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## EDITED BY

Sheng S. Zhang,  
United States Army Research Laboratory,  
United States

## REVIEWED BY

Xijun Liu,  
Guangxi University, China

## \*CORRESPONDENCE

Wonbong Choi,  
✉ Wonbong.choi@unt.edu

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# Lithium-CO<sub>2</sub> batteries and beyond

Anil D. Pathak<sup>1</sup>, Pashupati R. Adhikari<sup>2</sup> and Wonbong Choi<sup>1,2\*</sup>

<sup>1</sup>Department of Materials Science and Engineering, University of North Texas, Denton, TX, United States,

<sup>2</sup>Department of Mechanical Engineering, University of North Texas, Denton, TX, United States

Li-CO<sub>2</sub> batteries with a theoretical energy density of 1,876 Wh kg<sup>-1</sup> are attractive as a promising energy storage strategy and as an effective way to reduce greenhouse gas emissions by CO<sub>2</sub> reduction and the formation of discharge product Li<sub>2</sub>CO<sub>3</sub> and carbon. This article provides critical perspectives on the development of Li-CO<sub>2</sub> batteries as well as a description of current issues and challenges associated with cathode catalysts, electrolyte, and anode for Li-CO<sub>2</sub> batteries. Furthermore, the development and deployment of materials to overcome these challenges of Li-CO<sub>2</sub> batteries are discussed briefly. Finally, a systematic analysis of beyond Li-CO<sub>2</sub> batteries (other Metal-CO<sub>2</sub> batteries) as a potential research direction in the development of energy storage and CO<sub>2</sub> fixation and utilization in practical applications is provided.

## KEYWORDS

Li-CO<sub>2</sub> batteries, Li-O<sub>2</sub> batteries, metal-CO<sub>2</sub> batteries, CO<sub>2</sub> fixation, greenhouse emission

## 1 Introduction

Climate change is a global phenomenon that must be addressed to avoid major environmental consequences due to the non-renewable property of fossil fuels and excessive CO<sub>2</sub> emissions in the near future (Krane, 2017; Abbass et al., 2022). Even though significant progress has been made toward clean energy initiatives to mitigate the major cause of climate change, excessive greenhouse gas emission and usage of non-renewable fossil fuel still remain the dominant sources of climate crisis (Lelieveld et al., 2019). Among others, carbon dioxide (CO<sub>2</sub>), one of the leading greenhouse gases that arises from the use of fossil fuel, is accelerating climate change and likely will lead to global warming and endanger the sustainability of the planet Earth and its habitants. One way of preventing the emissions of CO<sub>2</sub> into the atmosphere is its capture, fix, storage and transportation in its liquid form, which requires further compression or liquefaction procedures. Such an approach could be highly costly, and the processes add higher energy consumption and hence unwanted additional greenhouse gas emission. To slow down the emission, to some extent, CO<sub>2</sub> could be used effectively in other energy forms by using metal-CO<sub>2</sub> batteries such as Li-CO<sub>2</sub> (Sun X. et al., 2021) and Zn-CO<sub>2</sub> (Xie and Wang, 2019; Wang et al., 2020; Hao et al., 2021; Yang et al., 2022a; Liu S. et al., 2022; Liu W. et al., 2022). In parallel, ultra-high energy density (11,680 Wh kg<sup>-1</sup>) metal-air batteries are also considered promising battery technology which is environmentally friendly (Cao et al., 2021) and utilized unlimited source of oxygen present in atmosphere. Metal-air batteries include primarily oxygen as air, and have received tremendous research interest in recent years (Li and Lu, 2017; Yang et al., 2022b; Zhang et al., 2014). A typical metal-air battery consists of an external cathode of oxygen (O<sub>2</sub>) present in the ambient air, aqueous or aprotic electrolyte, and metal anode.

Several Li-air batteries have been evolved over the years, employing lithium as an anode and O<sub>2</sub> or other gases as cathode including CO<sub>2</sub> (Li and Lu, 2017; Tang et al., 2022; Zhao et al., 2021; Zhang et al., 2021a) Among these batteries, Li-CO<sub>2</sub> batteries are of particular interest (Figure 1A) due to their high discharging voltage (~2.8 V) and very high theoretical

specific energy density (1,876 Wh kg<sup>-1</sup>). Also, Li-CO<sub>2</sub> electrochemistry can be a good strategy for CO<sub>2</sub> fixation by (Qiao et al., 2017) reduction of CO<sub>2</sub> and formation of Li<sub>2</sub>CO<sub>3</sub> and carbon *via* single step reaction. Thus, the Li-CO<sub>2</sub> batteries not only contribute to next-generation initiatives toward clean and sustainable energy but also relieve the detrimental impact of CO<sub>2</sub> on the environment. This mini review provides the state-of-the-art Li-CO<sub>2</sub> battery technology in comparing Li-O<sub>2</sub> batteries with their challenges and potential strategies to overcome the challenges. Furthermore, particular attention is devoted to the perspective and feasibility of the Li-CO<sub>2</sub> battery system in space applications such as Mars mission.

