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The development and prospect of lithium carbon dioxide battery

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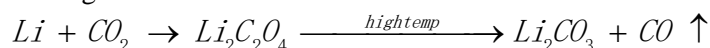
Abstract. With the rapid development of industry, the global warming is getting out of control. In order to figure out this urgent issue, energy scientists start to pay von on the mental carbon dioxide batteries. Among this kind of batteries, the lithium carbon dioxide battery is the relatively excellent. In this paper, we will focus on the momentous composing component of lithium carbon dioxide battery, like various electrolytes as well as anode and cathode materials. There are totally six sections in this paper, in the section 1 we will introduce the principle in the process of battery. Then, the topics of 2, 3, 4 orderly are the different properties of main component. At the last part, the application and prospects will be given. For the purpose of a better understanding, there is a brief comparison between the listed material in the end of each section.

1. Background

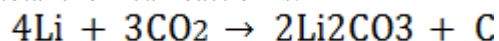
Human activities since the beginning of the Industrial Revolution (around 1750) have produced a 40% increase in the atmospheric concentration of carbon dioxide (CO₂), from 280 ppm in 1750 to 406 ppm in early 2017. [3] Carbon dioxide is not only the main greenhouse gases, but also is the significant carbon resources. Therefore, based on CCUS technology (the Carbon Capture, Utilization and Storage) as well as li-O₂ battery etc., the li-CO₂ battery continues to thrive with the target of Energy and Environment issues. [1][2] Like the li-O₂ battery, the li-CO₂ battery consists of the electrolyte, anode and materials, diaphragm and so on.

2. Mechanism

At first, Archer et al reported a primary Li-CO₂ battery which used pure carbon dioxide as cathode.[5]According to the chemical knowledge, Lithium metal can react with CO₂ to form lithium oxalate at room temperature. While at high temperatures, lithium oxalate decomposes to form lithium carbonate and carbon monoxide gas:



Based on the further measurement, the carbon monoxide wasn't the capital production of this reaction. Therefore, the total chemical reaction is:



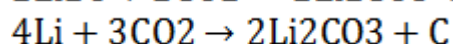
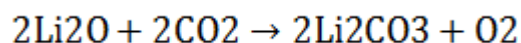
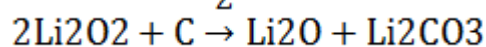
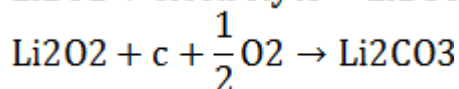
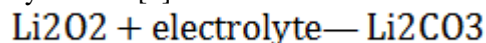
In order to make progress in the area of CO₂ capture and utilization, liu group developed rechargeable Li/CO₂-O₂ (2:1, volume ratio) batteries and even Li/CO₂ when lithium triflate (LiCF₃SO₃)-TEGDME is used as the electrolyte. In this research, Li₂CO₃ is the main product and can be decomposed reversibly. However, the reaction mechanism, thermo dynamic and kinetic properties are still not very clear. [6]

The accumulation of Li₂CO₃ during cycling will cause an increase in electrode impedance and lead to



a high overpotential during charging. [7][8] With the aim of solving the poor reversibility and low energy efficiency in the battery systems, Sixie Yang et al. reported the electrochemical decomposition mechanism of Li_2CO_3 by situ gas chromatography-mass spectrometry (GC-MS) measurements and an isotopic tracing method. In their report, the decomposition mechanism of Li_2CO_3 can be described as: Li_2CO_3 decomposes into CO_2 , superoxide radicals and O_2 (formed from the superoxide radicals). However, the O_2 and superoxide radicals fail to be detected, because they will react further with the tetraethylene glycol dimethyl ether electrolyte solvent. [9]

At present, these reactions are widely recognized with its in accordance with the laws of thermodynamics. [4]



In summary, the electrochemical reaction equation of Li- CO_2 battery has been basically determined, but the specific reaction mechanism remains to be explored. Meanwhile, the specific intermediate products and the types of partial pressure impurities still need to explore further.

2.1 Electrolyte

The development of electrolytes runs through the problems of electrolyte decomposition caused by CO_2 dissolution in Li- CO_2 batteries and superoxide generated by Li_2CO_3 , and corrosion caused by contact between Li anode and CO_2 . [12] [18]

In 2013, the Archer team first reported a primary Li- CO_2 battery using an ionic liquid electrolyte with a discharge capacity exceeding 2000 mah g⁻¹ at 60 °C. After this pioneering study, a rechargeable Li- CO_2 battery based on a lithium salt/tetraethylene glycol dimethyl ether liquid electrolyte was successfully developed. At a fixed capacity of 1000 mah g⁻¹, the battery showed only 7-20 discharge/charge cycles. Due to the high solubility of CO_2 in organic electrolyte solutions, the cycle performance of Li- CO_2 batteries is much lower than that of Li- O_2 batteries.

