

Electrochemistry of Metal-CO₂ Batteries: Principles and Applications

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Abstract. Overuse of non-renewable energy sources has raised fears about an energy deficit throughout the world. In addition, the burning of fossil fuels releases large quantities of greenhouse gases (mainly carbon dioxide (CO₂)) leading to serious environmental problems, particularly global warming. Metal-carbon dioxide batteries, which can capture and resourcefully utilize CO₂, are of great research significance. This article explores the importance of developing Metal-CO₂ batteries and their positive impact on the environment by introducing three Metal-CO₂ batteries. By describing the advantages that Metal-CO₂ batteries can offer in two locations, Earth and Mars, this article explores the prospects for their application in energy storage and transportation power. Among the three kinds of Metal-CO₂ batteries mentioned in this paper, Li-CO₂ batteries have high theoretical specific capacity, but the residual discharge product Li₂CO₃ will increase the polarization of the batteries by blocking the transport channels, which limits the cycle efficiency of the batteries. Na-CO₂ batteries perform electrochemically better than Li-CO₂ batteries, but the raw material Na is mainly prepared by electrolysis of molten sodium chloride or sodium hydroxide, which causes large energy consumption and environmental pollution. The raw material of Al-CO₂ battery is cheap and easy to obtain, but the specific power of the battery is low. All three types of batteries have the common problems of unclear reaction mechanisms and low charging and discharging efficiencies, and each faces different challenges that need to be investigated. This paper provides ideas for further research on Metal-CO₂ batteries, and we hope that Metal-CO₂ batteries can be really put into use in the future to alleviate the energy shortage and greenhouse effect to a certain extent.

Keywords: Global warming, energy storage, Metal-CO₂ batteries, electrochemistry.

1. Introduction

There are currently worries about an energy crisis all over the world due to the overabundance of non-renewable fossil fuels like coal, oil, and natural gas caused by the swift expansion of human society. Currently, the total annual energy consumption of human beings is 14 TW, which is expected to become triple by 2050 [1]. 83% of all energy is consumed through the use of fossil fuels, and the resulting CO₂ emissions have caused significant environmental issues like global warming. Atmospheric CO₂ levels have approached and exceeded 400 mg/L in recent years, and the resulting greenhouse effect has led to severe climate change. According to researchers at National Aeronautics and Space Administration (NASA) Goddard Institute for Space Studies, July 2003 was the warmest month on record since the agency began keeping statistics in 1880. Humanity must recognize that the vast amount of greenhouse gases emitted by the burning of fossil fuels has resulted in very catastrophic climate repercussions.

Given that energy sources are limited and utilizing fossil fuels harms the environment, there is a paradigm shift in the energy supply toward renewable energy-based sources including energy crops, sunlight, and wind. These renewable energy sources have substantial storage costs and are unreliable and highly intermittent. Therefore, resource-based conversion of CO₂ is an ideal approach to alleviate energy shortage. The carbon atom in CO₂, however, is in the state of oxidation with the maximum valence (+4). Direct conversion of CO₂ into other chemicals would cost a lot of energy and cause environmental pollution. Metal-CO₂ batteries are energy storage devices that use metals with negative electrode potentials, such as lithium, sodium, aluminum, and magnesium as the negative electrode, CO₂ as the positive active substance, and organic electrolyte as the electrolyte. Since Metal-CO₂ batteries can absorb and utilize CO₂, it is simple to discover that Metal-CO₂ batteries can not only cut

back on the usage of fossil fuels and lessen the impact of global warming, but they can also provide a sizable amount of electricity to meet people's daily energy needs.

This paper focuses on the environmental advantages of Metal-CO₂ batteries as well as the prospects for energy storage and transportation power in the future. First, the reaction mechanisms and advantages and disadvantages of three metal-carbon dioxide batteries are briefly introduced. Then, the great advantages that metal-carbon dioxide batteries can fulfill on Earth and Mars are elaborated. Finally, the solution ideas are given for the shortcomings of the current metal-carbon dioxide batteries.

