxide is not electrochemically active, despite the increased battery discharge capacity observed in the presence of CO_2. The mechanism does not adequately explain the observed improvement in capacity when CO_2 is introduced to a pure oxygen cell. It has been proposed that the capacity increase could be due to morphological change on the cathode, which increases the conductivity to facilitate the adsorption of CO_2 onto the surface and subsequent lithium carbonate formation. [104, 105] Lithium carbonate infilling would be expected to increase the cathode's performance, but due to the insulating nature of lithium carbonate, the theory for the observed capacity increase in Li-CO_2/O_2 cells using low donor number solvents requires further investigation. Wang et al. in 2020 demonstrated the application of CO_2 to a very different battery configuration using a sodium anode and phenanthrenequinone cathode, and found that the introduction of CO_2 allowed for the stabilization of a lower free energy product, resulting in a higher discharge voltage and increased capacity. [106] It is also possible that the introduction of CO_2 into a Li-O_2 cell similarly stabilizes the discharge product in a lower energy conformation.

The charge mechanism for Li-CO_2/O_2 batteries is poorly understood and without a generally agreed on mechanism. [21] However, there has been more research into the ion behaviors in Li-CO_2/O_2 batteries. Using first-principles calculations, in 2014 Ling et al. showed that the barrier towards Li_2CO_3 decomposition is the extraction of lithium ions from the cathode surface during charge. [107] In addition, in 2018 Qiao et al. showed that a high concentration of a lithium ion-coordinating salt can prevent the formation of Li_2CO_3 in a high donor number salt, leaving the peroxide intermediate, $Li_2C_2O_6$, as a final discharge product. [108] Under these conditions, Eq. (18) produces $C_2O_6^{2-}$, but the induced scarcity of Li^+ ions due to ionic shielding slows Eq. (19).

To develop a functional Li-CO_2 battery, the challenge of cycle stability must be addressed. Current research shows improvements, but a full understanding of the charge/discharge electrochemical mechanism is likely required for an ideal catalytic regime to be designed. This will further require the investigation of the charge mechanism of pure Li-CO_2 batteries. If a reduced oxygen species is a charge product, it will need to be quenched to stabilize the battery, which will require a full understanding of Li-CO_2/O_2 electrochemistry as well. The most powerful methods for investigating the electrochemical mechanism of Li-CO_2 batteries have been adapted from the studies in Li-O_2 batteries. However, it seems that these characterization methods have not been thoroughly applied to Li-CO_2/O_2 electrochemistry. The use of carbon isotope tracking paired with DEMS or a similar tool could provide insight into the charge mechanism of Li-CO_2/O_2 batteries.

5.2. Zn electrochemistry

Zinc-based batteries have also received a lot of attention compared to lithium-based batteries. Aqueous zinc-air batteries are considered an attractive alternative to Li-air batteries due to the fact of being relatively nontoxic, resilient to atmospheric conditions, cheap, and energy dense. Zn-air battery technology has a long history, where primary Zn-O_2 battery technology was being developed as early as 1997 as a possible energy storage solution for electric vehicles. [89] The research of ideal electrode structures and catalytic additives for Zn-air batteries has a similarly long history. [109] Catalysis of the oxygen reduction reaction is a broad research field of interest, in which Zn-O_2 batteries frequently benefit from. [10] In recent years, more attention has been placed on Zn-air batteries with CO_2 present. Metal-air batteries typically struggle in ambient air due to water and either oxygen or carbon dioxide. While membranes that can separate moisture from the atmosphere have shown some success, the large difficulty in separating oxygen from carbon dioxide in ambient air has led to research on Zn-CO_2/O_2 batteries where the gas separation is not necessary. As with lithium-CO_2 batteries, the study of Zn-CO_2 batteries has grown from increasing discharge capacities in Zn-CO_2 batteries to understanding the role carbon dioxide plays in a mixed air battery.

The history of Zn-air research is long enough so that the Zn-CO_2 cell can converge to a similar structure. In a typical Zn-CO_2 battery, it includes a Zn metal anode, an aqueous electrolyte, and a gas diffusion carbon cathode. In the electrolyte, there is a bifunctional membrane to separate the cathodic and anodic electrolytes which have different pH. The Zn^{2+} ions generated from the discharge process will form zincate, $Zn(OH)_4^{2-}$, in a basic electrolyte. [75] Zincate is much more soluble than zinc ions alone and is a preferable method for ion transport in most zinc-based batteries. However, the same basic solution can have parasitic reactions involving CO_2, therefore a separator is used to separate the catholyte and anolyte. Some batteries use an acidic anolyte instead, which allows the stripping and plating of the zinc to act as the anodic half reaction directly. [75] The aqueous electrolyte is very cheap and safe, but the relative ease of splitting water into hydrogen and oxygen gas during electrochemical cycling imposes several challenges when designing zinc-CO_2 batteries.

Xie et al. in 2018 demonstrated the first rechargeable Zn-CO_2 battery. [90] The catholyte was 1 M NaCl and 0.1 M HCOONa aqueous solution, while the anolyte was 1 M KOH and 0.02 M $Zn(CH_3COO)_2$ aqueous solution. The cathode was chosen carefully for its catalytic activity on the CO_2 reduction reaction (CDRR) and its specificity against the oxygen evolution reaction and hydrogen evolution reaction. Using the chosen cathode of interconnected palladium nanosheets, the authors observed the production of HCOOH in a low overpotential (0.38 V), high faradaic efficiency (89%) reaction. The proposed mechanism is shown in Eqs. (23) to (25).

$$2\,CO_2 + 2\,H^+ + 2\,e^- \leftrightarrow HCOOH \tag{23}$$

$$Zn^{2+} + 4\,OH^- \leftrightarrow Zn(OH)_4^{2-} \tag{24}$$

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + 2\,OH^- + H_2O \tag{25}$$

However, the discharge product in zinc-CO_2 batteries seems to be very dependent on the catalyst used. Wang et al. developed a Zn-CO_2

cell using a Ir@Au bimetal cathode, independently following the same principles to select the cathode. [56] The cell used a similar anolyte, 0.8 M KOH and 0.02 M $Zn(CH_3COO)_2$ aqueous solution, but a modified catholyte containing 0.8 M $KHCO_3$ in water. The authors identified the major discharge products to be $Zn(OH)_4{}^{2-}$ and CO by using XPS, *ex situ* Raman, and gas chromatography (GC). The discharge and charge mechanisms were proposed as shown in Eqs. (26) and (27). The discharge redox potential of the Zn-CO2 battery has a standard reaction potential of 1.677 V. This is lower than Li-CO_2 and Na-CO_2 batteries due to the higher standard electrode potential of Zinc, which is −0.76 V. While the discharge potential of Zn-CO_2 battery is low, Zn-CO_2 battery also has a relatively low theoretical specific energy due to its high molecular weight relative to its two-electron transfer discharge process. Nevertheless, considering the low cost of each component in a Zn-CO_2 battery, the Zn-CO_2 battery is still a significant energy storage technology for grid energy storage applications.

$$2\ Zn(OH)_4^{\ 2-} + 2\ H_2O\ \rightarrow\ 2\ Zn +\ O_2 + 2\ H^+ +\ 8\ OH^- \tag{26}$$

$$Zn +\ CO_2 +\ 2\ H^+ + 2\ OH^-\ \rightarrow\ Zn(OH)_4^{\ 2-} + CO + 2\ H_2O \tag{27}$$

Yang et al. in 2019 demonstrated a trifunctional cathode capable of catalyzing both a rechargeable Zn-CO_2 cell and Zn-O_2 cell. [34] The cathode was graphene codoped with Ni-N and P-O using pyrolysis. If supplied by CO_2, the cell could discharge and charge through the CDRR pathway. If supplied by oxygen the battery could discharge and charge through the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) pathway. The catholyte was 3 M $KHCO_3$ aqueous solution, while the aqueous anolyte contained 6 M KOH and 0.02 M $Zn(CH_3COO)_2$ aqueous solution. The codoped Ni-N and P-O had been previously shown to enable both CDR and ORR reactions, respectively. [110–112] During the charge process, the Zn-CO_2 battery mode was shown to evolve CO. [34]

Zn-CO_2 batteries show excellent promise for low-potential energy utilization and carbon capture. The cells are the safest configuration among all metal-CO_2 batteries. Recent research using super-high concentrated water-in-salt electrolytes have enabled stable cycling Zinc-air batteries by directly using ambient air. [69] However, the low discharge voltage and energy density prevent Zn-CO_2 batteries from widespread applications in portable devices and electrical vehicles which typically require high power and high capacity. In addition, the hydrogen evolution reaction during the charge process prevents Zn-CO_2 battery from reaching 100% Coulombic efficiency, which generates a flammable H_2 gas that may cause safety concerns.

5.3. Na electrochemistry

Sodium metal anode is a promising alternative to lithium metal anode due to its large abundance and inexpensiveness. Falling into the same alkaline group in the periodic table, advances from lithium battery research can be applied with some expectation of success to sodium battery research. Though sodium is more reactive and difficulty to handle than lithium, its high abundance and low cost would allow Na-CO_2 batteries to serve as alternatives to Li-CO_2 batteries in many applications.

