Review paper

Evaluating the potential of the lithium-carbon dioxide battery to replace the lithium-ion battery

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Abstract
A recent advance in battery research has yielded the discovery of a lithium carbon-dioxide battery (Li-CO_2). These batteries capture CO_2 from the atmosphere to store and discharge energy. Li-CO_2 batteries are an attempt at providing a large-scale battery solution for energy storage. They have a greater energy density (7x that of existing lithium-ion battery (LIB), are safe (fewer short circuit problems) and environmentally friendly (reduced harmful greenhouse gas). However, to date, Li-CO_2 batteries have not yet been actively pursued due to a variety of technical challenges in their implementation: an excess buildup of carbon that ruins the battery after a few cycles of charge and discharge, net energy capacity loss with discharge cycles, no definite catalyst to speed up the reaction and research being performed under 100% CO_2 partial pressure. By reviewing the current state of Li-CO_2 battery, we compare its performance with LIB, and analyze possible advancements in the technology needed before it can become widely available. The goal of this review is to analyze the advantages and drawbacks of the current technological state of Li-CO_2 batteries in comparison with the leading technology of LIB, by a techno-economic comparison. Our key findings are that LIBs are currently safer, last longer, discharge more, and are also more economically favorable than Li-CO_2 in terms of durability, and cost. However, Li-CO_2 batteries are more environmentally friendly, have a greater energy density, making them useful in energy grid balancing, mitigating large voltage fluctuations and in high volume transportation. There are potential applications for both batteries, and we propose steps that the field could take in order to address the challenges we have identified, that stop Li-CO_2 batteries from being widely adopted.

Keywords
Chemical engineering, Sustainable energy, Sustainable batteries, Alternative power, Lithium ion battery, Lithium carbon dioxide battery, Li-CO_2 battery, Energy density, Electrolyte, Metal Organic Framework

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1. Introduction

The lithium-ion battery (LIB) is a rechargeable battery to store and discharge energy. Batteries exist all around us and provide a convenient way to access and store energy. The "age of the battery" was marked with the introduction of the LIB in 1990 (1). LIB is the leading battery technology, having matured in the last 30 years (2). LIBs are also the biggest component in the transportation industry evolution, reaching a global market of $20 billion (about $62 per person in the US) in 2016 (3). From 1996-2016 the industry grew by a staggering 16% each year, making it the highest growth segment of all industry investments (3).

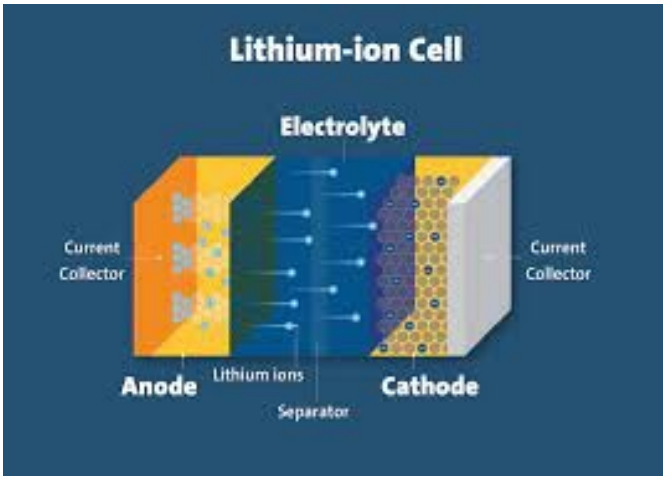

Figure 1: The current model of the LIB (4). During discharge Li metal is oxidized producing electrons and Li^+ ions, which both then combine with the Li metal oxide. During charge the exact opposite process occurs.

The LIB is made of 4 main components: the Li metal oxide cathode, graphite anode, organic electrolyte, and permeable separator (Figure 1, 4-6). The discharging phase of a LIB starts when lithium ions move from the negative anode to the positive cathode (5). This causes electrons to flow in the opposite direction, creating an electric current. When the battery is charged, the lithium ions move back to the cathode, and the electrons flow in the opposite direction (5). The electrolyte allows for the unimpeded movement of these ions and the separator physically keeps the cathode and anode from contacting each other (Figure 1, 4-5). The LIB reaction mechanism is as follows: Discharge: $Li(s) \rightarrow Li^+ + e^-$(Anode) and, CoO_2 (s) + Li^+ (aq) + $e^- \rightarrow LiCoO_2$ (s) (Cathode) (7). During the charge half reaction, this process is reversed, Charge: $Li^+ + e^-$ -> Li(s)(Cathode) and $LiCoO_2$ (s) $\rightarrow CoO_2$ (s) + Li^+ (aq) + e^- (Anode) (7). In this – and in most cases - the metal oxide is Lithium Cobalt Oxide (6). However, LIB's relatively low energy density is one of the major limitations in the field of transportation (more specifically electric vehicles (EV's)). Energy density is a measure of how much energy can be stored in a given battery size (typically (Wh/L) or (Wh/kg)). A

