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Progress in research on Li–CO₂ batteries: Mechanism, catalyst and performance

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ABSTRACT

Rechargeable Li–CO₂ batteries provide a promising new approach for carbon capture and energy storage technology. However, their practical application is limited by many challenges despite much progress in this technology. Recent development in Li–CO₂ batteries is presented. The reaction mechanism with an air cathode, operating temperatures used, electrochemical performance under different CO₂ concentrations, stability of the battery in different electrolytes, and utilization of different cathode materials were emphasized. At last, challenges and perspectives were also presented. This review provides a deep understanding of Li–CO₂ batteries and offers important guidelines for developing reversible and high efficiency Li–CO₂ batteries.

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1. Introduction

The total energy consumption worldwide is currently at 14 TW per year. Even it is projected to roughly triple by 2050 [1]. In 2009, close to 83% of current energy needs was met by the combustion of fossil fuels (e.g. coal, natural gas, and petroleum products). These fuels emit large amounts of CO₂ which is a leading greenhouse gas. CO₂ emission is now thousands of metric tons per year. Coal-fired power plants provide the largest CO₂ production [2–4]. Therefore, effective measures should be implemented to alleviate CO₂ emission. Several eco-friendly and high energy density battery systems, such as Li-ion or

Li-air batteries, have been developed to substitute traditional fossil fuels. Unfortunately, the energy limits of prevailing Li-ion batteries are insufficient to meet the demands of smart grids and electric vehicles for long distance transportation. Li–O₂ batteries were developed which can deliver a gravimetric energy density of ~3500 Wh/kg (from a simple reaction of Li with O₂) which is substantially higher than other systems (e.g., ~350 Wh/kg for a graphite/LiCoO₂ system) [5–8]. Recent studies have illustrated that the Li-air batteries can be made to sustain several hundreds of cycles by using a stable electrolyte, highly efficient catalyst, and optimized battery design. Despite these advances, the development of Li-air batteries is still relatively

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new. These batteries are limited by poor knowledge of their reaction mechanism and practical issues such as poor recyclability, high polarization, and low rate capability. Furthermore, the effect of the presence of non-O₂ components in air on the reaction mechanism in Li–air batteries remains unknown because previous studies were conducted in pure O₂. The influence of the other constituents of air (N₂, Ar, H₂O, and CO₂) on the operation of the Li–air battery should be elucidated to develop the Li–air battery technology for ambient conditions. Although N₂ and noble gases, such as Ar are more abundant in ambient air, the conventional cathode voltage of ~3 V cannot activate electrochemical reactions involving these gases and Li. For example, the formation potential is 0.444 V for the following reaction, where $\Delta_r G^\circ$ is standard Gibbs free energy:

H₂O is another component of air, accounting for 1.6 vol% in ambient air at 25 °C and 50% relative humidity (RH) [10]. Battery performance will deteriorate in the presence of water due to the corrosion of Li metal [11] and Li₂O₂ [7–12]. Moreover, SO₂ is a component of polluted air and an inherently harmful gas. A Li–SO₂ battery has been used in military and aerospace applications. However, the emission of SO₂ gas into the atmosphere will be undesirable when the battery is charged [13]. So the Li–SO₂ battery is still highly restricted for civil use.

In contrast, CO₂ can undergo electrochemical reactions with Li (some involving O₂ as well). The voltage for the formation of Li₂CO₃ is 3.82 V for the following reaction:

Moreover, Li₂CO₃ is more chemically stable than Li₂O₂ ($\Delta_r G^\circ(\text{Li}_2\text{O}_2) = -285.60 \text{ kJ/mol}$). The difference in chemical stability implies that Li₂O₂ is easily converted into Li₂CO₃ in the presence of CO₂ because of the thermodynamic driving force [14]. Furthermore, the high solubility of CO₂ gas in organic electrolytes (~50 times higher than O₂) [15] results in the high possibility of CO₂ participation in battery reactions although the CO₂ content in air is only 0.03 vol% [10]. Thus, the reactions involving CO₂ and the chemistry of Li₂CO₃ in a Li–air battery must be elucidated. CO₂ would have the most influence on the chemistry of Li–air batteries among the various constituents of air when moisture is removed by waterproof films. CO₂ is the working gas in Li–CO₂ batteries. Thus, exploring Li–CO₂ batteries is necessary.

