

# Challenges and prospects of lithium–CO<sub>2</sub> batteries

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## ABSTRACT

The key role played by carbon dioxide in global temperature cycles has stimulated constant research attention on carbon capture and storage. Among the various options, lithium–carbon dioxide batteries are intriguing, not only for the transformation of waste carbon dioxide to value-added products, but also for the storage of electricity from renewable power resources and balancing the carbon cycle. The development of this system is still in its early stages and faces tremendous hurdles caused by the introduction of carbon dioxide. In this review, detailed discussion on the critical problems faced by the electrode, the interface, and the electrolyte is provided, along with the rational strategies required to address these problematic issues for efficient carbon dioxide fixation and conversion. We hope that this review will provide a resource for a comprehensive understanding of lithium–carbon dioxide batteries and will serve as guidance for exploring reversible and rechargeable alkali metal-based carbon dioxide battery systems in the future.

## KEYWORDS

lithium (Li)–carbon dioxide batteries, Li metal, catalyst, mechanism, interface

## 1 Introduction

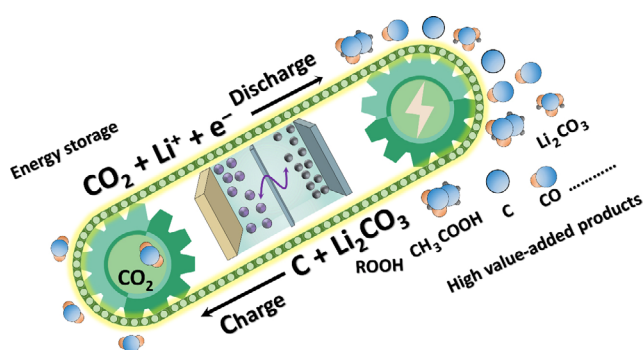
The gradual depletion of fossil fuels and the global CO<sub>2</sub> emission flux are two major energy concerns that have been challenges for the sustainability of human society since the industrial revolution. New energy storage technologies, especially renewable ones, will require switching to profoundly intermittent energy resources to partially replace fossil fuels for a low-carbon economy [1–3]. Developing accessible approaches for converting the energy produced by these renewable energy sources into models that can be stored are thus of great importance. On the other hand, the increasing concentration of the greenhouse gas CO<sub>2</sub> in the atmosphere has impacts that have extended beyond human society to world climate change. Novel efficient CO<sub>2</sub> utilization strategies, particularly ones to make value-added goods and driven in an efficient way, are currently being investigated.

Direct electrochemical recycling of the CO<sub>2</sub> in metal-CO<sub>2</sub> batteries possesses the unique merits of high efficiency and flexibility in both CO<sub>2</sub> fixation and energy storage. Among the different possibilities, Li–CO<sub>2</sub> batteries have been expected to be a promising system and have quickly drawn worldwide attention in the scientific community due to their high theoretical

specific energy density of 1,876 Wh·kg<sup>-1</sup> and high discharge potential at ~ 2.8 V (Fig. 1). Compared with other metal–CO<sub>2</sub> batteries, such as Na–CO<sub>2</sub> and Zn–CO<sub>2</sub> batteries, Li–CO<sub>2</sub> batteries are much more promising not only in delivering the highest operating voltage and energy density, but also in the aviation industry and aerospace exploration (particularly on Mars) for which lightweight materials are highly desirable. Importantly, suitable current chemistries and technologies derived from the Li metal batteries can be applied to Li–CO<sub>2</sub> batteries. The electrochemical reduction of CO<sub>2</sub> was firstly observed by Takechi et al. in the Li–O<sub>2</sub>/CO<sub>2</sub> system in 2011, and they revealed that with the existence of CO<sub>2</sub>, the discharge capacity could be dramatically increased compared with pure Li–O<sub>2</sub> batteries [4]. Two years later, Archer and co-workers assembled a pure primary Li–CO<sub>2</sub> battery based on a conductive carbon cathode in a novel ionic liquid electrolyte [5]. Subsequently, rechargeable Li–CO<sub>2</sub> batteries in pure CO<sub>2</sub> atmosphere have been realized, based on unique cathodes design and elaborate electrolyte formula to promote the decomposition of insulating Li<sub>2</sub>CO<sub>3</sub>. Considerable progress on rechargeable Li–CO<sub>2</sub> batteries has more recently been achieved in the past few years as a key direction with the participation of increasing numbers of groups.

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**Figure 1** Schematic illustration of the concept of Li-CO<sub>2</sub> batteries toward highlight efficient energy storage and CO<sub>2</sub> fixation.

Benefiting from the pioneering research in the early stages, current Li-CO<sub>2</sub> batteries can be operated with a high energy density, and lifespans of hundreds of cycles have been obtained from advanced cathodes and carefully chosen electrolytes. The development of Li-CO<sub>2</sub> battery technology has never encountered smooth sailing; however, its further practical application is still impeded by several hurdles since the first proposal, including inferior reversibility, inadequate understanding of the redox processes, large overpotential, and parasitic side reactions [6]. Recently, substantial efforts have been devoted to solving these problems, discovering the underlying reaction mechanism, and improving electrochemical performance of rechargeable Li-CO<sub>2</sub> batteries through various methodologies.

To spur more studies on nonaqueous Li-CO<sub>2</sub> batteries, in this review, we provide an overview of the critical challenges that have been recognized from researchers' efforts in the past few years. The detailed rationale behind battery reaction mechanisms and newly developed catalyst cathodes will be given, with the emphasis on how rechargeable Li-CO<sub>2</sub> batteries work to provide value-added CO<sub>2</sub> production and energy storage. Moreover, opportunities and guidelines will also be given for the design of practical Li-CO<sub>2</sub> batteries in the future. This review provides an intensive discussion and understanding of the Li-CO<sub>2</sub> batteries, which will be regarded as a useful handbook for further optimization of metal-CO<sub>2</sub> batteries.

## 2 Critical challenges for rechargeable Li-CO<sub>2</sub> batteries

An adequate understanding of the problematic issues for the nonaqueous Li-CO<sub>2</sub> batteries will stimulate their practical development. In the light of the previous research, we are making an attempt to exhaustively summarize the various challenges involving the cathode, interfaces, electrolyte, and anode, which need to be urgently overcome (Fig. 2(a)).

### 2.1 Challenges for the cathode electrode

Although the history of Li-CO<sub>2</sub> batteries is relatively short, great progress has been made on the electrochemical mechanism in less than a decade [7]. It is commonly accepted that a general Li-CO<sub>2</sub> battery consists of a Li metal anode, a nonaqueous electrolyte, and the CO<sub>2</sub> cathode, which is composed of carbon and binder materials with or without catalysts. Especially, the CO<sub>2</sub> cathode in Li-CO<sub>2</sub> batteries consists of a triple-phase zone, where the CO<sub>2</sub> reduction reaction (CRR) and the CO<sub>2</sub> evolution reaction (CER) take place, and there are multiphase interfacial reactions including gas (CO<sub>2</sub>), liquid (electrolyte),