greater energy density improves efficiency because more energy can be stored and used in a smaller amount of space, which is essential in the transportation and EV industry (8). Targets from this industry indicate that energy density values for future battery technology list a short-term goal of 400 Wh/kg and a long-term goal of 600 Wh/kg. LIB's currently fall short of this target (9-11, Table 1). There is a need for an alternative battery to increase adoption of EV's. This sector is currently 3% of the U.S. GDP, has grown at a rapid rate since it became an industry in 2010; and is predicted to continue to grow exponentially (12).

Good performance from batteries is needed in the field of transportation, especially for electric vehicles (EV), because batteries in EV's need to be environmentally friendly, long-lasting, energy dense, and cost effective (13). The future of EV's will need a lighter battery, cheaper manufacturing costs, and a greater range (13). Lithium carbon-dioxide (Li-CO_2) batteries have attracted attention due to their very high theoretical energy densities (14), greater power outputs (14) with the ability to sequester CO_2 from the atmosphere to store and discharge energy (15-16).

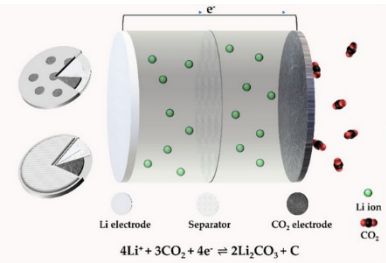

Figure 2. The structure of a Li–CO_2 battery.

Figure 2: The current model of the Li-CO_2 battery (16). During discharge, Li metal is oxidized, producing electrons and Li^+ ions, which combine with CO_2 to produce Li_2CO_3 and C. During charge, the decomposition of Li_2CO_3 and amorphous C occurs, to produce CO_2 and Li^+ ions.

Li-CO_2 batteries are composed of two electrodes: a positively charged lithium anode and a negatively charged porous carbon cathode (Figure 2, 16). This battery operates in the following way: in the discharge mode, CO_2 gas flows through the cathode and is reduced at catalyst sites *via* the half reaction ($3CO_2 + 2\ Li^+ + 2e^- \rightarrow 2Li_2CO_3 + C$) to the Li_2CO_3 species and Li is oxidized through the half reaction $2\ Li \rightarrow 2\ Li^+ + 2e^-$. (17) When the battery is charged, the reverse reactions occur, and CO_2 flows back out of the battery producing Li^+ ions (16-17). These are how the particular half reactions are derived for the cell, and combining these individual half reactions gives us our complete reaction mechanism: $3CO_2 + 4Li^+ + 4e^- \leftrightarrows 2Li_2CO_3 + C$ (16-17).

In this paper we compared Li-CO_2 with LIB on technical metrics of environmental friendliness, durability, reliability, and economics. For an economic comparison between these two

technologies, we estimated the current cost by using the energy density of the two batteries in $/kWh and also an annual battery cost for an accurate comparison. Section 5 will propose ideas on how to improve the maturity of Li-CO_2 technology and make it comparable or better than LIB in the not-too-distant future.

Metrics	Li-CO_2	LIB
Environmental (CO2 absorption kg/kg)	+ 907 (14, 21)	- 33 (19)
Durability (Peak Cycle Life)	~ 500 (21)	~ 1400 (22-23)
Energy Density (Wh/kg)	1876 (14, 33)	350 (22, 32)
Economic Comparison ($/kwh)	~ 58.6 (21, 47)	~ 50 (42-43)

Table 1: The performance of each battery (Li-CO_2 and LIB) in regard to performance + economic comparisons of CO_2 absorption, durability, energy density, and cost.

2. Performance Comparison

2.1 Environmental comparison

The first metric to compare Li-CO_2 with LIB is environmental impact. While implementing EV reduces transportation related emissions relative to gasoline vehicles, production and operation of EVs still produce significant carbon emissions (18); for example, a Tesla Model 3 releases 15,680 kg (about 16 tons) of CO_2 in the atmosphere while being manufactured (19). The typical weight of LIB in Tesla Model 3 is ~ 480.8 kg (20). In other words, for every kilogram of LIB, Tesla Model 3 manufacturing releases ~ 33 kg of CO_2 (Table 1).