2. Batteries and Reaction Mechanisms

2.1. Li-CO₂ Batteries

2.1.1. Primary Li-CO₂ batteries

Li-CO₂ batteries were the first Metal-CO₂ batteries to be developed. Takechi et al. [2] first suggested the idea of Li-CO₂ batteries in 2011 with a disposable Li-O₂/CO₂ battery. This groundbreaking discovery on Li-O₂/CO₂ batteries paved the path for further investigation of Li-CO₂ batteries and provided the world with a novel technique to capture CO₂ while also storing electricity. Then, as a new energy battery with great development prospect, Metal-CO₂ battery has been studied by more and more researchers.

The first pure CO₂ cathode lithium battery was introduced in 2013 by Archer et al. [3]. As the electrolyte, they used ionic liquid. The final discharge products of Li-CO₂ batteries are Li₂CO₃ and C, as given in equation (1), according to experimental data from differential electrochemical mass spectrometry and thermodynamic calculations. Based on this reversible process, Li-CO₂ batteries can theoretically provide energy densities as high as 1876 Wh/kg.



2.1.2. Rechargeable Li-CO₂ batteries

Li-CO₂ batteries typically include a catalytic positive electrode, a lithium metal negative electrode, and an electronically insulated diaphragm. When the battery is discharged, Li⁺ and e⁻ migrate from the negative electrode and flow through the electrolyte and external circuit to the positive electrode, where they combine with CO₂ to form Li₂CO₃ and C. The discharge capacity increases with the amount of Li⁺ that returns to the positive electrode. When the battery is charged, Li₂CO₃ and C are decomposed and Li⁺ and CO₂ are released at the positive electrode, and Li⁺ moves through the electrolyte to the negative electrode, where it is embedded in the micropores of the carbon, which has a layered structure at the negative electrode. The more Li⁺ is embedded, the higher the charging capacity. The total reaction process is shown in Fig. 1.

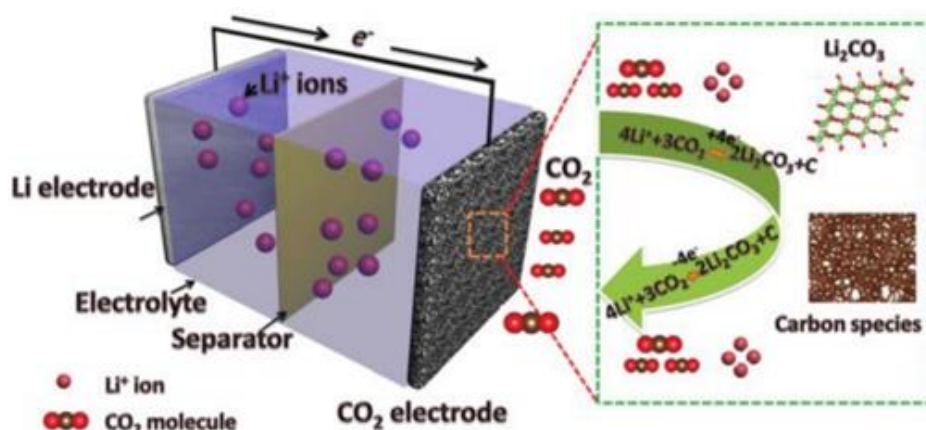
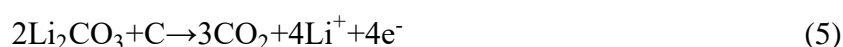
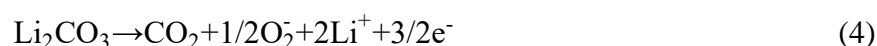
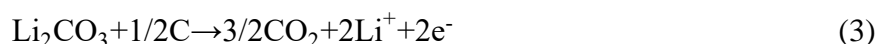


Figure 1. Schematic illustration of a reversible Li-CO₂ battery.