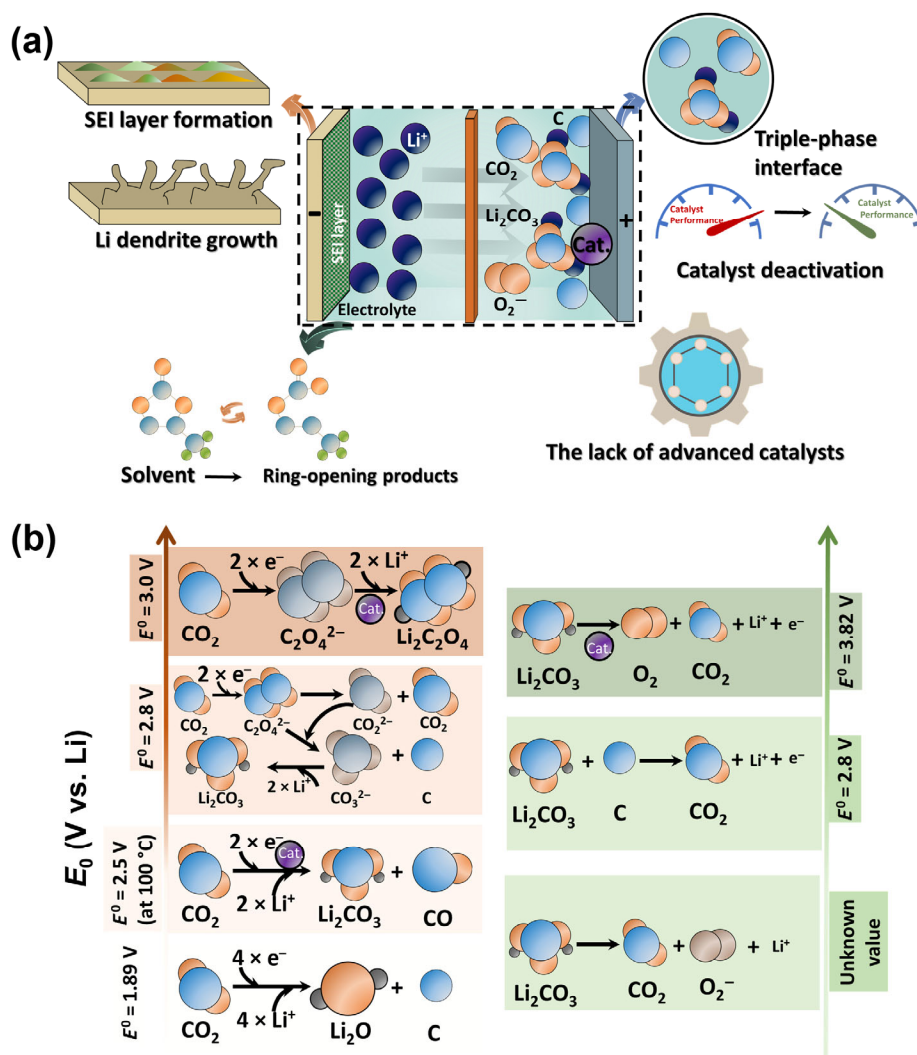
and solids (products and/or catalysts). With progress in research, mature investigations have provided convincing evidence that the cathode electrodes are facing problematic issues for reaching acceptable reversibility of the Li-CO<sub>2</sub> batteries, in which the problems are mainly associated with the unclear CRR and CER mechanisms, the lack of highly efficient catalysts, and catalyst deactivation.

#### 2.1.1 The controversial discharge and charge mechanisms

The exact pathway of the CO<sub>2</sub> reduction reaction is unknown when discharging the nonaqueous Li-CO<sub>2</sub> batteries, although researchers have reached a consensus that the CRR involves a multiple-electron transfer process. Based on experimental and simulation results, a reasonable assumption indicates that the CO<sub>2</sub> molecule is initially reduced to the intermediate C<sub>2</sub>O<sub>4</sub><sup>2-</sup> on the electrode's surface via a one-electron reaction [8]. The unstable C<sub>2</sub>O<sub>4</sub><sup>2-</sup> further experiences two steps of disproportionation reactions to form carbon species and CO<sub>3</sub><sup>2-</sup>. Finally, the thus-formed CO<sub>3</sub><sup>2-</sup> couples with Li<sup>+</sup> to produce crystalline Li<sub>2</sub>CO<sub>3</sub>. Therefore, the solid-state carbon and Li<sub>2</sub>CO<sub>3</sub> are widely acknowledged as discharge products formed and deposited on the cathode electrode surface, based on the reaction of  $4\text{Li} + 3\text{CO}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3 + \text{C}$ . Besides the abovementioned opinions, a few reports indicate that the main discharge product can be changed to the thermally unstable Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> by manipulating the electrocatalysts or to Li<sub>2</sub>O by adjusting the supply rate of CO<sub>2</sub>. Although Li<sub>2</sub>CO<sub>3</sub> is generally accepted as the final product, the detailed reaction path still seems controversial and needs more research attention in this field.

Unfortunately, the charging reaction is not just the reverse reaction of the discharge progress due to the variety of the discharge products and the corresponding physicochemical properties. Taking the discharge product of Li<sub>2</sub>CO<sub>3</sub> and C as an example, the CER process in Li-CO<sub>2</sub> batteries usually involves two main forms: Li<sub>2</sub>CO<sub>3</sub> self-decomposition and the decomposition of Li<sub>2</sub>CO<sub>3</sub> and C. This is mainly because of the wide band-gap character (band gap: 5.1 V) of the Li<sub>2</sub>CO<sub>3</sub> and the thermodynamic reaction barriers. Clearly, only the latter one is essentially reversible, holding promise for both CO<sub>2</sub> fixation and energy storage, while the former could only be called a rechargeable system with respect to CO<sub>2</sub> fixation. The possible reactions and corresponding thermodynamic potential (reversible potential) for CER processes are summarized in Fig. 2(b).

In short, when rechargeable Li-CO<sub>2</sub> batteries are discharged to Li<sub>2</sub>CO<sub>3</sub> and C products, they suffer a difficult and sluggish CRR process because (i) both Li<sub>2</sub>CO<sub>3</sub> and C are solids and insoluble in the organic electrolyte; (ii) the electronically insulating and thermodynamically stable (Gibbs free energy,  $\Delta_r G^\circ = -1132.1 \text{ kJ mol}^{-1}$ ) nature of Li<sub>2</sub>CO<sub>3</sub> results in the CER process taking place at a high voltage. As a result, a large overpotential will be finally required for CO<sub>2</sub> adsorption and reduction, as well as further deep CO<sub>2</sub> evolution. Here, the overpotential, which is defined as the energy gap between the actual potential and the theoretical equilibrium potential calculated by the Nernst equation, consists of two main parts in Li-CO<sub>2</sub> systems: the activation overpotential, caused by the sluggish decomposition of Li<sub>2</sub>CO<sub>3</sub>, which generally necessitates a charge voltage of 4.38 V, and the ohmic overpotential, induced by the insulating Li<sub>2</sub>CO<sub>3</sub> and its insolubility in organic electrolyte. This means that the high ohmic and activation components of the overpotential usually cause poor reversibility and low energy efficiency of Li-CO<sub>2</sub> batteries.



**Figure 2** (a) Critical challenges associated with the current Li-CO<sub>2</sub> batteries. The challenges can be mainly classified as anode issues, electrolyte issues, interfacial issues, and cathode issues. The cat. represents catalysts. (b) Possible discharge or charge reactions in Li-CO<sub>2</sub> batteries and the reversible potentials of corresponding reactions.