LIB's and Li-CO_2 batteries have similar production and manufacturing emissions, however Li-CO_2 batteries curb their environmental impact by carbon neutral; i.e. by capturing CO_2 from the atmosphere (14, 17, 21). The environmental advantage of carbon capture is when the battery is cycled, the carbon-dioxide that is released during charging the battery can be captured and reused in the discharge cycle, preventing it from being released into the atmosphere (22) and being trapped as a greenhouse gas. We can specifically measure the amount of CO_2 captured by one battery by making two assumptions. First, we assume the life of this battery is 500 cycles (see 2.2) (22). Second, we assume the discharge potential of the battery is 2.8 volts (see 2.3) (14). We convert its theoretical energy density (see 2.3) to units in 3600 J/kg per cycle, which is also equal to transferring 2.4 x 10^6 coulombs/cycle kg of the battery. We then use Faraday's constant and the cathodic half reaction to convert this number to 2238 grams/cycle kg of battery.

Multiplying by Li-CO_2 cycle life, we conclude that the Li-CO_2 battery absorbs ~ 1 ton of CO_2 from the atmosphere per kg of battery, during its lifetime, equivalent to 907 kg (Table 1). Comparing this to the CO_2 release of the LIB during manufacturing a car, it shows the potential of the Li-CO_2 battery in curbing a significant amount of CO_2 being released into the atmosphere if used as an EV battery. This capability of CO_2 capture of the Li-CO_2 battery allows for use in unique applications, which we explore in 5.2.

2.2 Durability comparison

The durability of batteries is typically characterized by the battery's cycle life, which is the number of charge and discharge cycles a battery withstand without losing more than 20% of its initial capacity. A new LIB charges to a peak voltage of 4.2V, which is also consistent with each individual cell of an EV battery. After ~ 800 cycles the peak voltage that can be reached during charging is reduced to 3.7V. Below 80% of initial capacity (3.0V) (the battery becomes non-usable) after ~1400 cycles (23, 24, Table 1). In other words, the average cycle life for LIB is ~1000 cycles (2).

Currently, Li-CO_2 batteries have a maximum life of 500 cycles, with a specific MoS_2 catalyst (22). This is a nanoflake catalyst that has specifically been proven to optimize the cycle life of Li-CO_2 batteries (22, Table 1). The reason as to why the cycle is currently lower for Li-CO_2 batteries is because of the high solubility of CO_2 in organic electrolyte solutions (26). This causes a parasitic side reaction (14). In other words, The Li_2CO_3 generated by the lithium anode with electrons and CO_2 generates a byproduct of carbon, which collects at the cathode and reduces its useful life (27). The CO_2 decomposes quickly in the electrolyte solution producing C + O_2, and this excess and unwanted carbon clogs the cathode, damaging/breaking the cathode and/or reducing the effective surface area available for the chemical reactions, limiting the movement of the Li^+ ions to and from the anode, causing a poor cycle life (22, 28).

Li-CO_2 and LIB are similar in safety measures. Dendrite growth and formation of an unstable Solid Electrolyte Interphase layer (SEI) layer are two major concerns (14). The SEI layer is an important component of a rechargeable battery (14). This layer forms between the electrode surface and the electrolyte and acts as a barrier to prevent unwanted chemical reactions (29). However, eventually the barrier breaks down and these unwanted chemical reactions occur, reducing battery life and possibly inflicting thermal runaway, extremely elevated temperatures which could lead to fires, or a surge of electrical current, a process known as a short circuit where a battery could catch on fire or explode (29-31). Furthermore, unwanted metal may deposit on this SEI layer in both batteries, called dendrites, which could compromise the layer (31). Dendrites accumulate at the anode over time due to the continuous charge and discharge of the battery (29-31). They can be very dangerous and cause a short circuit. Dendrite challenges are greater in Li-CO_2 batteries because they contain pure lithium metal as the anode rather than a lithium metal oxide, which comprises the cathode of LIB. This design is akin to that of a Li-O_2 (Lithium Air) battery (32). A pure lithium

electrode has very prevalent intrinsic dendrite growth, and the most direct way to prevent it, is swapping it with a lithium metal alloy (32). Although a metal oxide is not a metal alloy, the act of fusing together two different atoms represents an electrode with the potential for greater stability and safety.