5.3.1. Na-CO_2 electrochemistry

The first rechargeable Na-CO_2 battery was demonstrated in 2016 by Hu *et al.* [39] The authors created a battery using a Na-foil anode, a multi-walled carbon nanotube cathode, and an electrolyte of 1 M $NaClO_4$ in TEGDME. The electrolyte was chosen for its stability against sodium, low volatility, and high ionic conductivity. The electrochemical results are hindered by a partially capacitive charge and discharge process instead of a Faradic process, possibly caused by a very low mass loading of carbon nanotubes (CNT) on the nickel current collector. However, the investigation of the Na-CO_2 battery electrochemistry is still significant.

Hu et al. proposed a discharge reaction in which sodium ions react with the reduced CO_2 to form Na_2CO_3 and C. This discharge reaction, Eq. (28), is comparable to the lithium discharge reaction shown in Eq. (2). The authors proposed that this discharge reaction in sodium is fully reversible, in contrast to the Li-CO_2 battery discharge reaction. The reaction has a theoretical discharge potential of −4.07 V, which is comparable to Li-CO_2 batteries. If Eq. (28) does accurately represent the Na-CO_2 cell electrochemistry, the increase in Coulombic efficiency due to reversibly consuming the amorphous carbon could allow Na-CO_2 batteries to perform well without the addition of catalysts to tune the cell electrochemistry.

$$4\ Na^+ + 3\ CO_2 + 4\ e^- \leftrightarrow 2\ Na_2CO_3 + C \tag{28}$$

The production of Na_2CO_3 during discharge was observed by the authors by using *in-situ* Raman spectroscopy, XRD and XPS characterizations. The characterization of the charge process shows the complete degradation of the discharge products. **Fig. 7** displays both the Raman setup and the spectra showing the formation of Na_2CO_3 during discharge and Na_2CO_3 degradation during charge. The formation and degradation of carbon during discharge and charge was observed by applying electron energy loss spectroscopy to a cell using a silver cathode instead. Finally, the evolution of CO_2 gas during charge was observed using a mounted portable CO_2 analyzer which was found to closely match the theoretical value. A cathode prefilled with pure Na_2CO_3 showed a higher charge voltage than a cathode prefilled with Na_2CO_3 and C, suggesting that amorphous carbon could perhaps facilitate Na_2CO_3 degradation during the charge process. The physical evolution of polycrystalline Na_2CO_3 during discharge and charge was observed using TEM and EDS. [39]

Further research on Na-CO_2 batteries has continued to observe Na_2CO_3 as the main discharge product. Sun et al. in 2018 demonstrated a symmetric Na-CO_2 cell using a Super P/Al anode and a prefilled multi-walled CNT/Na_2CO_3 cathode. [30] The authors demonstrated the dendrite-free growth of Na on the anode during the charge and examined the charge electrochemical reaction using Raman and gas chromatography. The authors in addition optimized the Na_2CO_3/CNT ratio to lower the decomposition voltage using linear sweep voltammetry. These authors were able to support the previously observed charge/discharge reaction demonstrated by Hu *et al.* [39]

Thoka et al. in 2020 performed a study to compare the overpotential, cycle stability, and cycling behavior of the Li-CO_2 and Na-CO_2 batteries. [91] In both cases, a TEGDME solvent with added LiTFSI/NaTFSI salt was used as the electrolyte and a Ru catalyst doped CNT was used as the cathode. The ruthenium was shown to be essential to the cycling stability of the batteries, increasing the cycle life from 35 to 100 cycles. Thoka et al. proposed that the Ru catalyst decreased the overpotential of the metal carbonate degradation reaction during charge. In the electrochemical characterizations, the Na-CO_2 batteries were shown to have a lower overpotential both initially and after 100 cycles at a current density of 500 mA g^{-1}. The discharge product in both batteries was observed to not fully degrade after the 15th charge using Raman and XPS in both batteries. The authors did not observe carbon evolution given that a high carbon content cathode was used. [91] If the degradation of sodium carbonate in these batteries does consume amorphous carbon without the requirement of a catalyst, then the Na-CO_2 electrochemistry is a very appealing alternative to Li-CO_2.

5.3.2. Na-CO_2/O_2 electrochemistry

Unlike Li-CO_2 batteries Na-CO_2 batteries have not been observed or predicted to produce oxygen during the charge or discharge process. Therefore, it is less important to understand how the introduction of oxygen influences the Na-CO_2 battery electrochemistry. However, the application of Na-CO_2 batteries using direct atmospheric CO_2 is still likely to require an understanding of the roles of oxygen in the battery. Therefore, a summary of recent understandings of Na-O_2/CO_2 batteries is beneficial.

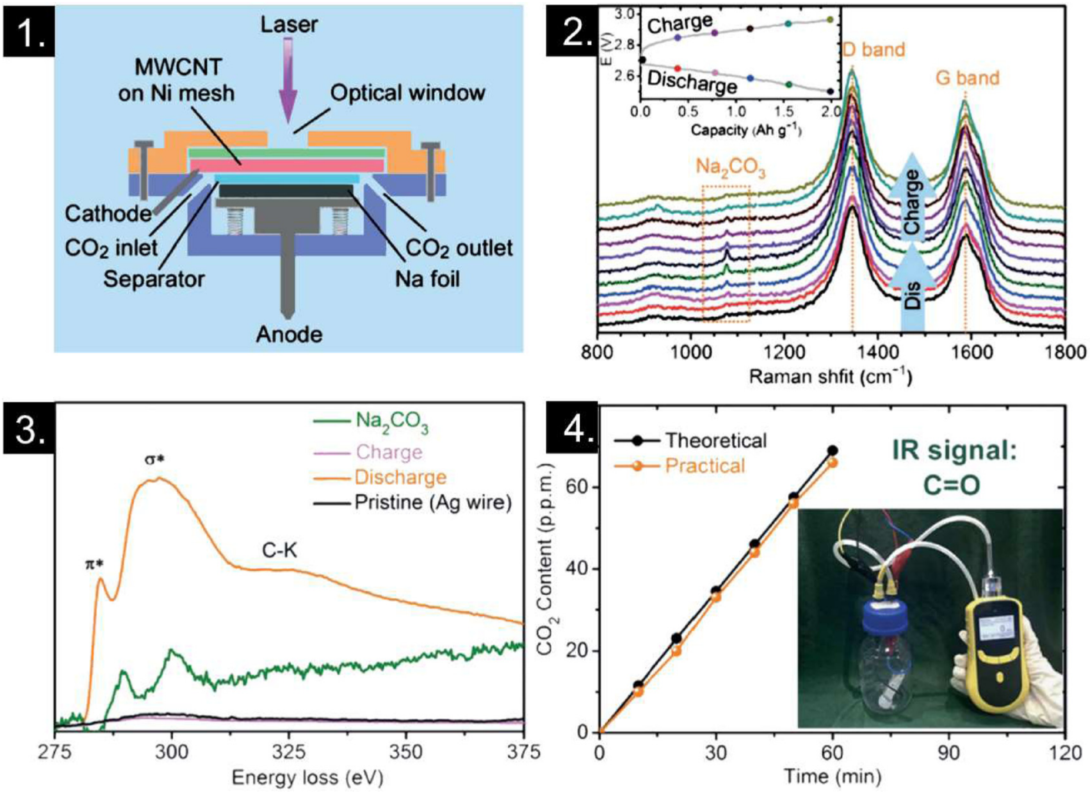

Fig. 7. Na-CO_2 battery characterization. **1.** A diagram of an *in-situ* Raman spectroscopy setup. **2.** Raman absorption spectra during discharge and charge. Inset of corresponding discharge/charge profiles. **3.** EELS of silver wire cathode at given states alongside Na_2CO_3 standard. **4.** CO_2 evolution data during discharge against proposed discharge mechanism. Inset of on-line CO_2 evolution detection. Reprinted in part with permission from [39]. Copyright 2016 Wiley-VCH.

Das, Xu, and Archer in 2012 introduced a mixed gas Na-O_2/CO_2 cell configuration by using a Super P carbon cathode, a Na foil anode and an electrolyte containing either $NaClO_4$ in TEGDME or $NaCF_3SO_3$ in 1-ethyl-3-methyl imidazolium trifluromethanesulfonate (ionic liquid). [31] Performance of the mixed gas Na-O_2/CO_2 cell was examined using pure oxygen, pure CO_2, and mixed gas atmospheres. Batteries using both electrolytes improve in capacity following the addition of CO_2 to the oxygen atmosphere. The authors examined the discharged electrodes using XRD and FTIR to understand the discharge products of the mixed gas Na-O_2/CO_2 battery. They further proposed several discharge reaction mechanisms to account for the observed discharge products. In agreement with the observations in Li-air batteries, oxygen was identified as the initially active species. [31] In the batteries with the TEGDME-based electrolyte, both $Na_2C_2O_4$ and Na_2CO_3 were observed as the discharge products. However, only $Na_2C_2O_4$ was observed in batteries using the ionic liquid electrolyte. The authors proposed three reaction mechanisms to explain these results, as shown in Eqs. (29) to (41).

$$4\ O_2 + 4\ e^- \rightarrow 4\ O_2^{\bullet -} \tag{29}$$

$$O_2^{\bullet -} + CO_2 \rightarrow CO_4^{\bullet -} \tag{30}$$

$$CO_4^{\bullet -} + CO_2 \rightarrow C_2O_6^{\bullet -} \tag{31}$$

$$C_2O_6^{\bullet -} + O_2^{\bullet -} \rightarrow C_2O_6^{2-} + O_2 \tag{32}$$

$$C_2O_6^{2-} + 2\ O_2^{\bullet -} + 4\ Na^+ \rightarrow 2\ Na_2CO_3 + 2\ O_2 \tag{33}$$