## 2 Li-CO<sub>2</sub> battery as a potential energy storage system

Li-ion batteries have dominated the portable electronics and electric vehicle market ever since their commercialization in 1991 (Ji and Nazar, 2010; Li et al., 2009; El Kharbachi et al., 2020; Mahmud et al., 2022). With the realization that Li-ion batteries have reached their practical limits (energy densities of 240–250 Wh kg<sup>-1</sup> and 550–600 Wh l<sup>-1</sup> (Cao et al., 2020), alternative battery systems with much higher energy storage capabilities need to be sought. Li-air batteries, the promising candidates for beyond Li-ion chemistry with high energy density have attracted much attention in recent years (Wang L. et al., 2018; Xiao et al., 2010; Huang et al., 2022; Li W. et al., 2021). Li-air batteries can deliver an ultra-high energy density of 11,680 Wh kg<sup>-1</sup>, which puts the Li-air battery on higher ground as compared to other battery systems (Imanishi and Yamamoto, 2014). The electrochemical reaction involved in Li-O<sub>2</sub> battery is  $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ , with the forward direction as discharge (formation of Li<sub>2</sub>O<sub>2</sub>), and reverse direction as a charge with decomposition of Li<sub>2</sub>O<sub>2</sub> (Chang et al., 2017). Mostly, Li-air batteries that have been tested are operated under pure oxygen, which can be costly considering the O<sub>2</sub> purification process and the associated costs. In the ambient air, other gases such as nitrogen (N<sub>2</sub>), argon (Ar), carbon dioxide (CO<sub>2</sub>) and water moisture are present. The influence of these gases or air on the reaction mechanism and electrochemical performance of Li-air batteries remains questionable (Cai et al., 2018). The inert nature of Ar and N<sub>2</sub> gases and the relatively high cathode voltage of 3.0 V are not able to activate the electrochemical reactions of lithium with Ar and N<sub>2</sub> (Nam et al., 2001). Water moisture present in the air (H<sub>2</sub>O) and CO<sub>2</sub> are active gases, and are theoretically expected to be involved in electrochemical reactions in Li-air cells. Water moisture in the ambient air potentially deteriorates cell performance due to the corrosion of the Li metal anode (Shui et al., 2013). Therefore, because of such issues with various Li-air batteries (also described in (Figure 1B)), overall, the development of Li-air batteries is hindered, mainly by selective filtration of O<sub>2</sub> from the air and unwanted side reactions with other elements in the air, such as water vapor, and carbon dioxide, which leads to the large cell overpotential, limited reversibility, and poor cyclability (Liu T. et al., 2020).

On the other hand, Li-CO<sub>2</sub> batteries, a type of metal-CO<sub>2</sub> batteries, are attractive (Figure 1C) due to their dual functionality of utilizing CO<sub>2</sub> gas and electrical energy storage, while demonstrating a high theoretical energy density (1,876 Wh kg<sup>-1</sup>;

Cai et al., 2018). However, the Li-CO<sub>2</sub> battery is an open cell configuration (Figure 1D), with Li metal anode, organic electrolyte and CO<sub>2</sub> porous-carbon cathode. In Li-CO<sub>2</sub> battery chemistry, during discharge, Li undergoes a redox reaction and react with CO<sub>2</sub> with the formation of Li<sub>2</sub>CO<sub>3</sub> and solid carbon at the cathode structure ( $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ ); whereas during charge, reverse reaction proceeded with decomposition of Li<sub>2</sub>CO<sub>3</sub>. Here, Li-CO<sub>2</sub> could be an alternative for using the CO<sub>2</sub> present in the air (or use of industrial CO<sub>2</sub> emission) while simultaneously contributing to reduced greenhouse emissions (Figure 1D). The following sections in this work summarize the critical understanding of issues involving the cathode-catalyst, electrolyte, and anode and their strategies, all of which can help to accelerate the practical development of Li-CO<sub>2</sub> batteries.