2.3 Energy density comparison

Energy density is the measure of the output of a battery based on relative size and is a determining factor for the future of battery technologies; an energy dense battery can produce/store multiple times more energy per unit weight. LIBs have a high discharge potential of 4.2 volts and can reach a maximum energy density of less than 350 Wh/kg. (Table 1, 23, 33). Li-CO_2 batteries have a relatively low discharge potential of 2.8 volts, but can reach a theoretical energy density of 1876 Wh/kg. (Table 1, 14, 34). When discharge potentials are compared, the LIB is more discharge efficient than the Li-CO_2 due to the chemistry of its system (35). A discharge potential below 3.0V is inefficient because not enough chemical energy is being converted to electrical energy (36). Li-CO_2 batteries have almost 7 times the theoretical energy density of LIB, allowing them to be used in a variety of applications; especially in electric vehicles. This is perhaps the biggest advantage of the Li-CO_2 battery. A 7x greater energy density compared with an LIB means that with a Li-CO_2 battery and LIB battery that produce the same energy, the battery of the Li-CO_2 will be 7 times lighter. This is especially valuable in the transportation industry. The gasoline used in gas powered cars currently has a practical energy density of 12,200 Wh/kg, significantly greater than the LIB of electric vehicles (26, 37). Using a Li-CO_2 cell in electric vehicles results in reduced weight and additional advantages of increased range and efficiency (38).

3. Economic Comparison

In spite of the last decade of battery improvements, batteries are needed that are not only durable, efficient, reliable, and environmentally friendly, but also cost-effective and accessible to buy and replace. We draw a comparison by evaluating current costs for LIB and Li-CO_2 batteries.

For manufacturing costs, the electrodes of the LIB and Li-CO2 batteries serve as valid comparators. The electrolyte and the separator of the batteries can be ignored because both batteries use a polyolefin polymer material as a separator, a plastic that is very porous, to prevent contact between anode and cathode and unwanted chemical reactions in the cell (39-40). Both the LIB and Li-CO_2 batteries use some form of a lithium salt-based electrolyte (17, 41). These costs are therefore comparable since the same material is used in both batteries.

Component	Weight	$/kg	$/kg Weight
Cathode (NCA)	51%	$25	$12.5
Anode (Graphite)	39%	$12	$4.7
Others	11%	$3	$0.3
Total Material Cost			$17.5/kg

Table 2. $/kg of LIB broken down by its components.

Artificial graphite is used as the anode in LIB. Graphite is relatively cheap due to its high abundance and has high energy density and very long cycle life (42). The graphite anode costs ~$12/kg (Table 2, 36, 41). A variety of cathode options exist for LIB, but the most common ones are: Lithium, Nickel-Cobalt-Aluminum Oxide (NCA) or a Layered Lithium Nickel Manganese Cobalt Oxide (NMC-111, NMC-442, NMC-532) (43). The typical cost for a NCA cathode is ~$25/kg (Table 2, 43). In terms of the total weight of the battery, the cathode accounts for ~50%, the anode accounts for ~39%, and any other material (mostly the casing) accounts for the remaining 11% (44). The total cost for LIB material cost is ~$17.5/kg (Table 2). Given that LIB can reach a maximum of 0.35 kWh/kg energy density, this translates to ~$50/kWh (=17.5/0.35), Table 1.

Component	Weight	$/kg	$/kg Weight
Cathode (Graphite)	41%	$12	$4.9
Anode (Li)	39%	$100	$39
Catalyst (MoS_2)	6%	$69	$11.04
Others	5%	$3	$0.15
Total Material Cost			$55.09/kg

Table 3. $/kg of Li-$CO_2$ broken down by its components

The Li-CO_2 batteries contain a carbon-based cathode, made up of carbon and other binder materials (14). The anode is pure lithium metal, and the cost is estimated ~$100/kg (Table 2, 45). The cost of graphite cathode in Li-CO_2 can be estimated using LIB as a proxy, to be ~$12/kg as presented in Table 2. The LIB and Li-CO_2 essentially have reversed materials for

anodes and cathodes, with the Li-CO_2 battery having a lithium-based anode and a graphite cathode. To power this reversed structure, a carbon supported cathode catalyst is needed to drive the reaction. Typical catalysts are usually carbon based for Li-CO_2 batteries (17). However, the longest recorded cycle life of the Li-CO_2 battery is with an MoS_2 nanoflake catalyst, hence the cost of this catalyst will be factored into the economic analysis (22). The Cost for the MoS_2 catalyst are predicted to be ~$69/kg (46, Table 3). We assume the catalyst to be 40% of the cathode cost in Li-CO_2.(Table 2, 47). The total material cost for Li-CO_2 is ~ $55/kg (Table 2). Given that Li-CO_2 can reach a maximum of 1.88 kWh/kg, this translates to ~$29.3/kWh (52/1.88). Li-$CO_2$ batteries hence have a lower cost per kWh compared to LIB, even though the technology is in its infancy.