2. Reaction mechanism on cathodes

The formation and decomposition mechanism of Li₂CO₃ has received much attention in recent years. Two conditions, namely, CO₂/O₂ mixture or pure CO₂ as working gas, have to be discussed when it comes to the reaction mechanism in a Li–CO₂ battery.

For the mechanism in CO₂/O₂ mixture gas, We [16] explored the electrochemical reaction mechanism of a Li–CO₂/O₂ battery with the gaseous tracer technique. An oxygen molecule is believed to be reduced to form a superoxide radical anion (O₂^{•−}) after extracting one electron from the carbon air electrode in the presence of O₂.

The resultant O₂^{•−} can coordinate with one Li⁺ to form an intermediate product, LiO₂ (Eq. (2)), precipitate on the air cathode, and/or attack a solvent molecule by the nucleophilic mechanism (Eq. (3)) [17]. Eqs. (2) and (3) are competitive depending on the stability of the solvent molecules in the vicinity of O₂^{•−}. LiO₂ is not thermodynamically stable and would convert to Li₂O₂ through either a chemical (Eq. (4)) and/or an electrochemical pathway (Eq. (5)). Auerbach et al. [18] suggested that Li₂O₂ was formed by the reaction of Li⁺ and a peroxide anion (O₂^{2−}), which was formed through the disproportionation and/or electrochemical reaction of superoxide radical anions. On the one hand, CO₂ is highly soluble in aprotic solvents and can easily react with the intermediate species O₂^{•−} to finally generate Li₂CO₃ [19]. On the other hand, Li₂O₂ prefers to form Li₂CO₃. The presence of Li₂CO₃ at cathodes mainly originated from the decomposition of the organic electrolyte [20], oxidation of carbon-based cathode [20–22], reactions between Li₂O₂ or Li and residual CO₂ from ambient air, as summarized in Table 1 [23–24].

For the mechanism in pure CO₂ gas, reversible Li₂CO₃ has also been confirmed as the final product [23]. A “thermal trigger” region was observed in a Li–CO₂ battery from 40 to 60 °C in which the discharge potential changed obviously (Fig. 1). The potential of a Li–CO₂ cell can be estimated from the electrochemical reactions using the formula $E = -\Delta G/zF$ [26], where ΔG is the change in Gibbs free energy, z represents the number of electrons transferred per mole of product, and F is the Faraday constant. The cell potential was estimated based on the thermodynamic data [27]. In Fig. 1, this is the dashed line assuming that the simplest known reaction between Li and CO₂, $2\text{Li} + 2\text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}$, dominates the discharge process. The measured cell potential initially approaches the calculated equilibrium potential, but then surpassed it. According to Tafel theory, the actual discharge potential cannot exceed the theoretical equilibrium potential, which implied that the proposed reaction is incorrect. Moreover, differential electrochemical mass spectrometry (DEMS) indicated that CO was not a reaction product. Thus, the reaction $4\text{Li} + 3\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ was considered (No. 5 in Table 1). The cell potential estimated based on this reaction is shown in Fig. 1 as the dotted line. The measured cell discharge potentials at elevated temperature were consistently lower than the equilibrium potentials, which implied that this reaction was relevant to the discharging mechanism of the Li–CO₂ battery.

Table 1
Possible reactions of Li₂CO₃ formation [25].

Number	Possible reactions	$\Delta G/(\text{kJ/mol})$
1	Li ₂ O ₂ + electrolyte → Li ₂ CO ₃	Uncertain
2	Li ₂ O ₂ + C + 1/2O ₂ → Li ₂ CO ₃	−561.0
3	2Li ₂ O ₂ + C → Li ₂ O + Li ₂ CO ₃	−551.2
4	2Li ₂ O ₂ + 2CO ₂ → 2Li ₂ CO ₃ + O ₂	−333.3
5	4Li + 3CO ₂ → 2Li ₂ CO ₃ + C	−1081.0

Fig. 1. Comparison of equilibrium potential with actual discharge potential. Reprinted with permission from Ref. [30]. Copyright 2013, Royal Society of Chemistry.