The first reaction mechanism, Eqs. (29) to (33), is quite similar to the formation of Li_2CO_3 during discharge of Li-O_2/CO_2 cells as proposed by Zhou et al., Eqs. (17) to (19). [104] Das et al. proposed this reaction mechanism as occurring in cells with TEGDME-based electrolytes. [31]

$$O_2 + e^- \rightarrow O_2^{\bullet -} \tag{34}$$

$$O_2 + 2\ e^- \rightarrow 2\ O_2^{2-} \tag{35}$$

$$CO_2 + O_2^{2-} \rightarrow CO_4^{2-} \tag{36}$$

$$CO_4^{2-} + CO_2 + 2\ Na^+ \rightarrow Na_2C_2O_4 + O_2 \tag{37}$$

The second mechanism, Eqs. (34) to (37), was proposed to occur alongside the first in the TEGDME electrolyte cells and dominate the ionic liquid electrolyte cells. Finally, the authors proposed a mechanism for the pure Na-CO_2 batteries examined in which a direct reduction of carbon reacts with sodium ions to produce both observed products, Eqs. (38) to (41).

$$2\ CO_2 + 2\ e^- \rightarrow C_2O_4^{2-} \tag{38}$$

$$2\ CO_2 + 2\ e^- \rightarrow CO_3^{2-} + CO \tag{39}$$

$$C_2O_4^{2-} + 2\ Na^+ \rightarrow Na_2C_2O_4 \tag{40}$$

$$CO_3^{2-} + 2\ Na^+ \rightarrow Na_2CO_3 \tag{41}$$

Notably the third proposed mechanism does not produce carbon as a discharge product, unlike what has been observed by Hu et al. in Li-CO_2 batteries. [39] In a later work, Xu et al. demonstrated a hybrid electrolyte using 1 M NaTFSI in propylene carbonate containing SiO_2 nanoparticles tethered to 1-methyl-3-propylimidazo-lium

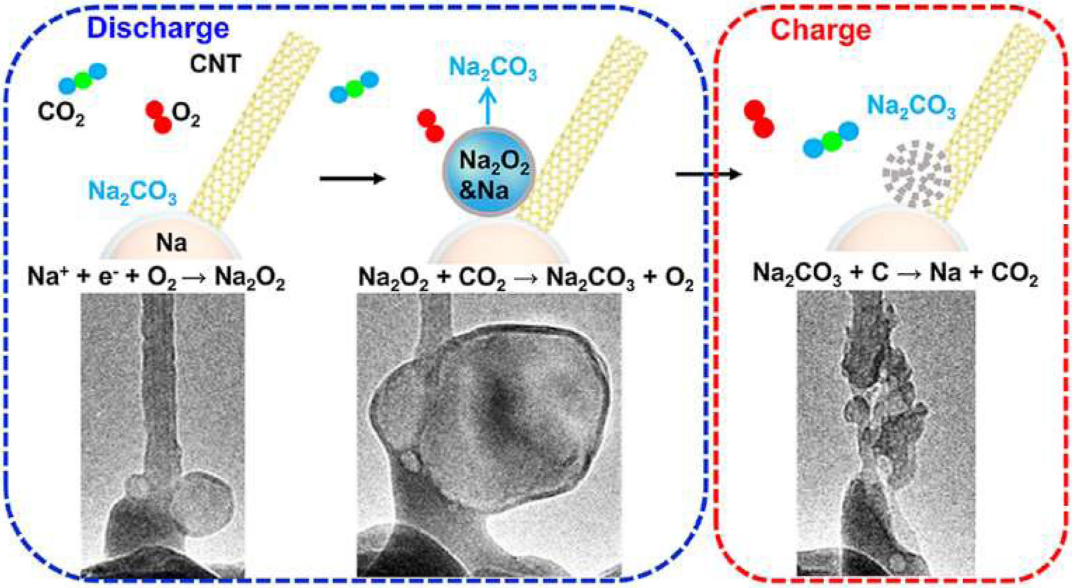

Fig. 8. Evolution of a nanowire cathode during discharge and charge. During discharge spherical structures of Na_2O_2 form before the development of a Na_2CO_3 coating. During charge the sphere shrinks to produce Na and CO_2. Reprinted with permission from [54]. Copyright 2020 American Chemical Society.

bis(trifluoromethanesulfone)imide (SiO_2-IL-TFSI) as an electrolyte additive for Na-CO_2 batteries. [55, 113, 114] This Na-CO_2 battery produces a discharge product of $NaHCO_3$. The proton source in $NaHCO_3$ was proposed to be the degradation of the electrolyte. The authors proposed a discharge electrochemical reaction based on the observed reaction potential, Eq. (42).

$$2\,Na + H_2 + 2\,CO_2 + O_2 \rightarrow NAHCO_3 \tag{42}$$

Though the degradation of the electrolyte is expected to cause a poorer cycling stability, the Na-CO_2 batteries were able to remain stable for over 20 cycles. Recent research by Frieberg et al. on Li-CO_2 batteries which identified a possible proton source in Li-CO_2 batteries may be relevant to understand the proton source in these batteries. [101]

Liu et al. recently examined the morphology and composition of the discharge cathode of a Na-O_2/CO_2 battery by using an environmental TEM assisted by electron dispersion pattern (EDP) and electron energy loss spectroscopy (EELS). [54] The authors were able to observe the morphology and structural evolution of the CNT cathode in real-time, as shown in **Fig. 8**. Some spherical structures were observed to grow on the CNT during discharge and shrink during discharge, and the structures were observed to shrink during discharge, with the spheres consisting of Na, Na_2O, and Na_2O_2 initially before decomposing to form Na_2CO_3. During the charge process, the Na_2CO_3 was observed to decompose to form Na and CO_2. These results are in excellent agreement with research on Li-O_2/CO_2 batteries, which suggests that the CO_2 species can decompose Li_2O_2 purely chemically. [104, 105] Liu et al. observed a more sluggish charge process under pure O_2 gas environment when discharging and charging a solid-state nanobattery under observation by TEM, implying that solid Na_2O_2 decomposition is slower than solid Na_2CO_3 decomposition. In addition, the same charge and discharge reaction mechanisms were observed on cells using both CNT and silver cathodes, although the charge process on the silver cathode was more sluggish. [54] This highlights the importance of carbon in facilitating the degradation of Na_2CO_3.

The discharge products in sodium-CO_2 batteries have been shown to be very dependent on the electrolyte compositions. The Na-CO_2 battery appears to discharge through a similar mechanism as the Li-CO_2 battery. But unlike Li-CO_2 batteries, the charge reaction of Na-CO_2 batteries does appear to reversibly consume the produced carbon. This characteristic should give Na-CO_2 batteries higher cycle stability and might contribute to a lower overpotential due to losses when charging. Building up of carbon, sodium carbonate, and unidentified products of parasitic reactions during charge and discharge has been observed in Na-CO_2 batteries, the exact source of which still remains unclear in terms of the reaction mechanism. [54]

5.4. Al electrochemistry

Al-CO_2 batteries are attractive primarily because of the high abundance of Al, its high capacity, and ease of manufacturing. Despite aluminum being significantly heavier than lithium, its three-electron transfer process gives aluminum the second highest theoretical specific capacity (2980 mAh/g) among all metal anodes discussed in the review.

Primary Al-CO_2 batteries were initially demonstrated as a proof-of-concept by Xu et al. in 2013. [57] The batteries however showed poor capacity and cyclability. The batteries used a conductive carbon as the cathode and an ionic liquid composed of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride as the electrolyte. [115] Sadat and Archer in 2016 demonstrated a primary Al-O_2/CO_2 cell with an exceptional discharge capacity of over 12,000 mAh/g. Informed by direct analysis in real-time mass spectrometry (DART-MS), SEM-EDS, XPS, and thermogravimetric analysis-FTIR (TGA-FTIR), the authors proposed a discharge mechanism for the cell with aluminum oxalate as the discharge product. [12] The authors observed the highest discharge capacity for the Al-O_2/CO_2 cell in an 80% CO_2 and 20% O_2 mixture gas environment, and a lower discharge capacity when the cell is discharged under either a 100% CO_2 or 100% O_2 gas environment. In their proposed discharge mechanism, as shown in Eqs. (43) to (48), superoxide and aluminum ions form first electrochemically. The discharge reaction then proceeds by reacting superoxide with carbon dioxide to form several reactive carbon species $CO_4^{\bullet-}$, CO_4^{2-}, and $C_2O_4^{2-}$. The oxalate ($C_2O_4^{2-}$) can then interact with the aluminum ions to form aluminum oxalate. Aluminum oxalate fragments were observed by using direct analysis in real-time mass spectrometry. Both XPS and EDS were also applied to observe ratios of aluminum, oxygen and carbon, which in turn suggests the approximately correct ratio for aluminum oxalate.