Even though the cost in $/kWh of LIB's is more than that for Li-CO_2 batteries, an alternate way to compare the lifetime costs is to relate their costs to their respective lifetimes. This will more accurately determine if Li-CO_2 batteries are more economically favorable compared to LIB's. To do this, we simply multiply our Li-CO_2 battery cost by two, since the LIB is expected to last ~1000 cycles before peak voltage drops below 80% capacity (battery non-usable) (23), twice that of the 500 operational cycles of Li-CO_2 battery (22). The cost for LIB's hence stays the same at $50/kWh, but that for Li-$CO_2$ increases to ~$58.6/kWh (Table 1). Furthermore, the life cycle for the Li-CO_2 batteries was calculated based on operation under specific conditions; the real time operating conditions may make the cycle life even lower, making the Li-CO_2 battery even more costly (22, 48). Hence, LIB is more economically favorable when calculated over its cycle life.

4. Uses of Lithium ion batteries and Li-CO_2 batteries

4.1 Lithium ion batteries

Portable electronics do not necessarily need to be powered with batteries that possess staggeringly high energy density or efficiency. Rather, the batteries that power them need to be affordable. For this reason, LIBs currently seem to be the most feasible because their cost has been optimized to be as low as possible for everyday affordability. With their high discharge potentials, they also are extremely efficient at converting the chemical energy in the cell to usable work, so the LIB is the perfect choice for an electronic device.

Medical devices are also ideal for continued LIB use. For medical devices, cycling is a significant challenge. They need to function for as long as possible before their battery has to be replaced, as lives depend on it (42). For this reason, LIBs seem the more feasible choice. Li-CO_2 batteries are less than ideal for use in these applications. Using Li-CO_2 batteries with everyday electronics or medical devices is not feasible because; among other limitations; they need an additional source of CO_2 at a high enough partial pressure.

4.2 Li-CO_2 batteries

There are numerous advantages a Li-CO_2 battery can have on grid scale energy storage when compared with a LIB, ultimately making them more efficient than a LIB for this particular use (49). Their relatively high theoretical energy density of 7x compared with

that of LIB's implies that Li-CO_2 batteries are indispensable in power surges or crises where stored energy is needed (14, 37). Li-CO_2 batteries are also more environmentally friendly than LIB's, as they can be used for CO_2 capture and sequestration while providing energy (14, 17). It hence appears that they are more advantageous than LIB for use in electrical grid scale energy storage.

The high specific energy density of Li-CO_2 batteries means that more energy can be stored per unit of space (14). This is extremely beneficial in EV's, where batteries need to be as powerful as possible, but are also space constrained by the rest of the vehicle components (50). Heavy duty transportation requires high energy densities. Li-CO_2 could provide a means to electrify these heavy-duty sectors of transportation, such as trucks, planes, boats, etc. (51). Apart from this, the significant amount of CO_2 a Li-CO_2 battery can capture (1 ton/kg battery) during its lifetime translates to ~500 tons of CO_2 capture in an entire EV (assuming Li-CO_2 and LIB weigh the same in the EV) (20). This provides for a more environmentally friendly EV as well.

Li-CO_2 batteries have also generated interest for potential Mars exploration (40). Mars has an atmosphere of 96% CO_2 (52), hence harnessing this CO_2 into efficient, renewable energy could prove to be a worthwhile consideration. However, the average surface temperature on Mars is ~ -65 degrees Celsius, significantly colder than Earth's climate (53). This is a limitation to this CO_2 abundant environment due to the fact that as temperature decreases, electrolyte viscosity increases, thereby decreasing the rate of CO_2 utilization at the cathode (14). This significantly decreases the rate capability of the battery thereby hindering its deployment. This problem and its solutions are not discussed in depth in this paper because the Li-CO_2 battery yet has to be deployed for real world applications.

Li-CO_2 batteries are also a novel attempt at carbon capture from the earth (14-15). Since its CO_2 cathode functions entirely on the premise of capturing carbon from the atmosphere, the battery can be utilized specifically for this function (14). The cell operates according to the reaction $3CO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2CO_3 + C$ (17). Whilst taking in CO_2 from the atmosphere, it produces carbon which accumulates at the cathode along with Li_2CO_3 (54). This carbon sequestration could be especially useful in the exhaust stream of natural gas plants, coal plants, or other industrial processes which result in carbon emissions. Capturing carbon in the exhaust stream is a novel way Li-CO_2 could be implemented, decreasing the CO_2 release into the atmosphere which, in turn, reduces air pollution and makes harnessing energy more environmentally friendly.