### 2.1.2 The lack of highly efficient catalysts

To predominantly solve the kinetic issue of the CO<sub>2</sub> cathode, heterogeneous cathode electrocatalysis and redox mediators have been intensively developed and employed [9, 10]. Mediators can regulate a targeted CO<sub>2</sub> redox reaction by introducing an extrinsic kinetically favourable redox couple that promotes the intrinsic CO<sub>2</sub> redox reactions. Typical redox mediators can stimulate the effective decomposition of Li<sub>2</sub>CO<sub>3</sub>, reduce the Li<sub>2</sub>CO<sub>3</sub> oxidation overpotential during charge, or facilitate indirect electrochemical reduction of CO<sub>2</sub> molecules in aprotic electrolytes [11–13]. The effectiveness of both inorganic (such as LiBr) and organic (such as quinones) redox mediators has been validated in previous research [14, 15]. The introduction of redox mediators (RMs) was widely used in Li-O<sub>2</sub> and Li-S batteries [16]. Among them, RMs are often referred as homogeneous mediators, a class of redox couples that undergo surface electroredox and diffuse to react with the active materials chemically. Therefore, such unique feature of RMs in Li-CO<sub>2</sub> batteries would be promising because immobile solid phases such as carbon and Li<sub>2</sub>CO<sub>3</sub> are the end products of oxidation and reduction reactions, respectively, making themselves difficult to achieve ideal contact with traditional

catalysts and thereafter to be “catalyzed”. Learning from conventional understanding of catalysis, the catalyst must have access to immobile phases if the reaction involves solid reactants, and the limited contact between solid catalysts and solid end products will therefore increase the overpotential of the Li-CO<sub>2</sub> batteries. The use of homogeneous mediators might be an ultimate solution to achieve an expedited full reaction scheme. Nevertheless, it should be pointed out that the redox mediators that are utilized at present are able to only satisfy certain requirements in CRR or CER process, and whether the RMs can facilitate participation of the carbon species in the decomposition reaction of Li<sub>2</sub>CO<sub>3</sub> remains unknown. In addition, the side reactions caused by the introduction of RMs are also perplexed to the anode electrode to achieve acceptable cyclability, so accordingly, more research attention should be paid in this field.

On the other hand, the introduction of capable electrocatalysts is intended to effectively promote the cathode redox kinetics by reducing the overpotential between CRR and CER processes (Table 1) [17–39]. So far, various electrocatalysts including carbonaceous materials, metals, metal compounds, and metal-organic complexes, have demonstrated their advantages in enhancing the reversibility, improving the rate response,

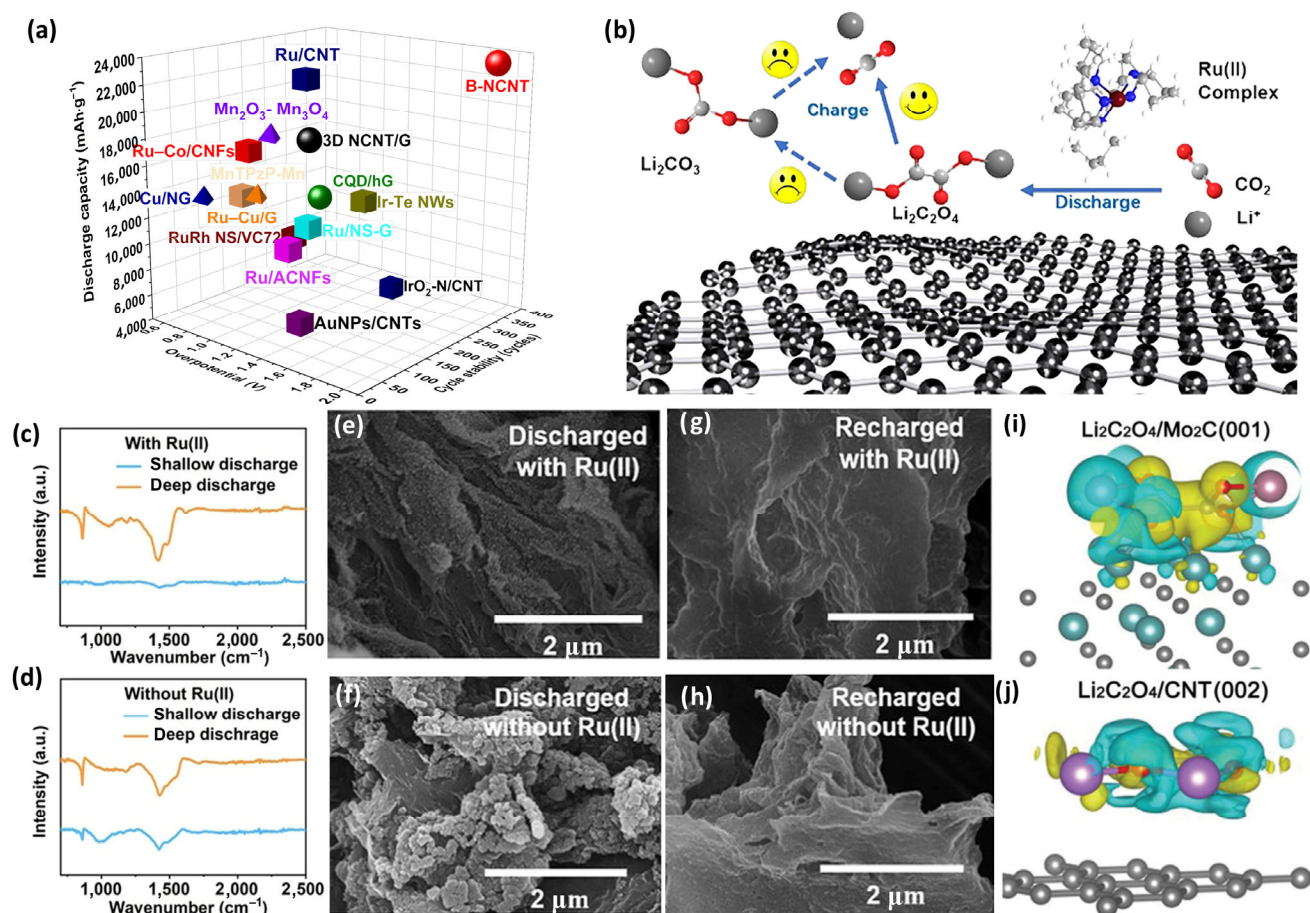
**Table 1** The performance of various cathodes and electrolytes in nonaqueous Li-CO<sub>2</sub> battery