$$2\,Al \leftrightarrow 2\,Al^{3+} + 6\,e^- \tag{43}$$

$$6\,O_2 + 6\,e^- \leftrightarrow 6\,O_2^{\bullet-} \tag{44}$$

$$3\ CO_2 + 3\ O_2^{\bullet -} \leftrightarrow 3\ CO_4^{\bullet -} \tag{45}$$

$$3\ CO_4^{\bullet -} + 3\ O_2^{\bullet -} \leftrightarrow 3\ CO_4^{2-} + 3\ O_2 \tag{46}$$

$$3\ CO_4^{2-} + 3\ CO_2 \leftrightarrow 3\ C_2O_4^{2-} + 3\ O_2 \tag{47}$$

$$2\ Al^{3+} + 3\ C_2O_4^{2-} \leftrightarrow Al_2(C_2O_4)_3 \tag{48}$$

Ma et al. in 2018 demonstrated the first rechargeable Al-CO_2 batteries. [29] The batteries used a chloroaluminate based ionic liquid as the electrolyte and palladium-coated nanoporous gold as the cathode. The Al-CO_2 batteries demonstrate stable cycles for over 30 cycles at a current density of 330 mA g^{-1}. In the voltage profile, a near constant charge plateau was observed. However, a decreasing discharge plateau over multiple cycles was also shown, which the authors explained as the buildup of the discharge products. The authors demonstrated that the primary discharge product is $Al_2(CO_3)_3$ by Raman spectroscopy, FTIR, and XPS. Thus, the authors proposed a reversible reaction mechanism similar to Li-CO_2 batteries, given in Eq. (49). Aluminum carbonate is not a well characterized chemical, whose theoretical discharge potential for this reaction is not easily obtainable. The observed discharge potential using a NPG@Pd cathode was 0.627 V. [29]

$$4\ Al + 9\ CO_2 \leftrightarrow 2\ Al_2(CO_3)_3 + 3\ C \tag{49}$$

The presence of aluminum carbonate was observed using Raman, XPS, electron energy-loss, and FTIR spectroscopy. [29] The authors argued that aluminum carbonate would be expected, given the prevalence of metal carbonate discharge products in other metal-CO_2 batteries. During charge the authors observed only most of the discharge product degrading, so the reversibility of this reaction is not fully demonstrated.

It is plausible that an Al-CO_2 cell during discharge would produce aluminum carbonate while an Al-CO_2/O_2 cell using a similar electrolyte would produce aluminum oxalate. Neither aluminum carbonate nor aluminum oxalate are well characterized, whose properties such as the Gibbs free energy of formation and conductivity are not reported. Sodium oxalate is reported to have a higher change in enthalpy of formation (−1318 kJ/mol to form the gas phase) than sodium carbonate (−1130.7 kJ/mol to form the crystal phase). [73] However, lithium oxalate is considered less stable than lithium carbonate. [116] It is plausible that the introduction of the more reactive oxygen could form a more stable discharge product, but the stability of both compounds is not well understood. A further investigation of the reaction mechanism of the Al-CO_2 battery is required before the Al-CO_2 battery technology can be adapted to practical applications.

5.5. Mg- and K-CO_2 electrochemistry

The first Mg-CO_2 battery was demonstrated by Xu *et al.* at the same time as the first Al-CO_2 battery. [57] The Mg-CO_2 battery was operated as a primary cell which showed relatively poor capacity. Das, Xu and Archer later demonstrated a mixed gas Mg-O_2/CO_2 cell alongside the Na-O_2/CO_2 cell. [31] Like the Na-O_2/CO_2 cell, the mixed gas Mg-O_2/CO_2 cell showed an increased capacity without changing the discharge potential. The cell used 1 M $Mg(ClO_4)_2$-propylene carbonate as the electrolyte and a Super P carbon as the cathode. The mixed gas Mg-O_2/CO_2 cell was demonstrated in a primary battery configuration.

Recently Kim et al. demonstrated a secondary Mg-CO_2 battery as a corollary to Zinc-CO_2 batteries. [77] The authors designed a cell with an aqueous electrolyte containing 1 M NaCl and 1 M KOH, an anode of a Mg alloy, and a gas evolution cathode consisting of carbon paper drop-casted with a catalytic ink (Pt/C+IrO_2). The electrochemical reaction mechanisms of the Mg-CO_2 battery were interrogated using galvanostatic measurements, FTIR, XRD, and gas chromatography. The cell was shown to consume CO_2 to produce H_2 gas during the discharge at a voltage over 0.75 V and produce Cl_2 and O_2 gas during charge at a voltage under 3.1 V. The Mg-CO_2 battery showed excellent cycling stability over 80 cycles at 20 mA cm^{-2}, however, a sluggish capacitive charge/discharge curve without obvious voltage plateau was observed. This Mg-CO_2 battery is of particular interest for producing three gas streams which is useful for industrial applications, but the relatively low discharge potential and specific capacity of the Mg-CO_2 battery hinder its application as an alternative to Li-ion batteries.

Among the anode materials used for metal-CO_2 batteries, investigation of potassium-CO_2 batteries is the most recent. Though the higher reactivity of potassium can pose significant safety issues when designing metal-CO_2 batteries, the material shares a similar theoretical discharge potential to sodium and a higher ion mobility. [37]

Zhang et al. in 2018 demonstrated solid-state K-CO_2 nanobatteries and analyzed their charge/discharge behavior in real-time using *in-situ* TEM, EDP, and EELS. [78] The batteries were constructed with a CNT cathode, K anode, and K_2O electrolyte. The researchers observed the formation of K_2CO_3 spheres on the CNT during discharge and their degradation during charge. The spheres of K_2CO_3 were observed to inflate during discharge and deflate during charge by *in-situ* TEM. In addition, the authors observed a shrinking of the CNT during the charge process, indicating carbon consumption. The authors used the information to propose the following reaction mechanism for the K-CO_2 nanobatteries.

$$2\ K + 2\ CO_2 \rightarrow K_2CO_3 + CO \tag{50}$$

$$K_2CO_3 + C \rightarrow 4\ K + CO_2 \tag{51}$$

According to this reaction the K-CO_2 battery produces CO gas during discharge while consuming carbon to produce CO_2 during charge. The discharge product was hollow shells of potassium carbonate filled with carbon monoxide. Due to this effect, the carbon monoxide produced during the discharge process was actually observed during the charge process when the K_2CO_3 shells degrade. The theoretical reaction potential of the K-CO_2 battery is 2.48 V, reflecting the thermodynamic properties of the anode. The production of carbon monoxide during discharge without being consumed during charge may prove to be a challenge for the cycling stability of K-CO_2 batteries. The same challenge also applies to the consumption of carbon during charge without its production during discharge. However, these challenges are not clearly visible in further work.

Zhang et al. in 2019 demonstrated a full K-CO_2 battery using a K anode, a TEGDME electrolyte with 1 M KTFSI salt, and cathodes of N-doped CNT and CNT/reduced graphene oxide. [37] This research focused on the fabrication of a suitable cathode for the K-CO_2 battery which was able to show the reversible formation and degradation of K_2CO_3 over 250 cycles at 100 mAh g^{-1}. This work did not significantly investigate the electrochemical mechanism of the K-CO_2 battery.

Lu et al. in 2021 demonstrated a K-CO_2 cell with significant modifications. [117] To prevent violent side reactions between anodic K and water, the authors chose a KSn alloy anode instead. The KSn alloy was also shown to significantly reduce dendrite formation, which was attributed to the alloying reaction between tin and potassium. The authors used multi-walled carbon nanotubes functionalized with carboxylic acid groups for their cathode. Due to the structural similarity between HCOOH and K_2CO_3, the authors proposed that strong ionic interactions between HCOOH groups and K_2CO_3 molecules can weaken the C = O double bonds in potassium carbonate which results in a lower charge potential of the battery. This effect was not conclusively shown by the authors, but the investigation of the K-CO_2 electrochemistry was significant. The authors proposed a reversible discharge mechanism as shown in Eq. (52).

$$4\ KSn + 3\ CO_2 \leftrightarrow 2\ K_2CO_3 + C + 4\ Sn \tag{52}$$

Lu et al. did not observe the formation of carbon monoxide during discharge and did observe both the formation of carbon during discharge and its consumption during charge as indicated in previous research. It is unclear if a KSn anode significantly changes the electrochemical reaction pathway of the K-CO_2 batteries.

Though the chemistries of these anode materials can be quite different, several similar commonalities of the anodes allow for development of metal-CO_2 batteries that share similar electrochemical reaction pathways. In most metal-CO_2 batteries, the reduction and evolution of carbon dioxide drives the discharge and charge reaction pathways. When oxygen is introduced in a metal-gas battery feed stream, the evolution and coordination of superoxide is expected to be the first step of discharge. We can therefore expect catalysts to be applicable across different anode materials. For this reason, a discussion of catalytic materials that have been applied in metal-CO_2 batteries is included in this review paper.

6. The catalysis

The common goals of many catalysts in metal-air batteries are to increase cycle stability and decrease high overpotential. Several excellent reviews already summarize great amounts of catalysis research into digestible formats. For examples, Mu et al. reviewed the catalysts in Li-CO_2 and Na-CO_2 batteries and Liu et al. comprehensively reviewed the catalysts of Li-CO_2 batteries. [19, 21] This section will focus on materials and methods that have been demonstrated in multiple metal-CO_2 batteries.

Most of the investigation of catalysts focuses on Li-CO_2 and Zn-CO_2 batteries, with many of the advances being applied to other cell structures. In both Li-CO_2 and Zn-CO_2 batteries, most catalytic materials are metals, which are usually integrated into the cathodes. The metals can be introduced directly, or in the form of oxides and carbides. The introduction is usually in the form of nanoparticles integrated into the conducting carbon matrix, with varying degrees of complexity for both nanoparticle and carbon matrix. The deposition of catalytic materials on the cathode is usually referred to as doping, and the added material is usually referred to as the dopant. Under the usual definition of doping this is not wholly accurate, as this deposition does not integrate atoms of a material into an existing crystalline structure. Due to the near-ubiquitous adoption of the term for this application, the integration of catalytic nanostructures into a larger cathode structure will be referred to here as doping.