Carbon is another discharge product besides Li_2CO_3 from reaction No. 5 in Table 1. Porous gold was used as a cathode in the Li- CO_2 battery to confirm the existence of carbon [28]. The discharge and charge curves of the Li- CO_2 battery with porous gold as cathode were similar to the battery with Ketjen black (KB) as cathode. Amorphous carbon was observed by surface-enhanced Raman spectroscopy and electron energy loss spectroscopy. Whether the reaction mechanism is the same in Li- CO_2 batteries with porous Au and KB as the cathode is unclear. Thus, the results with porous Au as the cathode were used as the reference.

The formation mechanism of Li_2CO_3 is relatively clear compared to the decomposition mechanism. A mechanism of Li_2CO_3 reversible decomposition remains unclear. The possible reactions of Li_2CO_3 decomposition are displayed in Table 2 [29]. Further studies should be performed to elucidate the decomposition mechanism to enhance the understanding of Li- CO_2 batteries.

3. Factors affecting the properties of Li- CO_2 batteries

The performance of a battery is affected by many factors such as operating temperature, active gas, electrolytes, and cathode materials.

3.1. Benefit of higher temperature

The performance of a Li- CO_2 battery can be affected by the temperature. A Li- CO_2 battery that consumes pure CO_2 gas exhibited a high discharge capacity of 2500 mAh/g at moderate temperature [30].

Fig. 2 shows the galvanostatic discharge curves of Li- CO_2 batteries at different temperatures in the range of 60–100 °C at

Fig. 2. Galvanostatic discharge curves of Li- CO_2 cells operated at various temperatures. Reprinted with permission from Ref. [30]. Copyright 2013, Royal Society of Chemistry.

a fixed current density of 0.05 mA/cm² and final potential of 2 V. The discharge potential increased with increasing temperature. A high operating temperature presents at least two beneficial effects. The higher temperature increases the solubility of Li_2CO_3 in the electrolyte and reduces its deposition on the electrode. Meanwhile, a higher temperature also reduces the transport barrier at the cathode-electrolyte interface. However, these data were obtained in the first discharge process, and changes in the performance in later cycles are not known.

3.2. Mixed CO_2/O_2 as the active gas

Aside from pure CO_2 , mixed CO_2/O_2 is also used as the active gas. Takechi et al. [19] first reported the application of a CO_2/O_2 mixed gas (from 0% to 100% volume CO_2) as the active material for Li- CO_2/O_2 batteries. The system using a mixed gas of CO_2 and O_2 delivered a very high discharge capacity which was three times that of a non-aqueous Li- O_2 battery.

The discharge profiles of the batteries with different CO_2

Fig. 3. Discharge curves of the Li- O_2/CO_2 batteries with various ratio of CO_2 in O_2/CO_2 mixed gas at 25 °C (current density 0.2 mA/cm²). Reprinted with permission from Ref. [19]. Copyright 2011, Royal Society of Chemistry.

Table 2

Possible reactions or pathways of Li_2CO_3 decomposition [25].

Number	Possible mechanisms or paths	E^0 / V
6	$\text{Li}_2\text{CO}_3 \rightarrow \text{CO}_2 + 1/2\text{O}_2 + 2\text{Li}^+ + 2\text{e}^-$	3.82
7	$\text{Li}_2\text{CO}_3 + 1/2\text{C} \rightarrow 3/2\text{CO}_2 + 2\text{Li}^+ + 2\text{e}^-$	2.80
8	$\text{Li}_2\text{CO}_3 + \text{electrolyte} \rightarrow \text{Unknown}$	Uncertain

concentrations are shown in Fig. 3. The Li–O₂/CO₂ battery (CO₂ ratio was 50%) had triple the discharge capacity compared with the Li–O₂ battery. Only a small capacity (66 mAh/g) was obtained when pure CO₂ was applied in the battery, contrary to the report by Liu et al. [28]. This difference may be due to the difference in the types of cathodes and electrolytes used.