Cathodes	Electrolytes	Discharge/charge voltage (current density)	Discharge capacity (current density)	Cycle stability (current density / cutoff capacity)	Ref.	
Carbon materials	3D NCNT/G	1 M LiTFSI/DMSO with 0.3 M LiNO <sub>3</sub>	2.77 V/3.9 V (100 mA·g <sup>-1</sup> )	17534.1 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	180 cycles (100 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[19]
	B,N-codoped holey graphene	1 M LiTFSI/TEGDME	2.75 V/— (300 mA·g <sup>-1</sup> )	16,033 mAh·g <sup>-1</sup> (300 mA·g <sup>-1</sup> )	200 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[20]
	Bamboo-like N-doped CNTs	1 M LiTFSI/TEGDME	2.72 V/3.98 V (50 mA·g <sup>-1</sup> ) 20 cycles	23,328 mAh·g <sup>-1</sup> (50 mA·g <sup>-1</sup> )	360 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[21]
	N,S-doped CNTs	1 M LiTFSI/TEGDME 1 g PVDF-HFP/4.0 g NMP 10 μL HMPP/3.0 g TMPET	2.63 V/4.3 V (200 mA·g <sup>-1</sup> )	23,560 mAh·g <sup>-1</sup> (200 mA·g <sup>-1</sup> )	538 cycles (200 mA·g <sup>-1</sup> /500 mAh·g <sup>-1</sup> )	[22]
	Vertically aligned N-doped carbon nanotube	2.5 mM Co-Pc in 2.4 g LiTFSI/1.6 g TEGDME, 4.0 g NMP/1.0 g PVDF-HFP, 0.01 g HMPP/3.0 g TMPET	~ 2.50 V/~ 4.30 V (100 mA·g <sup>-1</sup> )	18652.00 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	120 cycles (250 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[23]
Noble metal-based catalysts	Ru/N,S co-doped graphene	1 M LiTFSI/TEGDME	2.91 V/4.04 V (100 mA·g <sup>-1</sup> )	12,448 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	100 cycles (100 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[24]
	Ir/carbon nanofibers	1 M LiTFSI/TEGDME	2.76 V/4.14 V (100 mA·g <sup>-1</sup> )	21,528 mAh·g <sup>-1</sup> (50 mA·g <sup>-1</sup> )	120 cycles (20 μA/0.1 mAh·cm <sup>-2</sup> )	[25]
	Ru-Cu-G	1 M LiTFSI/TEGDME	—	13,590 mAh·g <sup>-1</sup> (400 mA·g <sup>-1</sup> )	100 cycles (400 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[26]
	COFs-Ru@CNT	1 M LiTFSI/TEGDME	2.64 V/4.45 V (200 mA·g <sup>-1</sup> )	27,348 mAh·g <sup>-1</sup> (200 mA·g <sup>-1</sup> )	200 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[27]
	AuNPs/CNTs	1 M LiTFSI/DMSO	~ 2.75 V/~ 4.5 V (100 mA·g <sup>-1</sup> )	6,399 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	46 cycles (200 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[28]
	RuRh NS/VC72	1 M LiTFSI/DMSO	~ 2.7 V/~ 3.75 V (200 mA·g <sup>-1</sup> )	9,600 mAh·g <sup>-1</sup> (200 mA·g <sup>-1</sup> )	180 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[29]
	RuCo/CNFs	1 M LiTFSI/DMSO	—/3.75 V (100 mA·g <sup>-1</sup> )	17,270 mAh·g <sup>-1</sup> (300 mA·g <sup>-1</sup> )	90 cycles (500 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[30]
	Ir-Te nanowires	DMSO	—/3.75 V (1,000 mA·g <sup>-1</sup> )	13441.8 mAh·g <sup>-1</sup> (200 mA·g <sup>-1</sup> )	200 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[31]
Ru/C	Quinary-molten salt electrolyte	—	44,000 mAh·g <sup>-1</sup> (10 A·g <sup>-1</sup> )	300 cycles (10 A·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[32]	
Nonprecious metal-based catalysts	Mn <sub>2</sub> O <sub>3</sub> -Mn <sub>3</sub> O <sub>4</sub>	1 M LiTFSI/TEGDME	—	19,024 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	69 cycles (100 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[33]
	NiO-CNT	1 M LiTFSI/TEGDME	~ 2.7 V/~ 4.1 V (100 mA·g <sup>-1</sup> )	9,000 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	40 cycles (50 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[34]
	Mo <sub>2</sub> C/CNT	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	~ 2.5 V/~ 3.5 V (20 μA)	1,150 μAh·cm <sup>-2</sup> (20 μA·cm <sup>-2</sup> )	40 cycles (20 μA/100 μAh)	[35]
	Co <sub>0.1</sub> Ni <sub>0.9</sub> O <sub>x</sub> /CNT	1M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	2.68 V/3.94 V (100 mA·g <sup>-1</sup> )	5871.41 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	50 cycles (100 mA·g <sup>-1</sup> /500 mAh·g <sup>-1</sup> )	[36]
	VN-NW GDC	1 M LiTFSI/DMSO	~ 2.75 V/~ 3.75 V (0.05 mA·cm <sup>-2</sup> )	5,915 μAh·cm <sup>-2</sup> (0.05 mA·cm <sup>-2</sup> )	100 cycles (0.05 mA cm <sup>-2</sup> /250 μAh·cm <sup>-2</sup> )	[37]
	Fe-ISA/N,S-HG	1 M LiTFSI 0.3 M LiNO <sub>3</sub> /DMSO	2.78 V/3.95 V (100 mA·g <sup>-1</sup> )	23,174 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	210 cycles (1,000 mA·g <sup>-1</sup> /1,000 mAh·g <sup>-1</sup> )	[38]
	MoS <sub>2</sub> nanoflakes	0.1 M LiTFSI in (EMIM-BF <sub>4</sub> )/DMSO	2.92 V/— (500 mA·g <sup>-1</sup> )	60,000 mAh·g <sup>-1</sup> (100 mA·g <sup>-1</sup> )	500 cycles (500 mA·g <sup>-1</sup> /500 mAh·g <sup>-1</sup> )	[39]

3D NCNT/G: N-doped double-layered 3D CNT/graphite; PVDF-HFP: poly(vinylidene fluoride-co-hexafluoropropylene); NMP: N-methyl-2-pyrrolidinone; HMPP: 2-hydroxy-2-methyl-1-phenyl-1-propanone, TMPET: trimethylolpropane ethoxylate triacrylate; Pc: phthalocyanine; COFs: covalent organic frameworks; VN-NW: vanadium nitride nanowire; GDC: carbon-free gas diffusion cathode; Fe-ISA: implanted single Fe atoms; N,S-HG: N,S-codoped holey graphene; EMIM: 1-ethyl-3-methylimidazolium tetrafluoroborate.

and extending the cycling lifespan (Fig. 3(a)) [5]. The early development of Li-CO<sub>2</sub> batteries relied on various commercial carbon materials, such as Super P and Ketjen black. Recently, a transition to nanoscale carbon materials, including carbon nanotubes (CNTs) and graphene, has drawn much attention owing to their advantages of tuneable structures, better electric conductivity, and higher surface area compared with the commercial carbon materials [5, 15, 40]. For instance, Dai and

co-authors have developed a series of functional carbon materials in Li-CO<sub>2</sub> batteries with a boosted redox kinetics [41, 42]. The intrinsically poor properties of carbon catalysts in terms of catalytic activity for both the CRR and the CER and electrochemical stability, however, make them less promising solely as catalysts. In principle, materials' catalytic properties are primarily controlled by their intrinsic electronic structures and related catalytic reactions should depend on the materials'



**Figure 3** (a) The state-of-the-art catalysts reported in current Li-CO<sub>2</sub> batteries. (b) Illustration of the function of the Ru<sup>II</sup> catalyst in Li-CO<sub>2</sub> electrochemistry. Reproduced with permission from Ref. [46], © Wiley-VCH Verlag 2021. (c) and (d) Fourier-transform infrared spectroscopy (FTIR) spectra of cathodes of the batteries (c) with or (d) without Ru<sup>II</sup> catalyst at different states of charge. (e)–(h) Scanning electron microscopy (SEM) images of ((e) and (f)) discharged and ((g) and (h)) recharged cathodes of the batteries ((e) and (g)) with or ((f) and (h)) without Ru<sup>II</sup> catalyst. Batteries in ((e) and (f)) were discharged to 1,000 mAh·g<sup>-1</sup>. Shallow or deep discharge herein denote that the batteries were discharged to 1,000 or 10,000 mAh·g<sup>-1</sup>, respectively. Reproduced with permission from Ref. [46], © Wiley-VCH Verlag 2021. (i) and (j) Charge density difference of Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> adsorbed on (i) Mo<sub>2</sub>C(001) surface and (j) CNT(002) surface, respectively. The yellow and light blue regions represent the charge accumulation and charge loss, respectively. The isosurface value is set to be 0.007 e·Å<sup>-3</sup>. Reproduced with permission from Ref. [47], © Wiley-VCH Verlag 2018.