Noble metals like ruthenium, iridium, and palladium, and transition metals like nickel, tin, and manganese are the most investigated metal catalysts for metal-CO_2 batteries. It is also common to see researchers investigating a combination of catalysts to explore synergistic effects, which are typically in the form of a combination of a metal catalyst with a nitrogen or boron elemental doping.

The effectiveness of a catalyst is typically demonstrated by using electrochemical characterization. These methods are typically simple to apply, however they do not provide significant insights on how the catalyst effects the electrochemical reaction pathway. **Fig. 9** displays the electrochemical results with different types of catalyst in metal-CO_2 batteries. The effectiveness of a catalyst can be observed through increased cycle stability, increased capacity, increased redox current during cyclic voltammetry, or decreased overpotential. A catalyst is not expected to change the discharge potential of a cell but can increase the capacity of the discharge reaction, which in some cases appears to increase the discharge potential by reducing the overpotential (as shown in Figure 9.3).

6.1. Noble metal catalysts

Noble metals are common catalysts for a variety of applications, being frequently useful for the coordination of reduction and oxidation reactions. [16] This makes them applicable for emerging battery chemistries where the specific reaction is not yet clear enough for the rational design of catalytic regimes. A common issue with noble metal catalysts is their scarcity and high cost, which prevent their use in large scale commercial batteries. Common noble metal catalysts that have been applied in metal-CO_2 batteries include ruthenium, iridium, and palladium. [8, 53, 81, 84, 90, 91, 118-121] **Fig. 10** shows some of the observed effects of ruthenium catalysts in metal-CO_2 batteries (Table 2).

Zhang et al. in 2019 examined the addition of ruthenium to N-doped CNT cathodes of Li-CO_2 and Li-O_2/CO_2 batteries. [120] The authors observed a decrease in overpotential due to the addition of Ru/N dopants, from 1.45 V to 1.06 V. The authors also observed an increase in cycle stability from 150 to 200 cycles across various atmospheres of O_2 and CO_2 with a current density of 500 mA g^{-1}. Failing cells were examined with most of the electrolyte consumed and deposits on the anode, which was proposed to be the decomposition of the electrolyte due to superoxide.

Zhang et al. fabricated Ru-Cu-graphene (Ru-Cu-G) nanoparticles using crystallization of hydroxyl groups in ethylene glycol. [121] The particles were co-dispersed across graphene cathodes, which was shown to significantly improve the cycling stability and overpotential of Li-CO_2 batteries. The interaction between Ru and Cu was shown to promote the dispersion of Li_2CO_3 during discharge to form ultra-thin plates that degrade without significant buildup. The authors observed no morphological change in the cathode after 10 cycles, though both Ru-G and Cu-G cathodes showed significant accumulation of Li_2CO_3 after the same period of cycling.

Guo et al. in 2019 demonstrated the applicability of ruthenium catalyst to Na-CO_2 batteries. [53] Cathodes with dispersed Ru nanoparticles on a ketjen black carbon cathode was shown to be stable over 130 cycles at 200 mA g^{-1}, compared to pure ketjen black cathodes which were significantly degraded after 90 cycles. In addition, the additive was shown to reduce the charge potential by 0.3 V and increase the discharge capacity from 6045 mAh g^{-1} to 11,537 mAh g^{-1}. Thoka et al. in 2021 performed a comparative study of Ni-CO_2 and Li-CO_2 cells with and without added Ru dispersed on the CNT cathode. [91] In both batteries, the addition of ruthenium was shown to increase cycle stability and lower overpotential.

6.2. Transition metal catalysts

Common metal oxide catalysts in metal-CO_2 batteries include manganese oxide, nickel oxide, and cobalt oxide. [32, 38, 91, 122-126] **Table 3** summarizes the recent research in transition metal catalysts, which is focused more on the application of manganese catalysts. When the subject of research is the integration of the metal catalyst into a larger structure, a manganese catalyst is typically used. Transition metal catalysts are most frequently introduced as metal oxides, though metal carbides, pure metals, and metal organic frameworks are also studied. **Fig. 11** shows the performance of some MnO catalysts in metal-CO_2 batteries.

Li et al. in 2019 demonstrated the efficacy of monodispersed MnO nanoparticles on an N-doped 3D graphene cathode in a Li-CO_2 cell. [32] The authors examined a series of different cathode structures to distinguish various properties of the cathode: bulk MnO, MnO dispersed on ketjen black, the metal-organic-framework (MOF) $Mn(C_2H_2N_3)_2$, and the pyrolized MOF MnO:NC without added graphene. The first catalyst, MnO:NC-G, was shown to provide the lowest overpotential, highest cycle stability, and highest durability. As in **Fig. 12**, SEM images show that Li_2CO_3 first forms inside the cathode and proceeds to coat thin flakes, ensuring a complete degradation on the recharge process to allow a longer cycle life cell. During initial discharge the surface of the cathode is not changed, indicating that initial deposition occurs inside pores of the cathode. Further discharge forms high surface area flakes coating the surface, which degrade fully during charge.

Following the success of mixed transition metal oxides as catalysts for oxygen evolution and reduction reactions, Fang et al. applied a Co_2MnO_x catalyst structure for Na-CO_2 batteries. [124] The catalysts were grown as nanowires on carbon fiber substrates. Com-

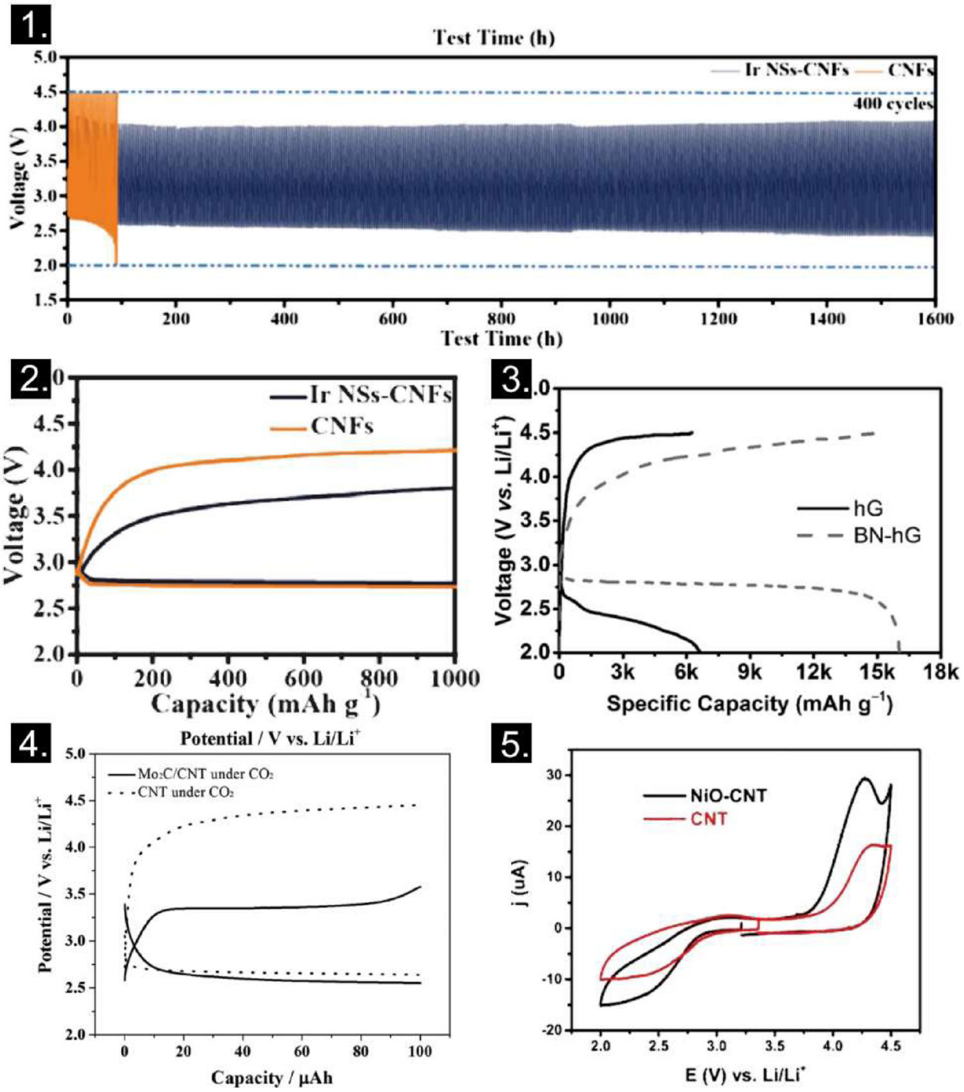

Fig. 9. The observation of catalytic effects. **1.** A higher cycle stability with added Ir nanosheets on N-doped carbon nanofibers in a Li-CO_2 cell implies a decrease in discharge product buildup. **2.** The significantly reduced charge potential with added Ir NSs-CNF cathode shows the catalyst's activity for Li_2CO_3 degradation. Reprinted in part with permission from [118]. Copyright 2018 Wiley-VCH. **3.** An increased discharge potential of a Li-CO_2 battery on a holey graphene cathode codoped with Boron and Nitrogen shows a higher activity for Li_2CO_3 formation. Reprinted in part with permission from [33]. Copyright 2017 Wiley-VCH. **4.** A decreased charge voltage in a Li-CO_2 cell with Mo-doped CNT cathode shows the catalyst's effectiveness for Li_2CO_3 degradation. Reprinted in part with permission from [9]. Copyright 2017 Wiley-VCH. **5.** The increase of anodic current of a Li-CO_2 cell during CV with added NiO–CNT shows an increased effectiveness for Li_2CO_3 decomposition. Reprinted in part with permission from [82]. Copyright 2018 Royal Society of Chemistry.