Another unique use of Li-CO_2 is to clean waste streams. Typically, waste streams contain unharnessed energy called waste to waste energy (55). Current methods to harness this energy are incineration, combustion, gasification, pyrolization, and anaerobic digestion (55, 56). However, all of these processes neglect CO_2 waste discharging into the environment. Cleaning out waste streams by scrubbing CO_2 at the same time as creating

energy that could be used in other applications, like EV's, is a potential advantage of Li-CO_2 batteries.

5.Advancements needed for Li-CO_2 batteries

5.1 Feasibly of implementation

The reaction $3CO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2CO_3 + C$ in a Li-CO_2 cell has inferior reversibility (14). This is because the high bond energy of Li_2CO_3 (1000 kJ/mol and insolubility in most organic electrolytes impede the charge reaction. Hence, there is often excess carbon collected (27). Having a more reversible Li-CO_2 battery would lead to the longer life of the battery because there would not be deposition of carbon at the cathode, clogging the battery and limiting its cycling. A rate capability is how efficiently a battery can deliver discharge rates. Due to the Li-CO_2 battery's low energy efficiency and poor cycle stability (57) it is not able to discharge energy efficiently or with stability, rendering the battery less useful. Additionally, the lifetime analysis also concludes that the inferior cycling of the Li-CO_2 battery also decreases its economic value, a big obstacle in battery implementation. Catalysts are substances that can increase the rate of a chemical reaction without being consumed themselves, and they are important for improving the efficiency or speed of reaction in batteries. LIB's do not need a catalyst because their driving chemical reaction is spontaneous and fast, although adding a catalyst has been debated (58). However, Li-CO_2 batteries need a cost-efficiant catalyst because of the slow and inefficient reaction (34).

Other than an improved catalyst, cycle life in Li-CO_2 may be improved by increasing the partial pressure of CO_2, ($P_{(CO2)}$), during its charge cycle. In a battery with the same problems as the Li-CO_2 battery, the Na-CO_2 battery, studies have been conducted showing more successful cycles in an environment where there were higher partial pressures for CO_2 (59). For the Na-CO_2 battery, cycling issues were caused by the poor reversibility of the discharge product, Na_2CO_3 (60). This is also the same challenge with the Li-CO_2 battery, as its discharge product Li_2CO_3 also has inferior reversibility (14). Since a more concentrated CO_2 environment improved reversibility in the Na-CO_2 battery going from ambient air into a fully CO_2 lab environment, a more concentrated CO_2 environment is promising for Li-CO_2 batteries as it also has to overcome the same challenge (59). This could be achieved in two ways: either through charging stations that maintain a high $P_{(CO2)}$ in the battery while charging, or with a small tank of pure CO_2 attached to the battery. Instead of implementing charging stations, having a small CO_2 tank in/or attached to the battery faces lesser design challenges, especially in practical applications like EV's (see 5.2). Furthermore the infrastructure necessities and economic concerns from implementing high $P_{(CO2)}$ charging stations do not seem practically viable. Instead, a CO_2 tank with the battery seems to be a probable proposition.

Further, there exists a challenge of the polarization gap as a function of the number of cycles in current Li-CO_2 batteries which needs to be addressed for real world implementation (22). Though Li-CO_2 batteries are accredited to have discharge potentials of ~ 2.8V (at 100% CO_2 atmosphere under room conditions), this

does not hold true as the battery is cycled. The lowest polarization gap after the first cycle was recorded to be 0.7V (22). After the first 100 cycles this increased to ~1.45V, and after 200 cycles, could increase to between 1.7 and 2.45V, rendering the battery essentially unusable (22). This challenge presents itself because of the accumulation of Li_2CO_3 and C species at the cathode (the former of which does not decompose fast enough due to the inferior reversibility of the reaction) (61).

There are four possible reactions that can occur during battery discharge. Since only Li_2CO_3 and C are observed to be formed during the reaction, the discharge is presumed to occur by reaction 4.

$2Li + 2CO_2 \rightarrow Li_2CO_3 + CO,$	$\Delta G = -4.82$ eV	Equation 1
$2Li + CO_2 \rightarrow Li_2O + CO,$	$\Delta G = -2.22$ eV	Equation 2
$4Li + CO_2 \rightarrow 2Li_2O + C,$	$\Delta G = +1.91$ eV	Equation 3
$2Li + 3/2CO_2 \rightarrow Li_2CO_3 + C,$	$\Delta G = -1.33$ eV	Equation 4

Following the initial adsorption of CO_2 on the catalyst surface, $\Delta G = -1.58$ eV), the dissociative adsorption of a second CO_2 molecule is also favorable ($\Delta G = -0.60$ eV), which leads to the formation of a co-adsorbed carbonate (CO_3^{-2}) and carbon monoxide (CO). The CO desorption is unfavorable by 2.23 eV, consistent with the experimental result wherein CO is not detected as a gaseous byproduct. Adsorbed CO_3^{-2} is assumed to react with Li^+ ions in solution to form Li_2CO_3. The process by which the amorphous carbon forms is suggested as follows: a third CO_2 could react catalyst containing adsorbed CO to form a second CO_3^{-2} and a single carbon atom (C), even though the ΔG for such a process = + 0.94 eV. It is speculated that that this process becomes favorable in the presence of defect sites on the catalyst or carbon product, leading to amorphous carbon growth.