electronic interactions with the located environment [43, 44]. Therefore, to endow excellent catalytic performance to the CRR and CER process, it is reasonable to focus on the manipulation of their electronic structures of the catalysts. Meanwhile, alternative catalysts, such as transition and noble metals, as well as their derivatives and compounds, are more interesting than carbonaceous catalysts due to their special electronic structures, particularly their changeable d-bond electron density of metals at Fermi level via electron transfer from hetero atoms [45]. For instance, the first reversible mechanism of pure Li-CO<sub>2</sub> battery electrochemistry was achieved by employing an Ru-based electrocatalyst, which was synthesised by coating an Ru film on a sputtered gold cathode without a carbon substrate [8]. With the help of the Ru catalyst, the charge potential plateau was decreased to around 3.6 V, lower than the thermodynamic potential for the Au-based cathode (> 4.0 V). A ruthenium-complex-based mobile catalyst was also reported to be beneficial to promoting CRR process and delaying carbonate formation, leading to lowered overpotential consequently (Figs. 3(b)–3(h)) [46]. Also, Hou et al. discovered that Mo<sub>2</sub>C catalyst could stably generate C<sub>2</sub>O<sub>4</sub><sup>2-</sup> in lieu of Li<sub>2</sub>CO<sub>3</sub> and carbon species, owing to the formation of a special bond

structure between Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Mo<sub>2</sub>C. Here, the discharge product of Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is more susceptible to decomposition than Li<sub>2</sub>CO<sub>3</sub> [35]. Zhou et al. attributed the mechanism to the electrons transfer from the Mo<sub>2</sub>C to O atoms in Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Because of lacking electrons transfer (Figs. 3(i) and 3(j)), Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> could not exist as a long-term product during the discharge process [47]. Also, a NiO-CNT nanosheet catalyst has been verified in the Li-CO<sub>2</sub> battery, demonstrating a stable 2.7 V discharge platform and a moderate 4.1 V charge platform (based on the Li<sub>2</sub>CO<sub>3</sub> self-decomposition mechanism) [34]. According to the previous studies, the selection and design of electrocatalysts are still serious issues which should be addressed because of the following facts: (i) Pure carbon materials exhibit almost no catalytic activity towards CRR and CER processes; (ii) precious metals and their composites are omnipotent electrocatalysts, yet their large-scale and industrial production is difficult to achieve due to their rare and costly nature; (iii) the catalytic performance of transition metal catalysts cannot fulfil the practical requirements of Li-CO<sub>2</sub> batteries, and only a few electrocatalysts are functional in both CRR and CER processes; (iv) elaborate characterization of the catalytic mechanism and electrochemical process is still lacking.

### 2.1.3 Catalyst deactivation

In principle, a catalyst can continuously increase the rate of a chemical reaction without itself undergoing any permanent chemical change, but catalyst deactivation by poisoning can occur when poisoning molecules or some reactants in the feed or by-products become irreversibly chemisorbed on the active sites, thereby reducing the availability of active sites for the reaction of interest [48]. Because the current Li-CO<sub>2</sub> batteries can only work for dozens of cycles with a low overpotential, even with the application of a state-of-the-art catalyst, it is reasonable to speculate that this is caused by the catalyst deactivation during the cycling. The possible catalyst deactivations in Li-CO<sub>2</sub> batteries may be influenced by two main factors: the self-degradation of the catalyst and variation due to the surrounding environment (discharge product or electrolyte). The self-degradation of catalysts indicates that the catalyst can be deactivated owing to change in the intrinsic factors, including the variation of nanoparticle size, phase distribution, and catalyst nanostructure during the catalytic procedure. For instance, previous work has demonstrated that Ru/TiO<sub>2</sub> catalyst in the CO methanation can be gradually ineffective due to the transformation of Ru particles from an active hemispherical to an inactive flat morphology [49]. Additionally, the variation due to the surrounding environment signifies that the catalyst will be affected by the limited surface accessibility and species contamination. For instance, the discharge products of insulating Li<sub>2</sub>O/Li<sub>2</sub>CO<sub>3</sub> and carbon species can be intensively aggregated and uncontrollably deposited on the cathode surface with the continuous cycling of Li-CO<sub>2</sub> batteries, which may only provide the catalyst with limited surface accessibility, leading to an inferior catalytic performance eventually [6, 8]. More importantly, most of the noble metal catalysts are very susceptible to contamination by sulphur compounds, such as mercapto groups, which are the main product in the solid-electrolyte interphase when using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)-based electrolyte [50–52]. The complexity of catalysts in Li-CO<sub>2</sub> batteries compared with the catalysts in general catalysis reaction suggests that observation of the phenomenon of catalyst deactivation is much more challenging and more attention should be paid to this topic. Obtaining structure-performance relationships of a catalyst under operating conditions is of the utmost importance for their knowledge-based development in Li-CO<sub>2</sub> batteries.

## 2.2 Challenges of the interfaces

The interfaces between the electrode and electrolyte in traditional Li-ion batteries strongly affect their electrochemical performance because the charge transfer causes the electrode redox reactions to begin at these interfaces [53, 54]. Understanding their surface structure, electronic structure, and chemical reactions at the interface is crucial to modulating the interfacial properties and designing a more compatible and stable interface. Except for the electrode-electrolyte interfaces, multiphase interfacial reactions can take place when considering the participation of solid catalyst/products, liquid electrolyte, and CO<sub>2</sub> gas on the cathode of Li-CO<sub>2</sub> batteries, which deserves investigation. Accordingly, the challenges for the interfaces can be exemplified by the triple-phase interfaces on the cathode and the anode-electrolyte interface.

### 2.2.1 Challenges for the triple-phase interface on the cathode

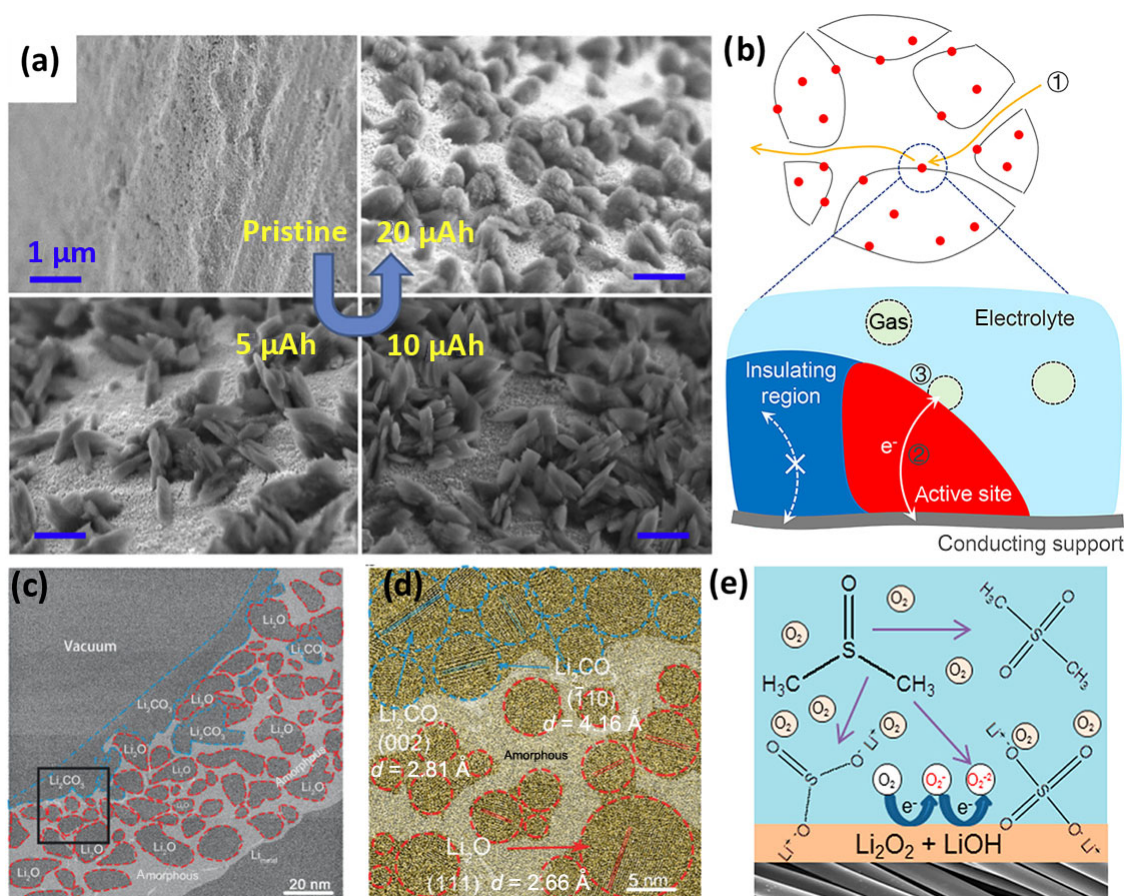
As we stated before, the introduction of gas phase of CO<sub>2</sub> in