Table 2

Summary of recent research on noble metal catalysts in metal-CO_2 batteries.

	Cathode / Anode	Current Density / Discharge Capacity	Coulombic Efficiency	Cycle Performance \ Conditions	Overpotential / Current Density	Ref.
Pd	3D Porous Pd / Zn	–	81.20%	100 cycles \ 0.56 mA cm^{-2}	0.19 V / 0.56 mA cm^{-2}	[77]
Ir	Ir/CNF / Li	50 mA g^{-1} / 21,528 mAh g^{-1}	93.10%	50 cycles \ 200 mAh g^{-1}	~1.4 V / 100 mAh g^{-1}	[45]
	Ir NSs-CNF / Li	166.7 mA g^{-1} / 7666.7 mAh g^{-1}	100%	400 cycles \ 500 mA g^{-1}	~0.8 V / 166.7 mA g^{-1}	[118]
Ru	Ru@Super P / Li	100 mA g-1 / 8229 mAh g^{-1}	86.20%	80 cycles \ 100 mA g^{-1}	~1 V / 100 mA g^{-1}	[83]
	RuO2/LDO / Li	100 mA g-1 / ~5500 mAh g^{-1}	–	60 cycles \ 166 mA g^{-1}	0.6 V / 166 mA g^{-1}	[90]
	Ru/CNT / Li	100 mA g-1 / ~23,102 mAh g^{-1}	71%	100 cycles \ 100 mA g^{-1}	1.39 V / 100 mA g^{-1}	[91]
	Ru/CNT / Na	100 mA g-1 / ~20,277 mAh g^{-1}	96.30%	100 cycles \ 100 mA g^{-1}	1.19 V / 100 mA g^{-1}	[91]
	Ru/KB / Li	10 A g-1 / 44,000 mAh g^{-1}	–	300 cycles \ 10 A g^{-1}	1 V / 1 A g^{-1} /	[119]
	Ru@KB / Li	100 mA g^{-1} / 11,537 mAh g^{-1}	94.10%	130 cycles \ 100 mA g^{-1}	~1.75 V / 100 mA g^{-1}	[53]
	Ru/ACNF / Li	100 mA g^{-1} / 11,495 mAh g^{-1}	93.20%	50 cycles \ 100 mA g^{-1}	1.43 V / 100 mA g^{-1}	[8]
	Ru/NC / Li	100 mA g^{-1} / 9300 mAh g^{-1}	–	140 cycles \ 100 mA g^{-1}	~1 V / 100 mA g^{-1}	[120]
	Ru-Cu-G / Li	400 mA g^{-1} / 13,590 mAh g^{-1}	96%	100 cycles \ 400 mA g^{-1}	~1.5 V / 400 mA g^{-1}	[121]

pared with cathodes containing either cobalt oxide or manganese oxide nanowires on carbon fiber, the cathodes with both kinds of nanowire were observed to lower the charge voltage and increase the discharge voltage.

Ma et al. in 2018 developed a porous Mn_2O_3 cathode for Li-CO_2 batteries. [127] The porous Mn was fabricated following a sol-gel method and mixed with ketjen black carbon and binder to fabricate the cathode. The catalyst was observed to not significantly increase the discharge capacity, but lowered the overpotential by ~0.39 V compared to a pure ketjen black cathode, which also significantly increased cycle stability.

Feng et al. in 2021 demonstrated a Li-CO_2 cell using a water-in-salt electrolyte and a molybdenum carbide catalyst. [98] The authors suggested that the WiSE is stable against the parasitic reactions common to organic electrolytes. Unlike many Li-CO_2 batteries, the main discharge product was observed to be lithium oxalate ($Li_2C_2O_4$). Using CO_2 consumption data, galvanostatic measurements and DFT simulation, the authors proposed that the molybdenum carbide catalyst cathode stabilized

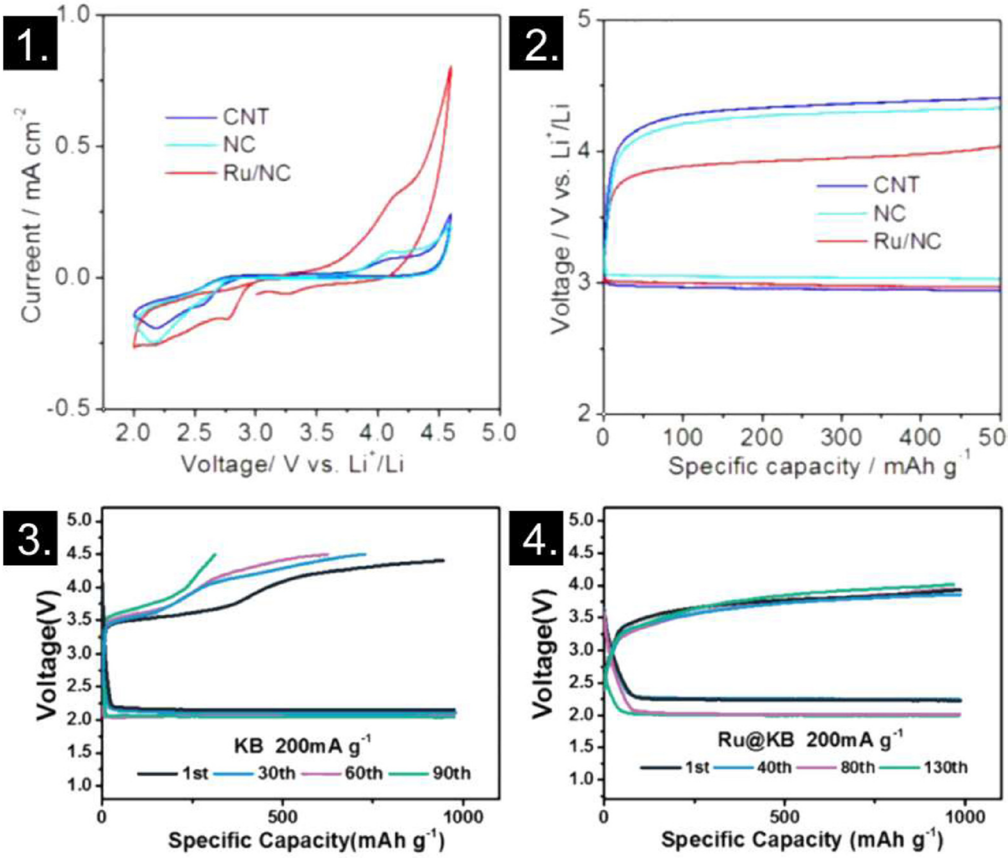

Fig. 10. Effects of Ruthenium catalysts on metal-CO_2 batteries. **1.** CV of Li-CO_2/O_2 carbon nanotube, nanoporous carbon, and nanoporous carbon/ruthenium cathodes. **2.** Charge/discharge profiles of Li-CO_2 cathodes under 4:1 CO_2:O_2 by volume. Reprinted in part with permission from [120]. Copyright 2019 Elsevier. **3, 4.** Cycling performance of Na-CO_2 batteries without and with ruthenium incorporated into a ketjen black cathode. Reprinted in part with permission from [53]. Copyright 2019 Royal Society of Chemistry.

Table 3
Summary of recent research of transition metal catalysts in metal-CO_2 batteries.

	Cathode / Anode	Current Density / Discharge Capacity	Coulombic Efficiency	Cycle Performance \ Conditions	Overpotential / Current Density	Ref.
Mn	MnO@NC-G / Li	50 mA g^{-1} / 25,021 mAh g^{-1}	95.20%	>200 cycles / 1000 mAh g^{-1}	0.88 V / 50 mA g^{-1}	[32]
	$CoMn_xO$@CF / Na	200 mA g^{-1} / 8448 mAh g^{-1}	80.20%	75 cycles / 500 mAh g^{-1}	1.77 V / 200 mA g^{-1}	[124]
	P-Mn_2O_3/KB / Li	50 mA g^{-1} / 1000 mAh g^{-1}	–	>50 cycles / 50 mA g^{-1}	1.40 V / 50 mA g^{-1}	[127]
	MnO_{2}_NCNT / Zn	–	–	50 cycles / 50 mA g^{-1}	~1.70 V / 50 mA g^{-1}	[122]
	MnO_2/CNT / Li	50 mA g^{-1} / 7134.1 mAh g^{-1}	100%	6 cycles / 100 mA g^{-1}	~1.40 V / 50 mA g^{-1}	[126]
Ni	Ni-N/P-O Graphene / Zn	–	–	–	2.11 V / 25 mA	[34]
	NiO–CNT / Li	100 mA g^{-1} / 9000 mAh g^{-1}	97.80%	42 cycles / 50 mA g^{-1}	~1.3 V / 50 mA g^{-1}	[84]
	$NiCo_2O_4$ / Li	400 mA g^{-1} / 22,000 mAh g^{-1}	–	140 cycles / 400 mAh g^{-1}	~0.9 V \ 400 mA g^{-1}	[38]
	Ni-NG / Li	100 mA g^{-1} / 17,625 mAh g^{-1}	55.6%	100 cycles / 100 mA g^{-1}	1.7 V / 100 mA g^{-1}	[96]
Co	Co/GO / Li	100 mA g^{-1} / 17,358 mAh g^{-1}	82.50%	100 cycles / 100 mA g^{-1}	~1.30 V / 100 mA g^{-1}	[35]
Zn	LiET-Zn / Li	–	–	–	0.95 V / ~23 mA cm^{-2}	[125]
Mo	Mo_2C/CNT / Li	20 mA / 1150 uAh	29.30%	40 cycles / 20 uA	~1 V / 20 uA	[9]
	Mo_2C/CNT / Li	–	79.00%	100 cycles / 100 mA g^{-1}	0.61 V / 100 mA g^{-1}	[98]
Ti	TiO_2/CC / Li	–	97.90%	30 cycles / 0.01 mAh cm^{-2}	~0.08 V / 0.01 mAh cm^{-2}	[128]
	$Ti_3C_2T_x$/CNT / Li	–	96.80%	40 cycles / 200 mAh g^{-1}	1.8 V / 200 mAh g^{-1}	[129]