The inset showed the relative discharge capacities of the Li–O₂/CO₂ battery with various CO₂ ratios in the mixed gas. The discharge capacity of the battery with 10% CO₂ in the mixed gas was the highest and was twice that of the standard Li–O₂ battery. Meanwhile, 30% CO₂ enhanced the performance of Li–O₂/CO₂ battery by almost three times that of the Li–O₂ battery. The appropriate CO₂ ratio to get the maximum capacity was from 30% to 70%. The capacity was dramatically reduced when the CO₂ ratio was higher than 80%. In contrast, the battery can operate well in pure CO₂ with different cathode materials. A reasonable explanation for the mechanism with these cathode materials remains to be established. Further work that elucidates the mechanism and properties of the Li–O₂/CO₂ batteries should be conducted to further improve the performance of the battery.

3.3. Stability of electrolytes

Lim et al. [31] investigated the reaction mechanism in the Li–O₂/CO₂ cell for various electrolyte conditions using quantum mechanical simulations combined with experimental verification. The subtle balance among the various reaction pathways can be modified by electrolyte solvation. Thus, a low dielectric electrolyte primarily forms Li₂O₂, while a high dielectric electrolyte is effective in electrochemically activating CO₂ and yielding only Li₂CO₃. A high dielectric medium, such as dimethyl sulfoxide (DMSO), can result in the reversible reaction of Li₂CO₃ over multiple cycles which may be due to minimizing side reactions.

The first reaction step can be reasonably taken to be an “oxygen reduction reaction step”. A radical nucleophile reagent is created after the capture of an electron by the O₂ molecule at the cathode. O₂^{•−} then reacts vigorously with a neutral or charged species in the battery, such as CO₂, Li⁺ or electrolyte.

Fig. 4 illustrates the possible reaction pathways for the initial complex formation. This includes the reaction energy (ΔE) and the activation barrier for the reaction in the three electrolytes (EC, DMSO, and DME). The reaction of O₂^{•−} with CO₂ in EC is more favored both thermodynamically and kinetically than its reaction with Li⁺ (Fig. 4(a)). However, a ring-opening reaction for O₂^{•−} with EC ($\Delta E = -29.7$ kJ/mol) is the most thermodynamically favored, from considering the surrounding electrolyte. Thus, although the activation barrier for reaction 2.3 is higher than reaction 2.2 (Fig. 4), the final resulting of reaction 2.3 is expected to drive the reaction pathway because of higher stability. However, the ring-opening reaction is not the most favored reaction in the DMSO (Fig. 4(b)) or DME (Fig. 4(c)) electrolytes. O₂^{•−} preferentially reacts with CO₂ over Li⁺ in DMSO. In contrast, the reaction of O₂^{•−} with Li⁺ is much more likely than the others in DME (Fig. 1(c)). The DFT results for other organic solvents are exhibited in Fig. 5. The reaction en-

Fig. 4. Activation barrier and binding reaction energy from discrete Fourier Transform (DFT) calculations at the initial complex formation (ICF) step with the use of ethylene carbonate (EC) (a), DMSO (b), and dimethyl ether (DME) (c) electrolytes. Reprinted with permission from Ref. [31]. Copyright 2013, American Chemical Society.

ergies decrease linearly with the increase of the inverse of the dielectric constant of the electrolyte, particularly for reaction 2.1. The effect by the dielectric constant is much less for the reaction of O₂^{•−} with CO₂. The contrasting behavior of these two reactions implied that O₂^{•−} was more likely to react with CO₂ in a high dielectric solvent and with Li⁺ in a low dielectric solvent in Li–O₂/CO₂ batteries. The possible discharge products in Li–O₂/CO₂ batteries are Li₂O₂ and Li₂CO₃. Thus, DMSO is a good choice for Li–O₂/CO₂ as the electrolyte. The effect of the electrolyte on Li–pure CO₂, however, should still be investigated. In addition, solid state electrolytes can be considered for use in Li–CO₂ batteries because of their good recycling performance [32].