## 3 Challenges and development of cathode for Li-CO<sub>2</sub> batteries

In general, Li-CO<sub>2</sub> battery cathodes should be porous, catalytically active and conducting in nature with wide electrochemical stability across the operating potential during charge and discharge. In most studies, porous carbon generally acts as the cathode material supporting the catalyst layer (e.g., Ru (Zhang P.-F. et al., 2020), Pt (Zhang et al., 2015), Au (Qiao et al., 2017), metal oxide (Liu L. et al., 2020), MoS<sub>2</sub> (Pipes et al., 2019), Mo<sub>2</sub>C (Yang et al., 2020)). However, the following critical challenges associated with the cathode-catalyst in the Li-CO<sub>2</sub> battery must be addressed; namely, i) sluggish CO<sub>2</sub> reduction reaction (CRR) and the CO<sub>2</sub> evolution reaction (CER), ii) complex three-phase (CO<sub>2</sub> gas-liquid electrolyte-solid cathode catalyst) interaction at electrode/electrolyte interface, iii) poor catalytic activity at electrode/electrolyte interface, iv) Li<sub>2</sub>CO<sub>3</sub> discharge product being insoluble in the organic electrolyte, electronically insulating in nature and thermodynamically more stable, v) Large overpotential during discharge and charge, vi) in sufficient ionic and electronic conductivity of cathode/catalyst structure, and vii) poor reversibility and low energy efficiency of catalytic-cathode structure.

Various electrocatalysts that have been explored to enhance the reaction kinetics and reversibility of the Li-CO<sub>2</sub> battery include carbon materials, transition metal, noble/precious metals, and organic frameworks and their compounds. The initial development of a Li-CO<sub>2</sub> battery used mainly commercial carbon-based material [Ketjen Black (KB), Super P] as cathode as well as catalyst (without adding additional catalyst elements). For example, Liu et al. (Liu et al., 2014) developed a KB cathode for rechargeable Li/CO<sub>2</sub>-O<sub>2</sub> and Li/CO<sub>2</sub> batteries having discharge specific capacities of 1,808 mA h g<sup>-1</sup> and 1,032 mA h g<sup>-1</sup>, respectively. However, the use of carbon nanomaterials [CNTs, Graphene, graphene oxide (r-GO)] is the good choice as a cathode structure due to its tunable morphology/porosity, electrical conductivity, high surface area and enhanced catalytic activity compared with conventional carbon materials. For instance, Zhang et al. (Zhang et al., 2015) first reported carbon nanotubes (CNTs) air cathodes with high electrical conductivity and porous three-dimensional networks for rechargeable Li-CO<sub>2</sub> batteries with an initial discharge capacity of 8,379 mAh g<sup>-1</sup>. Further, catalytic activity and electrochemical stability of carbon material can be