the lithium oxalate product through an increased interaction strength compared to bare CNT cathode, where $Li_2C_2O_4$ would degrade into lithium carbonate and carbon.

6.3. Homogeneous catalysts

Most catalytic research for metal-CO_2 batteries considers heterogenous catalysts, which are bound to the cathode surface. Recently, research in homogeneous catalysts that dissolve in the electrolyte has gained traction, particularly in Li-CO_2 batteries. Homogeneous catalysts will not be overly discussed here, as they have not been demonstrated in non- Li-CO_2 battery electrochemistries. As these homogeneous catalysts and redox mediators tend to be selected for their activity against carbon dioxide, a brief summary of the homogeneous catalysts is still included in this review.

A homogeneous catalyst has more restrictions than a heterogeneous catalyst. A homogeneous catalyst should be resilient to parasitic reactions with the battery components, products, and parasitic products from side reactions. A homogeneous catalyst should have a reversible redox reaction at a higher potential compared to carbon dioxide. A homogeneous catalyst should also be soluble in the electrolyte. Some catalysts are researched for their general function known as the redox me-

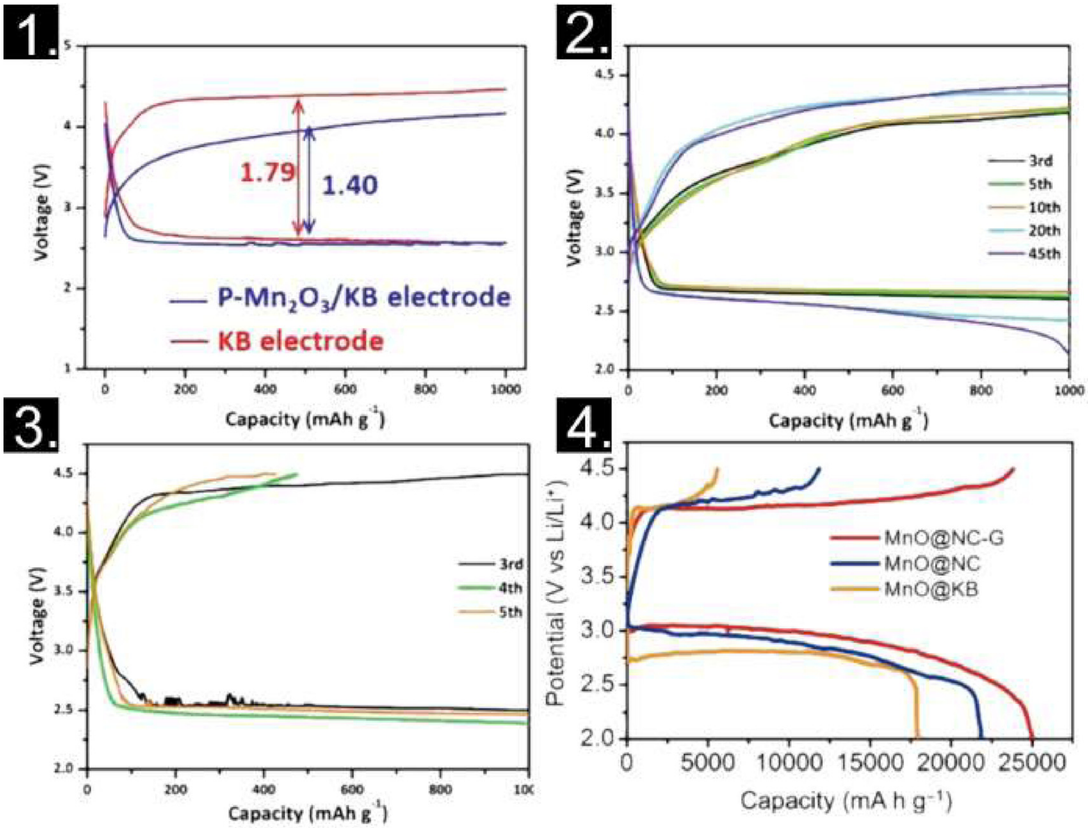

Fig. 11. Performance of manganese oxide catalysts. **1.** Second-cycle discharge/charge profiles of Li-CO_2 cells with and without added porous Mn_2O_3 catalyst. **2, 3.** Discharge/charge profiles of Li-CO_2 cells with and without porous Mn_2O_3 catalyst, respectively. Reprinted in part with permission from [127]. Copyright 2018 Royal Society of Chemistry. **4.** Discharge/charge profiles of Li-CO_2 cell cathodes containing MnO alongside ketjen black (MnO@KB), N-doped carbon framework (MnO@NC), and an N-doped carbon framework with 2D graphene support (MnO@NC-G). Reprinted in part with permission from [32]. Copyright 2019 Royal Society of Chemistry.

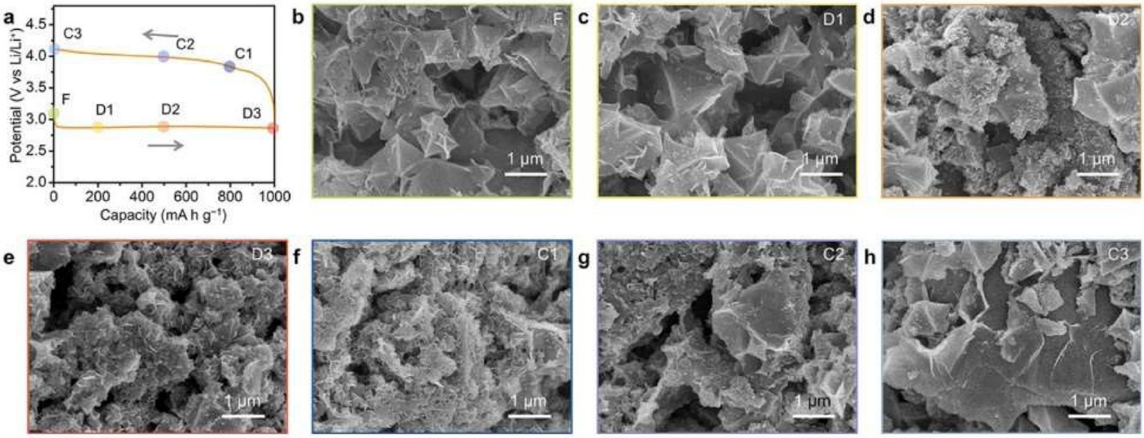

Fig. 12. Discharge/charge voltage profile and SEM images of a MnO- and N-doped interconnected graphene cathode in a Li-CO_2 battery. Reproduced with permission from [32]. Copyright 2019 Royal Society of Chemistry.

diators, for example bromine and iodine. [130–132] Other catalysts are researched due to their specific activity against carbon dioxide species, such as quinones and phenyl disulfide. [133, 134] In the case of these CO_2 specific redox mediators, the researchers proposed a reaction mechanism for the involved homogeneous catalytic species. While the initial results from these investigations are quite promising, it is apparent that further research in understanding the mechanism behind homogeneous catalysts is required for their successful application to metal-CO_2 electrochemistry.

Most research does not consider the role a catalyst plays in the discharge and charge mechanisms of an electrochemical cell. In several cases added catalysts have appeared to lower the activation energy of an alternate reaction pathway. For example, producing carbon monoxide over carbon during discharge of an Li-CO_2 cell, which stands as the most definitive evidence of the catalytic activity by altering the reaction pathway. [83] Researchers generally report the explicit evidence of catalytic effects, but do not confirm whether the catalyst is involved in the electrochemical mechanism and is subsequently regenerated. This is true for nitrogen-doped carbon cathodes as well, which are shown to improve the capacity and cycle stability. In terms of metal dopants, while there is little direct observation that metal dopants behave catalytically, metal catalysts are common to increase the electrochemical performance of metal-CO_2 batteries.