3.4. Diversity of cathodes for Li–CO₂ batteries

3.4.1. Ketjen black

Ketjen black is usually used as a cathode in Li–CO₂ batteries because of its excellent electrical conductivity, chain configuration, small particles and wide size distributions. Liu et al. [28]

Fig. 5. DFT predicted trend of activation barrier ($\Delta E^\ddagger$, dashed) and binding reaction energy (ΔE , solid) plotted against $(\text{dielectric constant})^{-1}$ for the ICF steps of the two reactions. Reprinted with permission from Ref. [31]. Copyright 2013, American Chemical Society.

reported rechargeable Li-CO₂/O₂ (2:1) and Li-CO₂ batteries using KB as the cathode and the catalyst operated at room temperature.

The profiles of charge and discharge are shown in Fig. 6. The discharge profiles of the three batteries are similar. The Li-CO₂/O₂ (2:1) battery showed the highest discharge voltage at 2.75 V versus Li⁺/Li. The Li-O₂ system showed a slope, while the other two systems mainly demonstrated a high charging plateau above 4.0 V versus Li⁺/Li. This result implied a higher polarization of CO₂-based batteries during charging. This characteristic may be caused by thermodynamic or kinetic factors, and needs future clarification.

The charge and discharge profiles, differential capacities, and polarization voltage of the Li-CO₂/O₂ (2:1) battery are shown in Fig. 7(a)–(c). Those for the Li-CO₂ battery are shown in Fig. 7(d)–(f). Li₂O₂ has a low conductivity. Garcia-Lastra et al. [33] showed that the charge transport of Li₂CO₃ was even poorer than that of Li₂O₂. The Li-CO₂ battery can operate reversibly, and the charging platform voltages were not higher than 4.3 V in the first five cycles. The round-trip efficiency of the Li-CO₂/O₂ (2:1) battery was 66.7% (the value is 66.3% for the Li-CO₂ battery). The polarization of the Li-CO₂ battery was slightly larger than that of the Li-CO₂/O₂ (2:1) battery. The battery can operate over tens of cycles without a catalyst and special cathode material at high CO₂ concentrations.

3.4.2. Graphene

Graphene has attracted much attention as an ideal cathode material for Li-O₂ batteries because of high electrical conductivity, large surface area, and high electrochemical stability. This material can play an important role in Li-CO₂ batteries because it also provides efficient diffusion channels, enough space, and active sites [34–37]. Zhang et al. [23] first introduced graphene into Li-CO₂ batteries.

Fig. 6. Charge-discharge curves of the Li-O₂ battery, Li-CO₂/O₂ (2: 1 in volume ratio) battery and Li-CO₂ battery. Reprinted with permission from Ref. [28]. Copyright 2014, Royal Society of Chemistry.

Fig. 8(a) displays the CV data to explore the catalytic activity of graphene and shows the evident cathodic and anodic peaks under CO₂ atmosphere. The graphene cathode delivered capacities of 14722 mAh/g and 6600 mAh/g (Fig. 8(b)) at a current densities of 50 mA/g and 100 mA/g, respectively. A stable discharge platform of 2.77 V was observed, which was extremely close to the equilibrium voltage of Li-CO₂ batteries [30]. The results indeed were greatly improved compared with those based on KB. The system exhibited a small discharge capacity when the working gas was Ar. The batteries showed good recycling performance over 20 cycles and the overpotential increased with cycle, which was attributed to the accumulation of inactive Li₂CO₃. Previous reports showed that Li-CO₂ batteries could only operate at high temperatures [30] or at a low current density (30 mA/g) [28]. Graphene showed a relatively

Fig. 7. Charge-discharge voltage profiles, differential capacity curve, and voltage hysteresis curves of the Li-CO₂/O₂ (2:1) and the Li-CO₂ battery. Reprinted with permission from Ref. [28]. Copyright 2014, Royal Society of Chemistry.

Fig. 8. (a) Cyclic voltammetry (CV) curves of batteries. (b) Initial discharge curves of the batteries. Curtailing capacity of 1000 mAh/g at current densities of 50 mA/g (c) and 100 mA/g (d). Reprinted with permission from Ref. [23]. Copyright 2015, Wiley VCH.

good performance but the instability of the battery system caused by the increased overpotential after 20 cycles needs further improvement.