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It follows that the charging process of Li-CO₂ batteries involves the decomposition of Li₂CO₃ and C. That is, a Li-CO₂ cell is considered reversible if Li₂CO₃ and C can be completely decomposed, and rechargeable if Li₂CO₃ and C cannot be completely decomposed. Yang et al. [4] proposed three possible pathways for the electrochemical oxidation of Li₂CO₃ by analyzing the results of mass spectrometry and infrared spectroscopy as shown in equations (2)-(4). Li et al. [5] synthesized a novel catalyst by simple pyrolysis. They embedded ultrafine MnO nanoparticles into graphene interconnected nitrogen-doped carbon frameworks to realize a reversible Li-CO₂ battery. The reversible reaction mechanism is shown in equation (5).



If N-doped graphene with three-dimensional porous structure is used as the cathode material in Li-CO₂ batteries, the first discharge specific capacity can be as high as 17625 mAh/g. However, although studies have been conducted to synthesize effective catalysts to realize the reversibility of Li-CO₂ batteries, researchers have not yet reached a unified conclusion on the reversible reaction process of Li₂CO₃ and C. Also, the thermodynamic and kinetic properties of the battery are also still unclear. In addition, although Li-CO₂ batteries can be continuously cycled for 100 cycles at a current density of 100 mA/g, a controlled specific capacity of 1000 mAh/g, and a low overpotential. Li₂CO₃, on the other hand, is an insulating substance with great thermodynamic stability and moderate breakdown kinetics. A higher electrochemical decomposition potential is required to induce the decomposition of Li₂CO₃ during battery charging. The electrolyte may decompose as the charging voltage approaches 4.5 V, and the liquid electrolyte also suffers from leaking and flammability. At the same time, Li₂CO₃ often does not decompose completely, so residual Li₂CO₃ builds up on the electrode surface, blocking the transport channels for substances and exacerbating the cell polarization. The cycling efficiency of Li-CO₂ batteries is thus limited, and the overall performance is reduced. As a result, a better mechanism is required for Li-CO₂ batteries. To increase the energy efficiency,

scientists must discover more stable electrolytes and effective catalysts that can lower the overpotential of charging and discharging.

2.2. Na-CO₂ Batteries

Na-CO₂ batteries are more recent than Li-CO₂ batteries in terms of development, but they have stable high cycle times and safe charging voltages, good electrochemical properties, and high energy densities. Na-CO₂ batteries perform far better than Li-CO₂ batteries, and there is a lot of potential for further research. In 2014, Archer et al. [6] reported to the world for the first time that the Na-CO₂/O₂ battery. This battery was mainly positioned as a primary battery. Due to the different electrolytes used, it produces different discharge products.

In 2016, Chen et al. [7] introduced more advanced Na-CO₂ batteries that can be charged and discharged. Through experimentation, they found that there was a reversible generation and decomposition of Na₂CO₃ during the reaction of the Na-CO₂ batteries. They also employed an Ag nanowire cathode to confirm that carbon was present in the discharge products. Additionally, they measured and analyzed the escaping gases during the charging and discharging of the Na-CO₂ battery with the aid of a portable carbon dioxide analyzer equipped with a thermoelectric infrared detector, and they verified the reversibility of CO₂, confirming that the reversible reaction is as shown in equation (6).



Chen et al. [8] constructed Na-CO₂ batteries employing Super P/Al as anode and Na₂CO₃ and multi-walled carbon nanotubes as cathode to further examine the charging mechanism. They demonstrated the charging reaction of the Na-CO₂ batteries as shown in equation (7) using characterization tools such as in situ Raman and gas chromatography, with no side reactions occurring. The battery could cycle steadily for 200 cycles at a current density of 1000 mA/g, a reversible specific capacity of 60,000 mAh/g, and a regulated specific capacity of 2,000 mAh/g, all while maintaining a charging voltage of less than 3.7 V during operation.