Since the discharge kinetics become unfavored due to C deposition, it is evident that if the desorption of CO from the catalyst were to be thermodynamically favorable, the downstream reaction on the catalyst containing defect sites; viz. $CO + CO_2 \rightarrow CO_3^{-2} + C$, would not occur. In this case, the effective discharge reaction would become Equation 1, yielding a greater E^o_{cell}. It has also been suggested that the oxidation potential of Li_2CO_3 is reduced if it is bound to the defects in the amorphous C. It is tempting to speculate that precise and deliberate engineering of the microstructure of the defect sites of the catalyst may alter reaction mechanisms or kinetics of both the discharge and charge processes and increase battery efficiency, life, discharge voltage and cycling. This proposition needs further research and investigation. The reaction mechanism pathway can be modulated by changing the MoS_2 catalyst to a Mo_2C catalyst. Such changes have been found to switch between the original reaction mechanism and others, which has the potential to overcome the challenges with

electrolyte oxidation and excessive irreversible electrolyte decomposition (62-64).

This excessive irreversible electrolyte decomposition often takes place because of the large potential difference in the cell. The electrolyte of any battery has to be stable at all the cell potentials which the battery could theoretically operate at, otherwise it becomes a safety hazard. As the Li^+ ions travel through the organic electrolyte during a cycle of the battery, they encounter O_2 derived free radicals at the double layer, which are present at the electrode interface and have an unpaired electron. This makes them extremely reactive. Concentrated electrolytes suppress free radical derived oxidative reactions and are also resistant to electrochemical reduction. These properties yield large and tunable electrochemical windows,which are indespensable for advanced batteries. The electrodeposition of Li metal from superconcentrated electrolyte solutions occurs in non-dendritic forms and exhibits greater reversibility. These superconcentrated solvents possess lower volatility, greater thermal stability and fire retardant properties which contribute to battery safety. The origin of these advantageous properties results from a lower thermodynamic activity of the solvent (water) molecules since a larger proportion are now coordinated to cations (Li^+). Furthermore, electrolyte decomposition forms a solid electrolyte interface (SEI) passivation layer on the anode that is ion conductive yet electron insulating to prolong the battery life.

5.2 Gaps

More testing needs to be done on the Li-CO_2 battery, especially with novel cathodes that have potential to fix the current reversibility challenge; that of carbon depositing at the cathode. These include Molybdenum Disulfide/Tin Disulfide Ultrathin Nanosheets, which have been tested to provide the highest cycle life ever recorded in a Li-CO_2 battery of 500 (22, 48).

A standardized catalyst is needed to improve the lifetime of Li-CO_2 batteries. The catalyst plays the most important role of cathode reversibility because it allows the battery to reach equilibrium faster, effectively helping with reversibility as well (64). There are numerous possible catalysts for the battery. Carbon-based catalysts have good electrical conductivity, a large surface area, and excellent stability (65). However, carbon interfered in systems with interface defects (battery thermal stability), and using this catalyst made the batteries less safe (22, 65). Noble metal-based catalysts exhibited excellent catalytic performance, but they were expensive due in part to limited reserves and resulted in an increase in the price (65). Transition metal compounds (oxides, sulfides, nitrides, metal single atom catalysts, etc.) have excellent energy efficiency and cycle life, and achieved catalytic activity comparable to noble based metals (65). Oxides and sulfides could convert a lot of energy to work, with easy preparation and abundant ores (65). Nitrides were low in price and abundant in resource, but they have an unstable structure that resulted in lowered efficiency (65). Single-metal atoms could improve efficiency while reducing agglomeration of metal particles, leading to

increased catalytic activity (65). Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) have the best potential for CO_2 capture, limiting greenhouse emissions, with desirable pore channel properties (65). Molecular catalysts have a large contact area and good catalytic efficiency (65).