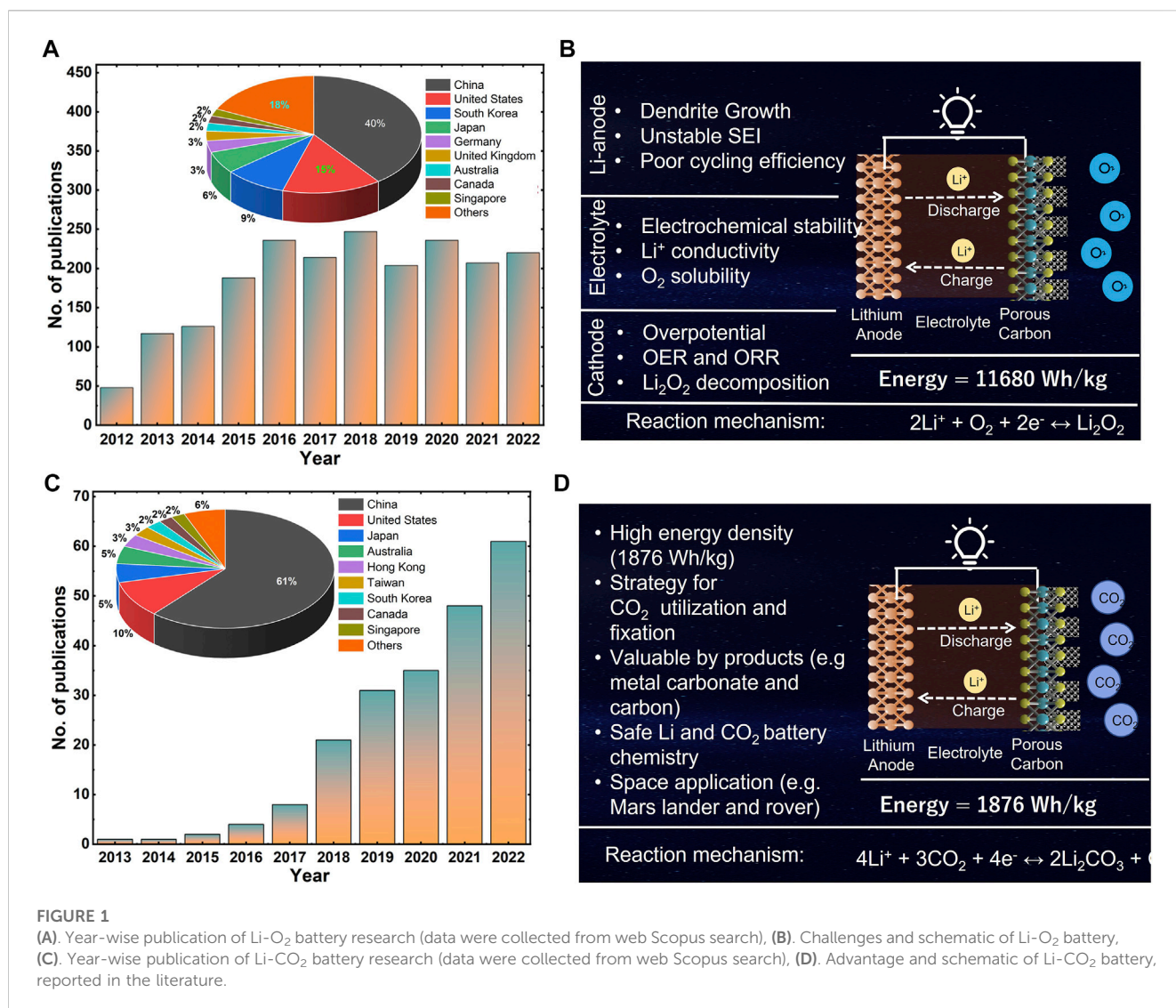


FIGURE 1

(A). Year-wise publication of Li-O<sub>2</sub> battery research (data were collected from web Scopus search), (B). Challenges and schematic of Li-O<sub>2</sub> battery, (C). Year-wise publication of Li-CO<sub>2</sub> battery research (data were collected from web Scopus search), (D). Advantage and schematic of Li-CO<sub>2</sub> battery, reported in the literature.

improved by adding defects in carbon structure such as voids, edges and doping heteroatoms. It has been observed that regulating the electronic structure and catalytic activity of pristine carbon material by heteroatoms doping is an effective strategy to improve the performance of Li-CO<sub>2</sub> batteries. Single-atom doping involves B, N, O, S, and F, (Zhou et al., 2022); however, N-doped carbon material has been used as an effective strategy in Li-CO<sub>2</sub> batteries (Jiao et al., 2021). In N-doping, electronegative N atoms placed near to a C atom alter the spin/charge density across the sp<sup>2</sup> carbon structure and thus improved adsorption energy (Zhang Z. et al., 2020) and enhanced electronic conductivity of the overall carbon structure (Yang et al., 2018). For example, N-doped carbon nanotubes as binder-free cathodes were utilized for high performance flexible quasi-solid-state Li-CO<sub>2</sub> batteries (Li X. et al., 2021). Here, N doping includes pyridinic, pyrrolic, quaternary nitrogen and pyridine-N-oxide structure, which provides low overpotential, good rate capability and high specific full discharge capacity, and long cycle life (1203 cycles). Furthermore, multiple atoms doping also enhances the overall catalytic, electronic conductivity and adsorption energy of

cathode structure. N, S-doped CNTs cathode catalyst can deliver a high discharge capacity of 23,560 mAh g<sup>-1</sup> for a quasi-solidus flexible Li-CO<sub>2</sub> battery (Song et al., 2020). Here, multi atom (e.g., N, S, Co, Ir) doping increases the defects to enhance the kinetics of the CO<sub>2</sub> fixing reaction with high adsorption of Li-ions and CO<sub>2</sub> gas molecules (Song et al., 2019; Rho et al., 2022).

Noble/precious metals are also a good choice as an effective electro-catalyst for Li-CO<sub>2</sub> battery applications due to their enhanced electrolytic properties, such as low over-potential, electrochemical stability against electrolyte, efficient CO<sub>2</sub> capture, and long-term durability over the operation. To the best of the author's knowledge, only three precious metals (Au, Ru, and Ir) have been explored as an electrocatalyst in the development of Li-CO<sub>2</sub> batteries. Ru metal has been observed to be an efficient electrocatalyst to improve the capacity and cycling stability by providing lower charging potential (3.6 V) compared to Au-based (>4.0 V) and Ir based (4.14 V) cathode (Qiao et al., 2017; Wang C. et al., 2018). The development of noble metal oxide (e.g., RuO), phosphides (e.g., RuP<sub>2</sub>) and their composite (IrO<sub>2</sub>/MnO<sub>2</sub>) is also an effective strategy to overcome electrocatalytic potential and

improve the CRR and CER of Li-CO<sub>2</sub> batteries. However, availability of the precious metal's precursors and their high processing cost can limit the usage of noble metals in large scale and commercial production of Li-CO<sub>2</sub> batteries.