Like all batteries, the electrolyte used in Na-CO₂ batteries suffers from a tendency to decompose at high potentials. As researchers continue to explore Na-CO₂ batteries, a semi-solid Na-CO₂ battery that is not easily combustible and has a stable electrolyte has been reported. With a current density of 500 mA/g and a controlled specific capacity of 1,000 mAh/g, the battery is capable of cycling 400 times. In particular, the amplified quasi-solid Na-CO₂ battery can discharge up to 1.1 Ah with a specific energy of 232 Wh/kg, and is capable of reversible cycling for 50 times. This kind of battery has a higher specific capacity and is safer than typical Na-CO₂ batteries.

It should be noted that the Na-CO₂ battery still has many problems to be solved before practical application. As with Li-CO₂ batteries, researchers have yet to agree on the principles of all the reactions within a Na-CO₂ battery when it is in operation and what is produced at each stage. During the operation of the battery, excessive Na is prone to form dendrites at the negative electrode, leading to short circuit of the battery, which is a potential safety hazard. At the same time, Na is primarily produced by electrolyzing molten sodium hydroxide or sodium chloride, which is an energy-intensive process that also pollutes the environment.

2.3. Al-CO₂ Batteries

Al makes up 8.3% of all the elements in the outermost layer of the earth and is the most prevalent metal there, coming in third behind silicon and oxygen. Compared with the two metals Li and Na, the use of Al has the advantages of low price, good safety and high specific energy (2980 Ah/kg). Although Al-CO₂ batteries were developed later, it has been studied that the electrochemical

performance of Al-CO₂ batteries with pure CO₂ as the cathode active material and Kochen black as the cathode conductive agent is poor. When a certain amount of O₂ was doped, the electrochemical performance of the battery was significantly improved.

Using 1-methyl-3-ethylimidazolium chloride/aluminum chloride as the electrolyte and O₂ as an auxiliary gas, Archer et al. [9] introduced an Al-CO₂ battery in 2016. They found that the principal discharge product of the system was identified as Al₂(C₂O₄)₃. Additionally, the specific capacity of discharge can be as high as 13 000 mAh/g under the condition of a current density of 70 mA/g, and the voltage of discharge can be controlled in the range of around 1.4 V. The total reaction is shown in equation (8).



Al-CO₂ batteries have a very high specific energy, with high economic value and application potential. However, the battery's general effectiveness must be increased, as the specific power of the battery is low and the charging and discharging speed is slow. In addition, Al-CO₂ batteries emit a large amount of heat during the reaction, so corresponding thermal management measures are needed to prevent the battery from overheating during operation. What's more, the reaction mechanism of Al-CO₂ batteries is not yet very clear, and Al-CO₂ batteries with pure CO₂ cathodes have not yet been studied.

3. Prospects for Metal-CO₂ Batteries

With the rapid progress of society and the continual innovation of science and technology, human beings' demand for energy is increasing, resulting in an oversupply of traditional energy sources. Furthermore, the use of fossil fuels results in significant emissions of CO₂-based greenhouse gases that worsen global warming and environmental degradation, a complex problem that now threatens human survival and is receiving a lot of attention from governments and researchers around the world. [10].