Additionally, the calculated voltage of the reaction $4\text{Li} + 3\text{CO}_2 = \text{C} + 2\text{Li}_2\text{CO}_3$ is 2.66 V, which was roughly consistent with the experimental data (2.8 V). Thus, this reaction can occur. A Pt net was used as the cathode to confirm the presence of carbon by electron energy loss spectroscopy. Whether the reaction mechanism is the same as that for Li- CO_2 batteries with a Pt net or graphene as the cathode remains ambiguous. Thus, the introduction of a Pt net was only used to confirm the presence of carbon as a reference. Although graphene cathodes have exhibited excellent electrochemical activity in Li- CO_2 batteries, their kinetic parameters still have to be much improved to enhance the efficiency of Li- O_2 batteries [34–38].

3.4.3. Carbon nanotubes (CNTs)

Similar to graphene, CNTs with a high electrical conductivity, large surface area, abundant channels, porosity, and 3D characteristics are considered to facilitate the transport of both electrons and gases, as well as the deposition of discharge products. Thus, CNTs were selected as cathode materials to enhance the electrochemical process and cycling stability of rechargeable Li- CO_2 batteries [39].

The SEM and TEM images of the CNTs are shown in Fig. 9.

Fig. 9. SEM (a) and TEM (b) images of the CNTs. Inset of (b) is the HRTEM image. Reprinted with permission from Ref. [39]. Copyright 2015, Royal Society of Chemistry.

The tubes stacked together and formed numerous pores and channels, which benefit the diffusion of CO_2 and electrolytes. The inset showed that the wall thickness of the CNTs was approximately 5 nm.

The first discharge curves of the batteries were evaluated in the voltage range of 2.2–4.3 V. The discharge capacities were obtained at current densities of 50 mA/g and 100 mA/g normalized to the weight of the CNTs. This is shown in Fig. 10(a). A low over-potential of 0.13 V can be clearly observed in Fig. 10(b) with a cut-off capacity of 1000 mAh/g at 50 mA/g, indicating the high electrochemical activity of CNTs cathodes. The lower discharge plateau appeared in Fig. 10(c) at 100 mA/g which may be attributed to the Ohmic resistance of the batteries.

They also thought that CNT cathodes enhanced the performances of the Li- CO_2 batteries because of their structural advantages. First, the good electrical conductivity of 1D CNTs is

Fig. 10. (a) Initial discharge curves of CNT cathodes at 50 and 100 mA/g. Recycling performance of the Li- CO_2 batteries at 50 mA/g (b) and 100 mA/g (c) under a cutoff capacity of 1000 mAh/g. Reprinted with permission from Ref. [39]. Copyright 2015, Royal Society of Chemistry.

Table 3Summary of cathode catalysts for Li–CO₂ batteries.