Transition metals and their compounds are effective and alternative electro-catalysts due to their multivalent nature of transition metal, tunable property (morphology, shape, pore size) and availability of precursor and cost effectiveness. Transitional metal-based materials such as oxide, carbides, nitrides and sulfides have also been explored in Li-CO<sub>2</sub> battery systems, and have improved reversibility of CRR and CER.

For example, Ge et al. (Ge et al., 2019) developed a Co-doped MnO<sub>2</sub> catalyst for high-performance Li-CO<sub>2</sub> batteries with a high initial capacity of 8,160 mA h g<sup>-1</sup> (at 100 mA g<sup>-1</sup>). The Co<sub>0.2</sub>Mn<sub>0.8</sub>O<sub>2</sub>/carbon cathode delivered an ultralong cycle life of 500 cycles with low overpotential (~0.73 V). Yuyang Hou et al. (Hou et al., 2017) show the type of catalyst used for Li-CO<sub>2</sub> batteries can alter their discharge product. For example, they have used a Mo<sub>2</sub>C/carbon nanotube composite cathode which can stabilize Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> as a final discharge product over insulating Li<sub>2</sub>CO<sub>3</sub>. The Mo<sub>2</sub>C/carbon nanotube composite cathode catalyst can be effective at lowering the decomposition of the discharge product below 3.5 V on charge with high energy efficiency (77%). Transition Metal Dichalcogenides (TMDs) can also be crucial catalysts for Li-CO<sub>2</sub> batteries due to their mixed 1T (metallic) + 2H (semiconducting) phase (Wonbong et al., 2017; Bhojate et al., 2021), which can provide a good catalytic effect with electronic conductivity to the structure. Further, NiO, (Zhang et al., 2018), Mn<sub>2</sub>O<sub>3</sub> (Ma et al., 2018b), TiO<sub>2</sub> (Pipes et al., 2018), MoS<sub>2</sub> (Ahmadiparidari et al., 2019), and ZnS (H. Wang et al., 2019) have been explored as cathode catalyst for Li-CO<sub>2</sub> batteries. However, there are other materials that can be explored for efficient catalyst including single metal-based compounds (Fe, Co, Ni, Ti, Zn and Cu), and mixed metal compounds (FeCoW, NiCoOx, CoFeOx, LaMnO<sub>3</sub>; C. Liu et al., 2012; Sun Y. et al., 2021). Furthermore, potential transition metal based catalysts can be reviewed in literature (Franco et al., 2020; Azaiza-Dabbah et al., 2022; Lv et al., 2022).

Unique properties such as ultrahigh porosity, versatile functionalities, long-range order, tunable pore sizes, synthetic versatility, CO<sub>2</sub> capture, and controllable structures (Zhao et al., 2018; Baumann et al., 2019; Zhu et al., 2019) of covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) certify them as being potential catalyst for Li-CO<sub>2</sub> batteries. Wang and co-authors (Li et al., 2018) have explored for the first time eight porous MOFs (Mn<sub>2</sub>(dobdc), Co<sub>2</sub>(dobdc), Ni<sub>2</sub>(dobdc), Mn(bdc), Fe(bdc), Cu(bdc), Mn(C<sub>2</sub>H<sub>2</sub>N<sub>3</sub>)<sub>2</sub>, and Mn(HCOO)<sub>2</sub>) and two non-porous materials (MnCO<sub>3</sub> and MnO) for Li-CO<sub>2</sub> batteries. However, Mn<sub>2</sub>(dobdc) porous MOF delivered excellent discharge capacity of 18,022 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup> with a low charge potential of 3.96 V; whereas Meng et al. (Huang et al., 2019) for the first time reported the case of COFs as a catalyst for Li-CO<sub>2</sub> batteries. They developed Graphene@COF as a catalyst, which delivered a high discharge capacity of 27,833 mAh g<sup>-1</sup> at 75 mA g<sup>-1</sup>, with a low charge potential of 3.5 V. Xing Li et al. (Li et al., 2019) introduced a hydrazone/hydrazide-containing COF-Ru@CNT as a cathode catalyst which shows a high capacity of 27,348 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup> with an accelerated decomposition of discharge product (low overpotential of 1.24 V).