metal-CO<sub>2</sub> batteries would complicate the interfacial reactions. Previous work has indicated that, when the 0.5 M LiClO<sub>4</sub>-dimethyl sulfoxide (DMSO) served as the liquid electrolyte in pure Li-CO<sub>2</sub> batteries, the growth of solid Li<sub>2</sub>CO<sub>3</sub> is obviously observed on the cathode surface, which severely passivates the cathode and thus lead to low discharge capacity even battery failure (Fig. 4(a)) [8]. In this case, it is reasonable to speculate that the CRR and CER processes preferentially occur at the cathode electrode in this kind of electrolyte system. When the electrochemical reactions take place at the interface, they prefer to taking place at the so-called triple-phase interfaces (TPIs) between the solid electrocatalyst (where a solid product may be also involved in CER process), the liquid (nonaqueous) electrolyte, and CO<sub>2</sub> reactant, where electrons and ions/molecules can come into continuously contact at catalytic active sites [55]. In other words, the electrocatalytic active sites, which can really boost the redox reactions, are restricted exclusively to those at the TPIs, and to the best of our knowledge, several critical steps are sequentially coupled with each other and significantly affect the reactivity: (i) mass diffusion in the electrolyte toward and from the TPIs; (ii) electron transfer from the cathode to the active sites; (iii) surface reactions involving the adsorption of reactants, interfacial charge transfer, and the desorption of the products at active sites (Fig. 4(b)) [55–57]. Having a clearer identification of the interfacial mechanisms for better reorganization and designation of Li-CO<sub>2</sub> batteries is quite significant. For instance, previous research work indicates that limiting the CO<sub>2</sub> availability by reducing the CO<sub>2</sub> supplement during battery testing can essentially change the conventional electrochemical reaction pathways, which may indicate that the accessibility of the catalyst to high concentrations of CO<sub>2</sub> molecules is crucial to changing electrochemical behaviour [8]. It can be mainly concluded that there are several key factors can impact the interfacial reactions in Li-CO<sub>2</sub> batteries: (i) the mass diffusion of the electrolyte and CO<sub>2</sub> gas; (ii) the electronic conductivity of both the current collector and catalysts at the cathode electrode; (iii) the accessibly interfacial active sites from the catalyst; (iv) the kinetics of the desorption and adsorption processes. Addressing these challenges facing Li-CO<sub>2</sub> batteries requires an advanced understanding of the Li-CO<sub>2</sub> reactions at the TPIs, but this is generally challenging and deficient.

### 2.2.2 Challenges in the anode-electrolyte interface

The solid-electrolyte interphase (SEI) layer formed on Li metal surface plays a key role in supporting the reversible cycling of Li metal batteries by passivating detrimental reactions between the active Li metal and the electrolyte, although uncontrolled SEI formation results in irreversible degradation reactions [1, 58, 59]. We will not comprehensively list all the interfacial problems that have been discovered on Li metal, such as the uneven distribution of components in the SEI layer, because there are already a few excellent reviews covering these phenomena [60, 61]. The major focus here is thus shifted to marshalling the critical problems that exist on the SEI layer for Li-CO<sub>2</sub> batteries.

In Li-CO<sub>2</sub> batteries, the generation of the SEI layer is not only influenced by the decomposition of electrolyte, but also by the reaction between Li and the dissolved CO<sub>2</sub> in the electrolyte [62]. The CO<sub>2</sub> atmosphere of the Li-CO<sub>2</sub> system complicates the issues for the SEI layer due to the presence of reactive species, such as superoxide radicals and oxygen formed during the CER process, promoting the accumulation of



**Figure 4** (a) SEM images of the cathodes harvested at various discharge depths, in comparison with the pristine cathode, the electrolyte is 0.5 M  $\text{LiClO}_4\text{-DMSO}$ . Reproduced with permission from Ref. [8], © Elsevier B.V. 2017. (b) Schematic representation of the gas-involving electrocatalysis. Three critical steps are coupled with each other, including (1) mass diffusion, (2) electron transfer, and (3) surface reaction. Reproduced with permission from Ref. [55], © American Chemical Society 2018. Cryogenic transmission electron microscopy (Cryo-TEM) images and elemental compositions of SEI structure in the blank (EC/DEC) electrolyte acquired using electron dosage  $\approx 100 \text{ e}^- \cdot \text{Å}^{-2}$ : (c) Phase map of the SEI; (d) magnified high-resolution transmission electron microscopy (HRTEM) image of the area marked by the black square in (c). Reproduced with permission from Ref. [65], © Wiley-VCH GmbH 2021. (e) Possible redox reactions in an aprotic  $\text{Li-O}_2$  cell. The superoxide radicals are considered as a strong Lewis base and electron-transfer agent, which may attack the electrolyte to produce byproducts. Reproduced with permission from Ref. [69], © American Chemical Society 2013.

insulating by-products ( $\text{Li}_2\text{O}$ ,  $\text{Li}_2\text{O}_2$ ,  $\text{Li}_2\text{CO}_3$ , etc.) on the anode surface. Although previously published results indicated that the  $\text{Li}_2\text{CO}_3$  in SEI layer could protect the Li metal from corrosion by other reactive species in the electrolyte, its stability in the SEI layer is a challenge, because the decomposition products of  $\text{Li}_2\text{CO}_3$  would continuously react with the electrolyte, leading to a porous SEI structure (Figs. 4(c) and 4(d)) [63–65]. Additionally, during cycling, the crossover of  $\text{CO}_2$  molecules from the cathode side and contaminations from the ether-based electrolyte (such as  $\text{H}_2\text{O}$  or redox mediator) to the anode side will have a detrimental effect on the performance of  $\text{Li-CO}_2$  due to direct reactions [6, 66]. Recently, the effect of  $\text{CO}_2$  crossover on the Li metal anode has been probed in a sulfone-based solvent system. With the help of X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) technique, Asadi et al. discovered that the Li foil could react with dissolved  $\text{CO}_2$  molecules and side-products that came from the electrolyte decomposition during cycling [67]. Zhou and co-authors also observed the phenomenon of  $\text{CO}_2$  gas crossover to Li anode in ether based electrolyte [64]. Accordingly, how to construct a stable SEI layer to alleviate the detriment from the introduction of  $\text{CO}_2$  gas in  $\text{Li-CO}_2$  batteries is still an open question.

### 2.3 Challenges for the liquid electrolyte

Designing a suitable electrolyte with high ionic conductivity, high ion migration, high stability, sufficient  $\text{CO}_2$  solubility, and excellent mechanical properties is desirable for practical  $\text{Li-CO}_2$  batteries. To fulfill the requirements in different scenarios, various electrolyte candidates have been developed and tested in  $\text{Li-CO}_2$  batteries, including liquid electrolytes (aqueous or organic-based), solid-state electrolytes (glass, ceramics, and polymers), hybrid electrolytes (liquid + solid), and ionic liquid electrolytes (e.g., 1-ethyl-3-methylimidazolium chloride) [10]. Although a great quantity of studies on  $\text{Li-CO}_2$  batteries are concentrated on organic-based liquid electrolytes, they still suffer from some intrinsic drawbacks in practical battery systems, such as the possible leakage, evaporation, and flammability for the semiopen cell structure [68]. Among the alternatives, solid-state or quasi-solid-state electrolytes can overcome the aforementioned obstacles and thus enhance the security; however, the large impedance of solid–solid interfaces between electrode and electrolyte leads to a relatively low ion conductivity and should be resolved before practical application. It is still challenging to develop and design a suitable solid-state electrolyte with high ionic conductivity and well interfacial compatibility in Li based batteries. Electrolytes based on ionic

liquids were regarded as very promising alternatives due to their excellent chemical/electrochemical stability toward intermediate product, yet the rapid development of ionic liquid is still hindered by the poor ionic conductivity and high viscosity in Li-CO<sub>2</sub> batteries. Since all electrolytes have more or less issues that must be addressed to achieve a highly reversible Li-CO<sub>2</sub> battery with long cycle life, we will mainly emphasise the prevalent liquid electrolytes in this part. In terms of liquid electrolyte, both the solvent and salts have a tremendous influence on the electrochemical performance of Li-CO<sub>2</sub>.