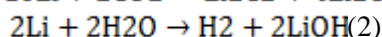
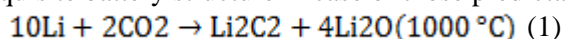
With the development of Li- CO_2 batteries, liquid electrolytes combined with porous carbon electrodes are widely used. Nevertheless, studies have confirmed that the discharge products are in an unstable state at a high charging potential. Both of two situations can cause decomposition of the electrolyte, resulting in low reversible capacity and short cycle life. In addition, liquid electrolytes lack a stable electrolyte/electrode structure, so it does not provide the required safety and flexibility. [12][18] Hu's team reported a quasi-solid polymer electrolyte (QPE) poly (vinylidene fluoride-co-hexafluoropropylene) - 4% SiO_2 / NaClO_4 -tetraethylene glycol dimethyl ether for Na- CO_2 batteries, energy density. However, the low ionic conductivity of the liquid-free electrolyte limits the cycle performance and reaction rate of the battery at room temperature. [18] Studies have suggested that the use of polymer electrolyte (PE) instead of liquid electrolyte. PE not only improves the safety of the battery, but also improves the battery's electricity. The course of events that the CO_2 dissolved in the chemical reaction can be limited to the PE/electrode surface is the main reason. In addition, PE can separate Li anode and CO_2 to avoid the occurrence of side reactions and to improve interface stability. Even so, PE as an electrolyte still has problems. Recently, a novel modified silyl-terminated polyether-based PE by a cross-linking manufacturing method has been proposed. The three-dimensional network of amorphous PE was found to have a high ionic conductivity of $3.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature, a stable electrochemical window of up to 5.0 V (vs. Li^+ / Li), and the electrode has excellent compatibility. [12] Similarly, the application of GPE in Li- CO_2 batteries was proposed by Li et al. A rechargeable Li- CO_2 battery with a CNT-based gas catalytic electrode is produced based on GPE. The discharge product has a particle shape with poor crystallinity, which promotes an improvement in

electrochemical performance. [19]

2.2. Anode

An anode is an electrode through which the conventional current enters into a polarized electrical device, at the same time, it will lose electrons because of an oxidation reaction.[10] Obviously, anode makes a significant impact on the capability of battery.

Compared with other battery, the anode of Li-CO₂ has its own character which is prone to react with water as well as carbon dioxide especially at high temperature. meanwhile, because of the ease of oxidizing, the anode even reacts with mid product and side product. Hence the scientists design the exquisite battery structure in case of those predictable bad consequences.



For the purpose of avoiding reaction (2) and (1), the majority li-air battery is layout to be waterproof and dry. There are two specific main methods which are widely adopted at present. The former measure is to adapt Organic electrolyte such as high dielectric medium of dimethyl sulfoxide (DMSO) in that organic electrolytes do not contain water and can properly consume CO₂. [11] While the latter way is employed Solid electrolyte, for example, the polymer electrolyte-based solid-state Li-CO₂ batteries because the PE can be applied on the anode to prevent it from CO₂ corrosion. [12] Definitely, the research on the anode of li-CO₂ is not so smooth. At first, Kensuke Takechi group researched and developed the original Li-CO₂ battery by li mental as anode. [13] However, with the consideration of safety, the Lithium embedded electrode was used to take place of Lithium mental. However, with the deepening of research, lithium shows excellent performance combing the corrosion resistant material.

Recently, the researches mainly focus on cathode material and electrolyte. Theoretically, the anode material still has some room to improve. Herein the scientists are supposed to pay attention on the anode to make breakthrough progress.