Cathode catalyst	Discharge capacity (mAh/g)	Applied current	Working gas (ratio by volume)	Working temperature (°C)	Electrolyte	Efficiency (%)	Ref.
Ketjen black	~5800	0.2 mA/cm ²	CO ₂ :O ₂ = 2:1	25	LiTFSI dissolved in EC/DEC	Unknown	[19]
	66	0.2 mA/cm ²	Prue CO ₂	25	LiTFSI dissolved in EC/DEC	Unknown	[19]
	1880	30 mA/g	CO ₂ :O ₂ = 2:1	25	LiCF ₃ SO ₃ dissolved in TEGDME	~98.6	[28]
	1032	30 mA/g	Prue CO ₂	25	LiCF ₃ SO ₃ dissolved in TEGDME	~96.2	[28]
	~2400	0.4 mA/cm ²	CO ₂ :O ₂ = 1:1	25	TBAPF ₆ dissolved in DMSO	Unknown	[31]
	~2200	0.4 mA/cm ²	CO ₂ :O ₂ = 9:1	25	TBAPF ₆ dissolved in DMSO	Unknown	[31]
	~2050	0.4 mA/cm ²	CO ₂ :O ₂ = 1:1	25	TBAPF ₆ dissolved in DME	Unknown	[31]
	~3800	0.4 mA/cm ²	CO ₂ :O ₂ = 9:1	25	TBAPF ₆ dissolved in DME	Unknown	[31]
Graphene	14722	50 mA/g	Prue CO ₂	25	LiTFSI dissolved in TEGDME	~40	[23]
	6600	100 mA/g	Prue CO ₂	25	LiTFSI dissolved in TEGDME	~36	[23]
Super P	~0	0.05 mA/cm ²	Prue CO ₂	25	LiTFSI dissolved in [bmim][Tf ₂ N]	Unknown	[30]
High surface area carbon	~750	0.05 mA/cm ²	Prue CO ₂	25	LiTFSI dissolved in [bmim][Tf ₂ N]	Unknown	[30]
Blending conductive carbon	~2000	0.05 mA/cm ²	Prue CO ₂	60	LiTFSI dissolved in [bmim][Tf ₂ N]	Unknown	[30]
	~2800	0.05 mA/cm ²	Prue CO ₂	80	LiTFSI dissolved in [bmim][Tf ₂ N]	Unknown	[30]
	~3800	0.05 mA/cm ²	Prue CO ₂	100	LiTFSI dissolved in [bmim][Tf ₂ N]	Unknown	[30]
CNTs	8379	50 mA/g	Prue CO ₂	25	LiTFSI dissolved in TEGDME	Unknown	[39]
	5786	100 mA/g	Prue CO ₂	25	LiTFSI dissolved in TEGDME	Unknown	[39]
Porous Au	~220	30 mA/g	Prue CO ₂	25	LiCF ₃ SO ₃ dissolved in TEGDME	~98	[23]

convenient for electron transport [40]. Second, the 3D networks formed from stackable and interlaced carbon nanotubes not only favorably allow electron transport in every direction [41], but also have more space for the deposition of discharged products. The space in the networks facilitates the transport of CO₂ and Li ions [42]. Moreover, other than layered graphene, which can only deposit Li₂CO₃ on the surface, excessive Li₂CO₃ prevents the transport of electrons. CNT cathodes can deposit Li₂CO₃ in their whole 3D networks and endow the batteries with improved recycling capability. Due to the considerable performance of the Li–CO₂ batteries, these batteries were extensively investigated before their commercialization [43]. This work can promote the realization of true Li–air batteries.

However, few reports on the application of metal catalysts in Li–CO₂ batteries are available. Wang et al. [44] clarified the effect of reducing parasitic reactions using a highly efficient Au/δ-MnO₂ catalytic electrode. TiC [45] and 3D porous Ru [46] were also used to reduce the polarization voltage. Introduction of soluble catalysts are a new approach to improve the round-trip efficiency of the battery [47].

Until now, carbon materials are commonly used as the cathode because of their superior electrical conductivity and high surface area. However, the reaction mechanism when charging the battery is unclear. A noble metal is expensive and difficult to fabricate as a porous electrode with high surface area, but it can reduce parasitic reactions and polarization. Moreover, the mechanism is easier to elucidate with a noble metal. Therefore, identifying new catalysts should be prioritized in Li–CO₂ batteries. Transition metal oxides are effective catalysts in lithium secondary batteries. Carbon/metal oxide

compositions may be suitable as cathodic catalysts for Li–CO₂ batteries. A summary of cathode catalysts for Li–CO₂ batteries is illustrated in Table 3. The deposition of Li₂CO₃ on the surface of the cathode will deteriorate the performance of the batteries. Li–CO₂ batteries with hybrid electrolytes [48] should be designed and studied in the future to prevent rapid blocking of the solid electrode surface by Li₂CO₃.