### 2.3.1 The problems associated with the solvents

In Li-CO<sub>2</sub> batteries, solvent molecules coordinate with Li<sup>+</sup>/CO<sub>2</sub> to facilitate Li<sup>+</sup>/CO<sub>2</sub> transportation through Li-CO<sub>2</sub> batteries and electrochemical reactions between CO<sub>2</sub> gas and Li metal anode. The diffusion of both CO<sub>2</sub> and Li<sup>+</sup> in the solvent can determine the kinetics of the batteries. Therefore, one of the criteria for solvent selection is good CO<sub>2</sub> solubility. Additionally, various aprotic solvents have been investigated for use in Li-CO<sub>2</sub> batteries including carbonates, ethers, and sulfones. Notably, owing to the negative electrochemical potential of Li metal anode (-3.04 V vs. standard hydrogen electrode (SHE)), almost all nonaqueous electrolytes will spontaneously react with Li metal to form the passivation SEI layer through a series of decomposition reactions, leading to unsatisfactory cycling performance due to electrolyte consumption. In other words, electrolyte decomposition, especially the decomposition of solvents, is correlated with the dramatic capacity fading of Li-based batteries. More importantly, the decomposition of electrolytes may be further accelerated owing to the highly reactive oxygen-containing substances generated in the redox reactions of Li-CO<sub>2</sub> batteries. For instance, previous work has demonstrated that the oxygen-containing substances, such as superoxide radicals, are considered as strong Lewis bases and electron-transfer agents, which can alleviate the problems of carbonate-based solvents (such as propylene carbonate), which suffer from a ring-opening reaction and generate different irreversible by-products (e.g., CO<sub>2</sub>, H<sub>2</sub>O, and Li-carboxylates) [69]. This failure mechanism may also apply to the sulfones-based electrolyte, such as DMSO solvent, although it was believed to be a promising solvent in Li-CO<sub>2</sub> batteries due to its high CO<sub>2</sub> solubility, high conductivity, and low viscosity (Fig. 4(e)). Yet, the formation of a stable SEI in DMSO solvents is still challenging. Therefore, both carbonate and DMSO-based electrolytes are less promising to be directly applied to pursue highly reversible Li-CO<sub>2</sub> electrochemistry. Alternatively, ether-based electrolytes, especially tetraethylene glycol dimethyl ether (TEGDME), have drawn much attention because of their relatively high oxidation potentials (> 4.5 V vs. Li/Li<sup>+</sup>) and stability against superoxide anions owing to the lack of electron-withdrawing functional groups in their molecular structures [70]. Yet, the ether solvents are susceptible to auto-oxidation. Bruce and co-workers found that the presence of highly electrophilic Li<sup>+</sup> in aprotic electrolytes can band with electronegative oxygen atoms in ether solvents in Li-air batteries, thereby accelerating the decomposition of polyether molecules through the conversion of alkoxy groups into better leaving groups [71]. This effect may be deteriorated in pure Li-CO<sub>2</sub> batteries. In addition, water molecular is a representative contaminant in ether-based electrolytes, which may react with CO<sub>2</sub> and Li metal to produce irreversible byproducts, such as hydroxides, peroxides, and protonated superoxides [72]. The

varied decomposition reactions of the electrolyte may be further enhanced in the presence of these byproducts.

More importantly, the donor number (DN) of a solvent has a great influence on the discharge process, as previously stated [3]. It was found that the formation of Li<sub>2</sub>CO<sub>3</sub> in O<sub>2</sub>-assisted Li-CO<sub>2</sub> batteries proceeded primarily via an “electrochemical solution route (high capacity but less stability)” in high-DN solvents, whereas in low-DN solvents, Li<sub>2</sub>O<sub>2</sub> reacted with CO<sub>2</sub> to form Li<sub>2</sub>CO<sub>3</sub> via a “chemical surface route (low capacity but high stability)” [3]. However, the growth of solid Li<sub>2</sub>CO<sub>3</sub> was obviously observed on the cathode surface in the 0.5 M LiClO<sub>4</sub>-DMSO electrolyte, in which DMSO is a kind of solvent with high DN value. Actually, the impact of the DN number on determining the mechanism pathway in pure Li-CO<sub>2</sub> batteries needs more investigation. The selection of the solvent also requires consideration of the trade-off between the capacity and the electrolyte stability.

In summary, the main problematic issues associated with the solvents in Li-CO<sub>2</sub> batteries can be concluded as follows: (i) the parasitic reactions of solvents with both CO<sub>2</sub> gas and Li metal. (ii) Continues decomposition of solvents to form unstable SEI layer. (iii) Unclear mechanism of changing the DN number of solvents on electrochemical performance.

### 2.3.2 The problem associated with the salts

The electrolyte salts are as important as the solvent for the stability and ionic conductivity of the electrolyte, and they may participate in SEI formation. The traditional lithium salts generally contain LiBF<sub>4</sub>, LiClO<sub>4</sub>, LiTFSI, lithium bis(fluorosulfonyl)imide (LiFSI), LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, etc. [68]. The state-of-the-art LiPF<sub>6</sub> salt in Li ion batteries has been excluded in Li-CO<sub>2</sub> batteries, however, because it is unstable with the attack of oxygen intermediates generated during redox reactions [73]. Inspired by the successful electrolytes applied in Li-air batteries, the vast majority of electrolytes in Li-CO<sub>2</sub> batteries employ relatively limited choices, such as LiTFSI and LiCF<sub>3</sub>SO<sub>3</sub> [68]. Unfortunately, the problem of the poor stability of Li metal in LiTFSI-based electrolyte under CO<sub>2</sub> atmosphere remains unsettled, which causes that the conducting lithium salt still represents as one of the bottlenecks in stabilizing the operation of Li-CO<sub>2</sub> batteries [74].

## 2.4 Challenges for the anode

Stabilizing the plating/stripping process of the Li metal anode is a key aspect in achieving not only long-life Li metal batteries but also Li-CO<sub>2</sub> batteries. Unlike Li-ion batteries, Li-CO<sub>2</sub> batteries utilize Li metal foil as their anode material. The electron and ion transfer at the electrolyte/electrode interface is always involved in charge and discharge processes of an Li-CO<sub>2</sub> battery. The instability of the SEI layer has always been a problem, as we have discussed above. Apart from the issues of the protective SEI layer, the Li metal is further suffering from huge dendrite growth on its surface. The dendrites may continuously grow and consequently penetrate the separator film to result in a short circuit of the cell and serious safety problems within the Li-CO<sub>2</sub> batteries. Previous work indicates that the growth of dendrites is closely related to the nonuniform nucleation of Li metal, since the actual electrode interface cannot be atomically smooth. Dendrites can gradually detach from the Li anode to form “dead lithium”, leading to the loss of anode materials. Notably, more attention should be paid to the correlation between electrolyte solvents or additives with different DN values and the Li metal. Previous work indicates



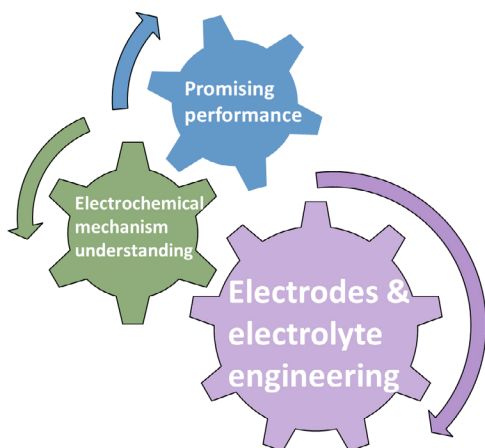
that a few solvents with high DN values are instable to the Li metal, such as 1-methylimidazole, which will dramatically affect the composition of the SEI layer and Li dendrite formation [75]. Therefore, the formation of an unstable SEI layer and the dendritic growth of Li metal are major hurdles to be conquered for the development of practical Li-CO<sub>2</sub> batteries.