The metal catalysts make up the bulk of research on the application of catalysts to metal-CO_2 batteries. However, the field of catalysis is quite broad, therefore it is not practical to include all catalytic elements and configurations in metal-CO_2 batteries. Investigation of electrochemical carbon dioxide reduction shows some common catalytically active materials that have not been explored for metal-CO_2 batteries. [16, 17] In this field, carbon dioxide reduction is frequently catalyzed by heteroatom-doped carbon nanostructures containing nitrogen, boron, or both. Nitrogen doping is quite typical in metal-CO_2 research, but a boron, nitrogen-codoped carbon has not yet been investigated in metal-CO_2 batteries. For metal catalysts, cobalt and cobalt oxide are quite commonly used to reduce carbon dioxide to carbon monoxide or formate. Other noble metals and metal oxides such as silver, nickel, and tin oxide have seen applications as catalysts in both electrochemical CO_2 reduction and metal-CO_2 batteries. Copper catalysts, particularly nanostructured heterometal catalysts containing copper, tin, and palladium, are common on electrochemical CO_2 reduction but rarely seen in metal-CO_2 battery research. [17] It is worth comparing the effects of common catalysts that have been applied in both electrochemical CO_2 reduction and metal-CO_2 batteries in order to rationally design catalysts for both applications.

7. The applications

Although promising, metal-CO_2 batteries still face several challenges for practical applications. Even the best performing metal-CO_2 batteries are still not comparable to state-of-the-art Li-ion batteries. The ion intercalation mechanism of Li-ion batteries allows for low dendrite growth and charging overpotentials, and the exaggerated impact these issues have on metal-CO_2 batteries must be addressed before the technology can be competitive against Li-ion batteries. Each metal-CO_2 battery also faces unique challenges, such as sensitivity to electrolyte impurities and active material volatility. If these challenges can be adequately addressed, we can predict specific applications for each metal-CO_2 battery.

7.1. Li/Na as energy storage, Al/Zn as CO_2 reduction

In a review of metal-CO_2 batteries covering different metal anodes including lithium, sodium, zinc, and aluminum, Xie et al. proposed that lithium-CO_2 and sodium-CO_2 batteries would best serve as energy storage for a renewable energy grid application. They argued that aluminum-CO_2 and zinc-CO_2 batteries would be better applied for carbon capture and the production of industrial feedstocks. [15] Li-CO_2 batteries are well suited to store energy due to their high capacity and power, though hindered by the cost and scarcity of the materials. Among the cheaper alternatives, sodium-CO_2, aluminum-CO_2, and magnesium-CO_2 batteries have the potential to provide comparable capacity and power at a lower price.

Zinc-CO_2 and magnesium-CO_2 batteries have the greatest potential for conversion of carbon dioxide to useful feedstocks due to the adoption of aqueous electrolytes. These two battery electrochemistries allow these batteries to take advantage of knowledge gained of electrochemical carbon reduction, which is typically done in aqueous electrolytes. Researchers use zinc-CO_2 batteries to demonstrate the effect of a given catalyst for CO_2 electrochemical reduction. [135] Furthermore, zinc-air batteries have by this point shown the most success at reversible cycling in atmospheric conditions. [69] Xie et al. identified aluminum-based batteries as suitable for ambient air conditions, though the low compatibility with water and current expensive electrolytes aluminum-based batteries use pose a challenge.

Potassium-CO_2 batteries are limited to a low specific capacity by the one-electron transfer process and high molecular weight. However, the comparable reaction potential furnishes this electrochemistry with a high discharge potential compared to the other lithium-CO_2 battery alternatives. The low cost and high potential make the potassium-CO_2 battery as a useful alternative to capacitive fast charging for electric vehicles.

7.2. High CO_2 environments

The proposed applications of the metal CO_2 batteries require batteries that are stable in ambient air environments. Though developing a stable metal-CO_2 cell that can be used in dry air conditions seems feasible, extending a battery's operating conditions to real-world variations in temperature and humidity pose another challenge. For a more approachable application of metal-CO_2 batteries, attention can be turned to environments with high CO_2 concentrations. Batteries operating in these conditions do not need to be as stable against oxygen, water, or other atmospheric pollutants. The surface of mars, for example, contains approximately 95% carbon dioxide. [136] A metal-CO_2 battery, likely lithium-based, could provide a high energy density and stable energy storage solution to power devices on the surface of Mars. Even on the earth, the concentration of CO_2 in the flue gas exhaust from a coal-fired power plant is typically 3–13% by volume. [137] By integrating metal-CO_2 batteries with the power plant to utilize CO_2 in the flue gas, one can expect the metal-CO_2 batteries to generate electricity from the flue gas during the on-peak times and to charge the batteries and concentrate CO_2 during the off-peak times. Developing carbon capture systems for use alongside CO_2-emitting infrastructure is important to reduce the inertial barrier that pre-existing CO_2 emission sources present against mitigating climate change. [138]

7.3. Pairing of metal-CO_2 and metal-O_2 for functional batteries

A metal-CO_2 cell that functions properly in the atmospheric environment will need to account for the presence of oxygen. It has been shown in lithium-air and aluminum-air batteries, the introduction of oxygen into a carbon dioxide cell electrochemistry significantly changes the discharge and charge mechanism. As the more reactive species involved in the battery, the electrochemical reduction has been shown to start with the oxygen. [12, 94] Similarly, a metal-oxygen cell functioning in atmosphere will need to deal with the presence of carbon dioxide. It is common to observe metal carbonates as the products of parasitic reactions between the electrolyte and carbon dioxide in metal-oxygen batteries. By routing oxygen and carbon dioxide into suitable metal-air batteries, a combined battery structure using both metal-carbon dioxide and metal-oxygen batteries could provide a high stability and high-capacity energy storage solution for a renewable energy supply network.

8. Conclusion and perspectives

Recent advancements in our understanding of metal-CO_2 chemistries have been substantial, but the fundamental understanding of the electrochemistry is still lacking. In Li-CO_2 batteries, the well accepted charge mechanism produces an excited oxygen species, yet the identity of this species has not been directly determined. Furthermore, while many strategies to handle the excited oxygen species and to prevent its parasitic reaction have been proposed, none of them have been convincingly demonstrated. Qiao et al. were able to observe oxygen evolution during charge at a high charge rate, but this observation has not been well addressed by subsequent research investigating this missing oxygen. [97] Lastly, the possibility of oxygen evolution in the cell causing Li-CO_2/O_2 electrochemistry has not been addressed. However, the understanding of Li-CO_2 battery electrochemistry is now progressed enough to plausibly allow the rational design of catalysts in Li-CO_2 batteries. [116]

Zinc-CO_2 batteries are the closest battery electrochemistry for commercial application due to its low volatility and toxicity. The main challenges of the Zinc-CO_2 batteries are to promote the charge reaction and hinder hydrogen evolution, and to exclude oxygen from the battery electrochemistry. To this purpose, an effective catalyst is required, but no essential modification of the battery electrochemistry is likely needed. Current efforts do not address the challenges of Zinc-CO_2 batteries adequately, but water-in-salt electrolytes together with already identified catalysts may prove sufficient.

Our understanding of sodium-CO_2 and potassium-CO_2 batteries is not adequate for the rational design of cost-effective catalysts to facilitate the electrochemical reactions in these batteries. The understanding of Li-CO_2 battery electrochemistry cannot be copied onto the heavier alkali metals, but these cheaper alternatives can be predicted to behave in similar ways. It has been observed that the discharge reaction product of all alkali-CO_2 batteries discharge is metal carbonates. However, there is a degree of complexity in the electrochemical mechanisms of Li-CO_2 batteries that is not observed in either sodium-CO_2 or potassium-CO_2 batteries.

Aluminum-CO_2 and magnesium-CO_2 batteries are even less understood than the alkali metal CO_2 batteries. While the discharge products have been identified in both battery chemistries, the characterization is still not sufficient. Al-CO_2 batteries have been identified to produce aluminum oxalate ($Al_2(C_2O_4)_3$) and aluminum carbonate ($Al_2(CO_3)_3$) as the discharge products, while Mg-CO_2 batteries have been observed to produce magnesium bicarbonate ($Mg(HCO_3)_2$). However, aluminum carbonate is an almost entirely uncharacterized material. It is also understood that magnesium bicarbonate will spontaneously decompose if removed from an aqueous solution. [139] Since the discharge products in the aluminum-CO_2 and magnesium-CO_2 batteries were observed to deposit on the battery cathode, more information is needed before these discharge products can be fully characterized.

The application of electrocatalysis and other surface modification has shown excellent results to apply dopants to improve the cell lifetime in various metal-CO_2 battery electrochemistries. However, the understanding of the effects of catalysts is not sufficient. Noble metal catalysts are limited by the high cost and low availability of the materials. The identification of the role of a transition metal catalyst plays in the electrochemistry of the metal-CO_2 battery can be used to rationally design cathode materials.

Despite these challenges, current research toward practical metal-CO_2 batteries is quite promising. The fundamental issues in metal-CO_2 batteries include the stability of metal carbonates, the stability of electrolytes the interphases, and dendrite growth. The catalytic effects on metal carbonate degradation have been highly studied, where carbon nanostructures co-doped with nitrogen and a metal or metal oxide catalyst show good results as cheap catalytic cathodes. Applications of in situ spectroscopies to investigate discharge mechanisms in lithium-CO_2 batteries has provided good insight into the electrolyte's behavior. DEMS during charge and discharge has also provided excellent insight into lithium-CO_2 batteries. These methods can provide the standard for the investigation of electrochemical reaction mechanisms in other metal-CO_2 battery chemistries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

C.F. wrote the original draft, revised, and edited the manuscript. **C.C.** revised and edited the manuscript. **X-D. Z.** conceptualized and supervised the project. **S.W.** conceptualized, supervised the project and revised the manuscript.

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