Metal-CO₂ batteries, which employ metal as the anode material and CO₂ as the cathode raw material, can not only catch CO₂ in the atmosphere, but also use CO₂ efficiently. In addition to creating useful compounds when the batteries are operating, they also turn CO₂ into electricity. To put it another way, the creation of metal-carbon dioxide batteries and their widespread use will give the world a new, effective way to store energy while reducing greenhouse gas emissions. Thanks to the efforts of people from all walks of life in the previous decade or so, the development and application of lithium-ion batteries have been a great success. Because of their lengthy longevity and great energy density, lithium-ion batteries have become the industry standard for electric vehicles. Currently, the energy density of power batteries for pure electric vehicles equipped with lithium-ion batteries is 250 Wh/kg. However, standard lithium-ion batteries with conventional intercalation chemistries have a maximum theoretical energy density of 300 Wh/kg, and even if lithium-ion battery technology were to be further developed so that the energy density of batteries could be increased by 30% from today's level to reach the theoretical value, it would still fall far short of the energy density needed for the pursuit of carbon neutral energy storage in the future. It can be seen that the current power battery system is still difficult to fully meet the stringent requirements of high energy and power density, low price, high security, extended life, no pollution and other aspects. Li-CO₂ battery theoretically has an energy density of up to 1876 Wh/kg, which is seven times higher than that of the traditional lithium-ion battery, and thus has a huge advantage in long-distance transportation [11]. In addition, due to the low price and good safety performance of metal Al, Al-CO₂ batteries also have great economic value and application potential in the field of transportation power.

It is reasonable to assume that Metal-CO₂ batteries are the best options to store energy for long-distance transportation since they produce sustainable power and have a wide range of applications in the power storage and transportation power sectors. Future power batteries made of Metal-CO₂ are

also advancing the growth of the electric car sector in a more cost-effective, sustainable, and green path.

It is also worth noting that Metal-CO₂ batteries can play a more unique role in the aerospace field. Compared with other planets, Mars is the most similar to earth. If humans colonize in the future, Mars is likely to be the preferred destination. The CO₂ content of the Martian atmosphere is as high as 95.3%. Metal-CO₂ batteries can capture a large amount of CO₂ from the Martian atmosphere as the raw material for battery work, convert CO₂ into electricity, provide energy for Mars rovers and research bases, and even provide energy support for future Martian immigrants. Currently, the International Space Station (ISS) relies mainly on lithium-ion batteries shipped from Earth, and transportation over such a long distance would consume a lot of energy and money. Therefore, it is necessary to research and develop energy storage devices that can be produced directly on Mars. However, there is very little metallic Li on Mars, and the production of Li-CO₂ batteries would be limited by the lack of raw materials. Mars, on the other hand, contains a certain amount of Na. As a high-energy density battery in development, Na-CO₂ batteries are predicted to creatively harness the plentiful CO₂ in the Martian atmosphere and become a new generation of space energy. Additionally, it is anticipated that exploration robots, medical devices, and portable wireless communication devices will all use rechargeable Metal-CO₂ batteries.

4. Conclusion

Increasing global warming and environmental degradation have become thorny issues that threaten the survival of mankind and have attracted great attention from governments and researchers around the world. Metal-CO₂ batteries can capture and resourcefully utilize atmospheric CO₂, and have good application prospects for energy storage and transportation electricity on Earth and Mars. This paper briefly summarizes the development history and research status of Metal-CO₂ batteries, and highlights the charging and discharging mechanisms, advantages and disadvantages of three Metal-CO₂ batteries. Li-CO₂ batteries stand out among three batteries for having a high theoretical specific capacity. However, Li₂CO₃ cannot be decomposed completely, and the residual material will block the transmission channel, thus limiting the cycling efficiency of the battery. Na-CO₂ batteries have a stable high number of cycles and a safe charging voltage, but the preparation of raw material Na for the batteries through the electrolysis of molten sodium chloride or sodium hydroxide generates a large amount of energy consumption and causes environmental pollution. Al-CO₂ batteries have high specific energy and the raw material Al is abundant in the earth's crust. However, the battery has the disadvantages of slow charging and discharging speed and low battery efficiency. All three batteries share the common problems of unclear reaction mechanisms and low cell efficiency. Only when the above problems are solved can Metal-CO₂ batteries be expected to be put into large-scale production and truly applied in the field of energy storage and transportation electricity. This paper provides ideas for understanding and further research on metal-carbon dioxide batteries.

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