## 4 Challenges and development of electrolyte system for Li-CO<sub>2</sub> batteries

The efficient electrochemical performance of Li-CO<sub>2</sub> batteries requires appropriate electrolyte chemistries that should be compatible with other integral parts of the battery, particularly with the cathode-catalyst. Some challenges associated with the electrolyte system of Li-CO<sub>2</sub> batteries that need to be addressed include, i) interface stability with cathode catalyst during the cycle, ii) limited CO<sub>2</sub> diffusion and solubility, iii) self-decomposition under high voltage during charging, flammability, leakage, and evaporation of liquid electrolyte, iv) Li-ion conductivity and diffusivity (particularly for quasi and all solid-state electrolyte), and v) electrochemical stability against intermediates (particularly C and O based radicals) that form during reaction.

The majority of reports on Li-CO<sub>2</sub> batteries have relied on very limited electrolytes, either sulfones-based dimethyl sulfoxide (DMSO) or ethers based tetraethylene glycol dimethyl ether (TEGDME). DMSO solvent is promising because of its high CO<sub>2</sub> solubility, dielectric-strength, high conductivity, and low viscosity (Zhang et al., 2022; Zhao et al., 2019). However, DMSO solvent caused failure of the Li-CO<sub>2</sub> battery with lasting depletion *via* evaporation and side reactions (Lu et al., 2022); whereas TEGDME electrolyte was used in Li-CO<sub>2</sub> batteries due to its low evaporation loss, high oxidation potentials (>4.5 V vs. Li/Li<sup>+</sup>), high boiling point and stability against intermediates (Xu, 2004; Zhang et al., 2022). However, lithium trifluoromethanesulfonate (1 M LiCF<sub>3</sub>SO<sub>3</sub>) and lithium bis(trifluoromethanesulfonyl)imide (1 M LiTFSI) have been explored as promising salts for Li-CO<sub>2</sub> battery development. Quasi-solid electrolytes (gel polymer electrolyte (Li et al., 2017), composite polymer electrolyte (Hu et al., 2017a) and all solid state electrolytes (e.g., Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP); Guan et al., 2022), lithium aluminum titanium phosphate (LATP; Na et al., 2022) have also been explored for the development of Li-CO<sub>2</sub> batteries, and provide electrolyte stability, safety and a way forward to achieve high energy density.

## 5 Challenges and progress of lithium anode for Li-CO<sub>2</sub> batteries

Lithium metal anode is an important component to improve the performance of Li-CO<sub>2</sub> batteries.

Critical challenges that need to be considered for safe and high energy density Li-CO<sub>2</sub> batteries include, particularly, i) corrosion of Li-anode with CO<sub>2</sub> and formation insulating Li<sub>2</sub>CO<sub>3</sub> on surface, ii) stability of Li anode with organic electrolyte, iv) unstable solid electrolyte interface (SEI) on Li-anode and, v) unwanted and unsafe growth of Li dendrites.

Very limited work has been explored for the development of Li anode in Li-CO<sub>2</sub> battery application. However, Li corrosion due to reaction between diffused CO<sub>2</sub> gas (passed through electrolyte) and Li surface which forms Li<sub>2</sub>CO<sub>3</sub> as a corrosion product considered as critical issues of Li-CO<sub>2</sub> battery. Zhang et al. (Zhang et al., 2021b) constructed Li-ethylenediamine (LE) layer on a Li anode to overcome Li anode issues in a Li-CO<sub>2</sub> battery such as dendrite, side reaction, passivation/pulverization, and interfacial impedance. However, other approaches that can be adopted to overcome Li-