Overall, the Li-CO_2 battery is aimed at being the most environmentally friendly battery, and one of the current challenges is increasing the porosity of the materials of the cell so it can have better rate capability and efficiency. The current catalysts that have been used with this battery are carbon based, but they pose limitations with the rate capability (17). Although not experimented with before, MOFs show the most promise as a catalyst in the Li-CO_2 cell as they have the potential towards carbon capture and sequestration towards a greener future in this battery technology, as well as a promise of better current efficiency and rate capabilities (14, 17).

Additionally, by tailoring the defect sites on a catalyst, further insight toward a desirable reaction mechanism can be obtained. Research has been conducted on this pressing issue and it was concluded that interface defect sites on the catalyst of Li-CO_2 improve the electrochemical performance of the battery (22, 66). Catalyst engineering is a field that has been extensively studied, especially for the determination of reaction mechanisms.

Type	Category	Uses
XPS	Electronic States	Oxidation states, magnitude of discharge reversibility (68)
SEM	Material Characteristics	Defect sites at a 100 to 1000 nm scale
XRD	Material Characteristics	Confirmation of Discharge Products (67)
TEM	Material Characteristics	Defect sites at a < 100 nm scale
FTIR	Performance	Confirmation of Discharge Products and in situ reaction mechanism (67)
EXAFS	Material Characteristics	Coordination Number
C-NMR	Performance	Identification of Molecules present

Table 4. Analytical Techniques Important to assess the future development of Li-CO_2 batteries.

With regard to the still questioned reaction mechanism, characterizing the dominant ones with potential to bring future development in the battery could be accentuated through analytical techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), fourier transform Infrared spectroscopy (FTIR), extended x-ray absorption fine structure (EXAFS), and carbon nuclear magnetic resonance spectroscopy (C-NMR). These techniques can be grouped into three categories, each with a different advantage to aiding future Li-CO_2 development (Table 4). The instrumental techniques that provide the best insight onto the active site (XPS) are categorized under "electronic state"(Table 4). Those providing the best information on the observable species in the reaction (FTIR, C-NMR) are categorized under "performance"(Table 4). Finally, those providing best details on the defects under the crystal structure (TEM, SEM, XRD, EXAFS) are categorized under "material characteristics" (Table 4). Electronic state techniques provide signatures of oxidation states during the reaction, potentially answering open ended questions on the reaction mechanism of the battery. Performance techniques identify the molecules that are present during a cycle of the battery, thus enabling researchers to determine rate-limiting and rate-determining reactions of the battery. By examining material characteristic techniques, active crystal structures during the reaction are revealed, further helping researchers engineer catalyst materials, and materials with specified defects for Li-CO_2.

In addition, for real world applicability, the battery will have to operate in a atmosphere of primarily N_2 and O_2; unlike current testing in labs, which is performed in a pure CO_2 environment (22). Thus, according to its remedial chemistry, a fourth reaction mechanism for the battery may be introduced, with the battery partially functioning as a Li-O_2 battery as well (66). This is a major disadvantage for Li-CO_2 batteries currently. To combat this issue a possible solution would be a small tank of pure CO_2 attached to the battery, which would be the reactant when discharging and the product when charging. In ambient air the CO_2 concentration is too low to be used in the battery. A CO_2 tank would be a potential solution, especially in EV's. Additionally, if the product CO_2 could be captured during the charging cycle, and recycled back into the CO_2 tank (possibly with an engineered pore zeolite gas separator), the battery would effectively function without any CO_2 emissions. There would hence be no need to visit a CO_2 filling station; a major advantage for the battery. However, the disadvantage to using a CO_2 tank with the battery is that it no longer would be capturing CO_2 from the environment, no longer rendering the battery "environmentally friendly". However, CO_2 sequestered by the battery from other applications such as the waste streams (discussed in 4.2) could be used in these tanks. This is a viable alternative as the CO_2 would still be captured, and used in the tank.

6. Conclusion

In summary, LIB's and Li-CO_2 batteries are two types of batteries with distinct chemistry, performance, and potential applications. LIB's

have a well-established track record of cost effectiveness; long cycle life; and widespread use in consumer electronics, EVs, and energy storage systems. Li-CO_2 batteries have the potential to offer even higher energy density and environmental advantages. Improvements are needed regarding their cycling capability and polarization gap, discharge depth and electrode degradation. Deliberate and precise electrolyte choice, catalyst choice, catalyst microstructure defect engineering, tuning of electolyte electochemical windows and control of parasitic reactions are needed to deliver these improvements. Simultaneous delivery of reactant CO_2 in the discharge cycle and its capture in the charge cycle with a companion compressed CO_2 tank make these batteries carbon-neutral. As research and development in battery technology continues to advance, both LIB's and Li-CO_2 batteries are likely to play important roles in the future of the battery revolution.

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