2.3. Cathode materials and catalyst

The evolution of the cathode material runs through the development of Li-CO₂ batteries, such as low discharge capacity, high charging voltage, difficult decomposition of the discharge product Li₂CO₃, and poverty reversibility. [15]

The Archer team first experimented with lithium-carbon dioxide batteries (without oxygen) and found that the battery can only display discharge capacity at high temperatures. Subsequently, Xu's team reported a new primary lithium carbon dioxide battery, which has a high discharge capacity of about 2500 mAhg⁻¹ at moderate temperatures, and a discharge capacity of 1000% higher at 40 °C than at 40 °C. For higher surface area carbon cathodes, the temperature dependence is significantly reduced. [15][17][23] For the first time, Zhang's team applied graphene as a cathode to lithium carbon dioxide. At a current density of 50 mA g⁻¹, the battery can provide a discharge capacity of up to 14774 mAhg⁻¹ and can perform 20 stable cycles. [21][22] However, as the current density increases, the discharge capacity of the cathode also decreases. Moreover, the discharge product Li₂CO₃ is difficult to decompose, and the cathode potential is raised, which brings problems such as poor reversibility and insufficient safety to the battery. [20][24] Therefore, current batteries are still operating at low current densities and high overvoltage conditions. However, it provides a direction for future research on cathode materials. Materials with excellent conductivity, porous structure and catalytic activity will be ideal cathode materials for lithium carbon dioxide batteries. [15][21][22]

For the problem of poor reversibility of the battery caused by the discharge product Li₂CO₃ being difficult to decompose during recharging, Zhang's team took the lead in applying high-conductivity and multi-space three-dimensional network carbon nanotubes (CNTs) to the air cathode of rechargeable lithium carbon dioxide batteries. At a current density of 100 mA g⁻¹, the battery can operate stably for more than 20 cycles with a cutoff capacity of 1000 mAhg⁻¹ and an initial discharge capacity of up to 8379 mAhg⁻¹. [17][22] The excellent electrical conductivity and three-dimensional network structure of CNTs not only facilitate the transmission of electrons in all directions, but also provide more space for

the deposition of discharge products. Therefore, the CNT cathode can improve the cycle performance of the lithium carbon dioxide battery and improve the battery performance. [14] Even so, the overpotential during charging was still very high, and after 20 cycles of the current density of 100 mA g⁻¹, it was observed that the limit charging voltage increased to over 4.5V. The high overpotential will undoubtedly lead to the decomposition of the electrolyte, affecting the cycle performance of the battery. [24] Carbon materials are widely used as cathodes in rechargeable Li-CO₂ batteries due to their good electrical conductivity, excellent porous structure, and large surface area. However, a pure carbon material acts as a cathode in a Li-CO₂ battery, and at a high charging potential, a superoxide radical generated by Li₂CO₃ will further oxidize the electrolyte solvent and cause decomposition of the electrolyte, thereby compromising the stability of the Li-CO₂ battery. [15][20][21] In order to improve the performance of Li-CO₂ batteries, humans began to explore more active catalysts. It has been reported that boron and carbon co-doped porous graphene have been introduced into Li-CO₂ batteries. The doping of heteroatoms improves the catalytic activity of graphene, resulting in a significant decrease in polarization, excellent rate performance, and excellent long-term cycle stability. [14][16]

It has been found that the addition of metal nanoparticles with high catalytic activity can limit side reactions and accelerate the reaction of Li₂CO₃ and C. In addition, the attachment of metal carbides or the surface modification of carbon materials can also lead to unexpected electrochemical performance. [15] Metal Ni has also been explored for use in Li-CO₂ cells, and highly dispersed Ni nanoparticles on graphene act as active sites in the reaction of Li with CO₂. [16] The battery exhibits excellent performance due to its excellent ability to capture reactants (CO₂ and Li).

With the emergence of various new cathode materials, Li-CO₂ battery capture technology has been developed, and the reversibility and efficiency of the battery have also been continuously achieved. Recently, some scientists have focused on the research of Li-CO₂ batteries, how to convert CO₂ into valuable by-products with high efficiency and high selectivity. Xie's team first used PF-Zn as a cathode in Li-CO₂ batteries to realize the first Li-CO₂ battery system with fuel gas CO as its main product. The CO generation can be easily adjusted by adjusting the discharge current over a wide range and achieves a Faraday efficiency of up to 67%. The selectivity of Zn as a catalyst for converting CO₂ to CO exceeds 70% and Zn has high porosity and high electrochemical active surface area. Therefore, the three-dimensional porous fractal Zn material has excellent electrocatalyst activity and selectivity for the reaction of electrochemical CO₂ reduction to CO. [14]

3. Exception and conclusion

With the requirement of energy-saving and environmental protection, li-CO₂ battery owns enormous potential as the technology to capture and vitalize carbon resource, although it just at the star stage. According to the least research worldwide, the material of battery anode and oxygen reduction catalyst has made great process, nevertheless, there are still quite a few obstacles to be solved, such as improvement on the cycle performance of the battery and reduction in the overvoltage of the battery charge and discharge.

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