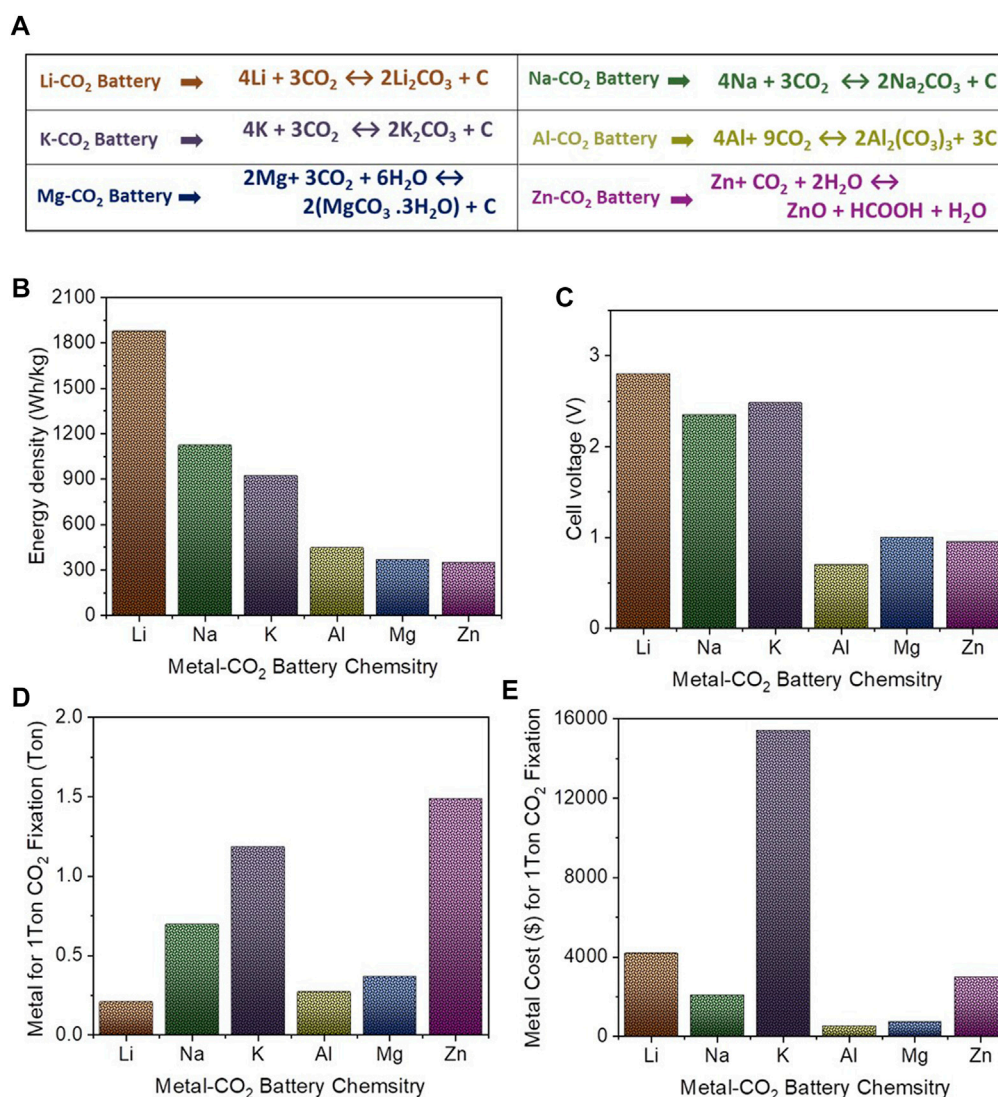


FIGURE 2

(A). Thermodynamic reaction of Li-CO<sub>2</sub> (Sun X. et al., 2021), Na-CO<sub>2</sub> (Hu et al., 2017b), K-CO<sub>2</sub> (Zhang W. et al., 2020), Al-CO<sub>2</sub> (Ma et al., 2018a), Mg-CO<sub>2</sub> (Zhang W. et al., 2020), and Zn-CO<sub>2</sub> (Xie et al., 2018), battery chemistries, (B). Comparative theoretical energy density of metal-CO<sub>2</sub> batteries, (C). Comparative discharge potential of metal-CO<sub>2</sub> batteries, (D). Comparative amount of metal anode required for 1 ton CO<sub>2</sub> fixation in metal-CO<sub>2</sub> batteries, (E). Comparative cost (\$) of metal anode required for 1 ton CO<sub>2</sub> fixation in metal-CO<sub>2</sub> batteries [unit cost of metal is taken from Ref (Chao et al., 2020)].

anode issues such as deploying artificial SEI (Yu et al., 2020), developing electrolyte additive (Li L. et al., 2021), and coating of protection layer (Cha et al., 2018).

## 6 Li-CO<sub>2</sub> battery application on Earth and Mars atmosphere

To consider the practical operation of Li-CO<sub>2</sub> batteries on Earth atmosphere, the source of pure CO<sub>2</sub> needs to be onboard/supplemented, particularly for electric vehicles (EVs) and grid applications. However, it is all about the economics and technical feasibility of extracting CO<sub>2</sub> from the Earth atmosphere to operate the Li-CO<sub>2</sub> battery in “CO<sub>2</sub> breathing mode”. D. W. Keith et al.

(Keith et al., 2018) provided a systematic cost analysis for capturing CO<sub>2</sub> (1 ton/year) from the atmosphere. Here, atmospheric air is directed through towers that contain potassium hydroxide (KOH) solution. As CO<sub>2</sub> contains air in contact with KOH, it forms potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). Further, K<sub>2</sub>CO<sub>3</sub> is heated with calcium carbonate (CaCO<sub>3</sub>), which releases CO<sub>2</sub> and is pressurized in a pipeline for underground storage. Capturing a ton of CO<sub>2</sub> has been calculated and analyzed potentially to cost about \$232, and can drop to below \$100 per ton. Here, instead of feeding the CO<sub>2</sub> collected gas and transporting it to ground, it is wise to use the strategy of metal-CO<sub>2</sub> battery for better utilization and provide alternative energy resource.