4. Conclusions and perspective

Recent studies on the reaction mechanism, electrolyte, working gas, operating temperature, and different cathode materials for Li–CO₂ batteries were reviewed. Superoxide radicals anion (O₂^{•−}) generated during discharge chemically attack carbonate electrolyte solvents when a CO₂/O₂ mixed gas is used. However, ether-based, amide-based, and DMSO electrolytes are reasonably stable against the superoxide during discharge. The use of a high dielectric electrolyte helps preserve the reversible reaction of Li₂CO₃ by electrochemically activating CO₂. Thus, DMSO is the optimal electrolyte for a Li–CO₂ battery. The properties of the battery can be improved by using a mixed gas of O₂ and CO₂ as the working gas. The capacity was improved in the range of 30%–70% CO₂. A high temperature improved the capacity of the battery. CNTs and graphene as air cathodes of the Li–CO₂ battery delivered a high discharge capacity and sustained stable recyclability. These materials have excellent electrical conductivity, a porous structure, and catalytic activity, and they can be used as references. In addition, adopting noble metal or soluble catalysts is a new approach to improve the round-trip efficiency of the battery. Li–CO₂ batter-

ies with hybrid electrolytes should be designed and studied in the future. The reaction mechanism in the battery is still unclear, especially for the charging process, and should receive attention in future investigations.

This paper reviewed recent progress on stable Li-CO₂ batteries. Li-CO₂ batteries provide a promising new approach for CO₂ capture and generation of electrical energy. However, the reaction mechanism, thermodynamic and kinetic properties are still unknown and require further investigation. A better understanding of the electrochemical mechanism in Li-CO₂ systems is important. A stable Li-CO₂ system depends on finding stable electrolytes and effective catalysts to reduce the discharge/charge over-potential and improve energy efficiency.

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Graphical Abstract

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Progress in research on Li-CO₂ batteries: Mechanism, catalyst and performance

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The Li-CO₂ battery system is a promising potential technology for CO₂ capture and next-generation energy storage. It is indispensable to understand these fundamental issues including organic electrolyte, cathode catalysts, and reaction mechanisms.

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Li–CO₂ 电池机理、催化剂和性能研究进展

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摘要: 对化石能源依赖所造成的能源安全和环境污染等问题限制了人类社会的可持续发展。Li–CO₂ 电池能量密度高、原材料成本低廉且结构简单, 因而被认为是开发和利用可再生清洁能源的有力技术, 在住宅能量存储、电动汽车驱动和智能电网等领域具备良好的应用前景。此外, CO₂ 等温室气体的大量排放是全球变暖的主要原因, Li–CO₂ 电池放电时可将空气中的 CO₂ 还原固定, 生成的碳材料可用作燃料和化工原料, 在资源利用化上提供了新途径。Li–CO₂ 电池是建立在锂-空气电池的基础上。相比大气中的其他成分, H₂O 与 CO₂ 对该电池的影响很大。防水膜可以减少水的影响; 而在放电过程中, CO₂ 的存在会生成 Li₂CO₃, Li₂CO₃ 是可以分解的。由此可见, CO₂ 在可充放的锂电池中作为正极活性成分储能, 从而被利用起来。目前 Li–CO₂ 电池至少面临三个问题: (1) 电池充放电的机理尚不完全清楚, 并且以 O₂ 和 CO₂ 混合气为活性气体的机理与以纯 CO₂ 为活性气体的机理是有差别的, Li₂CO₃ 的生成与分解的机制仍在探索中; (2) 电解液的稳定性; (3) 寻找高效的正极催化材料。

本文介绍了 Li–CO₂ 电池的发展历程, 讨论了 Li–CO₂ 电池的充放电机理、电解液的影响以及正极催化材料的选取等。综述了活性气体为纯 CO₂ 和 CO₂–O₂ 混合气时机理的差别, 以及 CO₂/O₂ 混合比对电池性能的影响。选取电解液应考虑其粘度和介电性。高效能的正极催化材料大多具有高导电性、多孔结构和大的比表面积等特点。而温度也是影响 Li–CO₂ 电池性能的因素之一。虽然 Li–CO₂ 电池的概念相对较新, 但可实现 CO₂ 在能源储存与转化领域中的应用, 并为 Li–O₂ 电池向锂空气电池飞跃提供了重要参考。本文以如何提高正极材料的催化性能和 Li₂CO₃ 的生成和分解机理为重点, 总结了正极材料所具有的导电性、比表面积、特殊结构等特点, 以及相关机理。

关键词: 锂-二氧化碳电池; 正极反应机理; 催化剂设计; 固碳

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