Beyond planet Earth, recently, with the accelerated Mars exploration from different countries, the possibility of a Li-CO<sub>2</sub>

battery in the Mars mission has been discussed heavily. According to National Aeronautics and Space Administration (NASA), Mars Perseverance carried Li-ion batteries that weighed 26.5 kg to power herself, which is a significant weight coming only from the battery. The batteries in Mars landers are used during descent, landing operations, and support during the initial deployments until the solar panels are in full operation. To make these missions more efficient and economically feasible, the vehicles should have batteries with higher specific energy density and lightweight, so as to help reduce overall mission cost and significantly increase payload. Some feasibility studies have been conducted at the research level on whether the Li-CO<sub>2</sub> battery system is suitable for Mars missions. Sharma et al. were the first to develop a working prototype of a Li-CO<sub>2</sub> battery operated at simulated Martian gases atmosphere (Pathak and Sharma, 2021), and confirmed the feasibility of Li-CO<sub>2</sub> battery operated in simulated Martian atmosphere consisting of 95% CO<sub>2</sub> gas. Further, Jiabin Li et al. (Li et al., 2020) developed 1,3-dioxolane-based electrolytes and iridium-based cathodes for ultra-low-temperature Li-CO<sub>2</sub> batteries which were operated at realistic temperature fluctuations of Mars atmosphere. Knowing the feasibility of Li-CO<sub>2</sub> battery in saturated air (100% humidity) and low-pressure (~6 mbar) conditions of Mars has been interesting. However, current efforts to the development of Li-CO<sub>2</sub> battery design for the Mars mission have the potential of reducing significant payload and cost of the overall mission spacecraft.

## 7 Beyond Li-CO<sub>2</sub> batteries

The theoretical energy density of metal-CO<sub>2</sub> batteries is calculated based on thermodynamic reaction as described in Figure 2A. Theoretical energy density and average discharge potential of metal-CO<sub>2</sub> systems (Figures 2B,C) provide a comparison of these parameters. Li-CO<sub>2</sub> batteries have great potential in terms of high specific energy density (1,876 Wh kg<sup>-1</sup>) with high discharge potential (-2.8 V) compared to other metal-CO<sub>2</sub> batteries such as Na-CO<sub>2</sub>, K-CO<sub>2</sub>, Al-CO<sub>2</sub>, Mg-CO<sub>2</sub>, and Zn-CO<sub>2</sub> batteries. Here, the energy density and potential of Mg-CO<sub>2</sub>, and Zn-CO<sub>2</sub> batteries are limited due to the use of an aqueous electrolyte which limits cell voltage greatly. Therefore, developing a non-aqueous electrolyte system for Mg-CO<sub>2</sub>, and Zn-CO<sub>2</sub> that can improve overall energy density and overcoming the issues of anode corrosion and hydrogen evolution is highly suggested.

Further, the amount of metal anode required for 1 ton CO<sub>2</sub> fixation was also calculated (based on thermodynamic reaction) and compared with the cost of metal anode (Figures 2C,D). In metal anode chemistry, Al-CO<sub>2</sub> batteries show comparatively good

potential that requires 0.27 tons of Al for fixing 1 ton of CO<sub>2</sub> at a cost of ~\$545 and that can produce energy density of 447 W h/kg. Also worth noting is that Al is a better choice when considering the availability and safety of alkali metals (e.g., Li, Na, K).

## 8 Summary

A Li-CO<sub>2</sub> battery system based on a CO<sub>2</sub> fixation and energy conversion mechanism can transform CO<sub>2</sub> gases into electrical energy directly without using additional electricity/energy input. The system can be sustainable in terms of continuous utilization of CO<sub>2</sub>, production of electricity and other valuable products (e.g., methane in case of Zn-CO<sub>2</sub> battery) in a CO<sub>2</sub> environment. A metal-CO<sub>2</sub> battery system can provide a competitive and cheaper technology for carbon capture and would open an industrial, scalable route for CO<sub>2</sub> fixation and electrical energy generation. For example, the Al-CO<sub>2</sub> system can capture 1 ton of CO<sub>2</sub> with usage of approximately 0.27 tons of aluminum at the low cost of ~\$545. Also, a Li-CO<sub>2</sub> battery system that can demonstrate high energy density seems to be a promising technology for energy storage for future Mars missions. Despite the advancements in development of Li-CO<sub>2</sub> batteries, strategies to maximize their energy density and cycle life for practical application are still in great demand.

## Author contributions

Writing, and original manuscript preparation: AP; writing, and review: PA; writing, editing and overall management: WC.

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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