## 2.5 Challenges for large-scale Li-CO<sub>2</sub> batteries

As can be seen, various types of liquid electrolytes, electrocatalysts, and additives have been reported as indispensable components that can dramatically improve electrochemical performance with thousands of milliamp-hours of specific capacities over hundreds of cycles [23, 26]. However, these numbers have mostly been calculated from the energy per the mass of only the active material and have excluded those of other required components (such as binders, and electrolytes). The practical cell-scale cyclability and energy density of the Li-CO<sub>2</sub> battery system have not been reported and established. In addition, for currently reported Li-CO<sub>2</sub> batteries, CO<sub>2</sub> gas is supplied to the test container from a compressed gas cylinder under laboratory testing, which is hardly used for practical applications. To further realize the practical deployment, applying for CO<sub>2</sub> gas captured from the greenhouse gases or industrial waste gases is one of the key challenges. Reports of a series of novel materials for CO<sub>2</sub> capture with high efficiency, low cost, and high-performance CO<sub>2</sub> fixation and conversion under real conditions are still lacking. In short, although the Li-CO<sub>2</sub> batteries appear to be a promising blueprint for a sustainable development society, the proposed restrictions listed here that are blocking the achievement of highly efficient CO<sub>2</sub> and high energy density fixation are worth attention and should be highlighted.

## 3 Guidelines for future Li-CO<sub>2</sub> batteries

In order to realize the intrinsic advantages of Li-CO<sub>2</sub> batteries, high energy density and highly efficient CO<sub>2</sub> fixation, the application of Li-CO<sub>2</sub> batteries demands recruitment of a highly efficient catalyst, an optimized electrolyte formula, a stabilized interface, and a dendrite-free Li metal anode. In this section, to address the challenges with regard to the uncertain mechanism, ineffective catalyst selection, the susceptible interphase, and the rapid failure of Li metal, the following directions call for extensive attention, which is expected to lead to essential advances in future (Fig. 5).



**Figure 5** The schematic illustration of the catalyst design toward Li-CO<sub>2</sub> batteries with highly efficient CO<sub>2</sub> fixation and energy storage.

## 3.1 Approaches for next-generation cathode design

The ideal cathode in Li-CO<sub>2</sub> batteries should meet the requirements of high catalytic activity, high electronic and ionic conductivity, rational structural design, rapid CO<sub>2</sub> diffusion, fast intermediate/product separation, and high working stability. The use of a functional catalyst, as the most important part in the cathode electrode, has been proven to be an efficient way to achieving reversible reaction pathways for LiCO<sub>3</sub> with C during the charging process [10, 76]. Therefore, in this part, we will mainly focus on the design of novel functional catalysts. In consideration of the challenges faced by the current catalysts, our strategies will be proposed as follows: the catalyst screening, the catalyst engineering, and the *in situ* characterization of the catalytic process.

### 3.1.1 Catalyst screening

Although only a few catalysts have been validated in aprotic Li-CO<sub>2</sub> batteries, there is great progress in developing highly efficient aqueous-based CO<sub>2</sub> electrochemistry. For instance, it has been widely recognized that a vast number of electrocatalysts are promising for the aqueous-based CRR reaction, such as Bi, Sn, and Pd through a 2 e<sup>-</sup> process, Cu<sub>2</sub>O and SnO<sub>2</sub> through a 6e<sup>-</sup> process, and Cu through an 8e<sup>-</sup> process, while Ir and Ru-based catalysts are efficient for the CER process in aqueous-based electrolytes [77]. In addition, some catalyst candidates used in CO<sub>2</sub> photoreduction is also received tremendous attention to be another appealing solution in Li-CO<sub>2</sub> batteries, such as TiO<sub>2</sub> and CdS, which hold the promise in photoelectrocatalytic Li-CO<sub>2</sub> batteries, although the potential application of these devices needs to be further examined [78]. Besides, the introduction of bifunctional electrolytes will not only change the discharge/charge mechanism, but also reduce the overpotential of the CRR and CER process, thus providing excellent reversibility. Since Ru-based catalysts are effective in reversible CER processes in aprotic Li-CO<sub>2</sub> batteries, it is thus interesting to examine the Bi or Sn, even metal oxides in aprotic Li-CO<sub>2</sub> batteries. Additionally, the cathode reaction of the Li-CO<sub>2</sub> batteries inevitably involves both CRR and CER processes, which require different electrocatalysts and correspond to the discharge potential and the charge potential, respectively. Screening out a bifunctional electrocatalyst that possesses activities toward both the CRR and CER reactions will be more promising. Integrating CRR/CER catalysts in the cathode of Li-CO<sub>2</sub> batteries would endow the cathode electrode with bifunctional catalytic activity. Potential concepts may be involved bimetallic catalysts and so on.

### 3.1.2 Catalyst engineering

To artificially endow materials with desirable properties that they do not exist originally possess through material engineering is not only a challenging and intriguing task to the research fields, but also is conducive to potential application. Although the pursuit of highly efficient catalysts in Li-CO<sub>2</sub> batteries is still challenging, catalyst engineering will be served as an approach to synthesis the catalyst with desirable structure, dimensions, physicochemical properties, and performance. Since the electronic structure can dramatically determine the catalytic sites of the electrocatalyst and the surrounding environment has a significant influence on the catalytic activity, we will herein focus on the available protocols for manipulating these two aspects, which can be roughly classified

into two parts: intrinsic factors (such as doping effect, defect effect, and framework-based engineering) and extrinsic factors (such as porosity, phases, and dimensions).

### 3.1.2.1 Heteroatom doping effects

Despite pristine carbon materials have intrinsically poor activities for either CRR or CER process, heteroatoms, such as B, N, O, S, and F, can dope the carbon materials to tailor their electronic structure and thus donate the catalytic ability to pristine carbon materials. It is generally believed that doped carbons will reduce the band gap, regardless of whether the doping involves single atoms or multiple atoms, along with promotion of electron mobility within the carbons and optimization of donor–acceptor functions. Here, the definition of the band gap is the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). As a result, the heteroatom-doped carbon materials hold the potential to change the reaction pathways of the CRR and the CER processes and manipulate the absorption/desorption of intermediates or discharge products. Among all the heteroatom doped carbons verified so far, N-doped carbon has received the most attention in Li–CO<sub>2</sub> batteries because the kinetics of both the CRR and the CER processes can be accelerated by certain N–C species, such as pyridinic sites [79]. Except for carbon substrates, the heteroatom doping strategy can be further extended to other substrates, such as transitional metal oxide and C<sub>3</sub>N<sub>4</sub>, which hold the potential in pure Li–CO<sub>2</sub> batteries or photo-assisted Li–CO<sub>2</sub> batteries.

Among the N doped carbon materials, jointly atomic-metal and nitrogen-doped carbons (MNCs) are currently one of the most prevalent non-metallic materials, since they are capable of reducing CO<sub>2</sub> in aqueous electrolytes selectively. In these materials, the N atoms are always introduced and combined with C atoms, establishing a large number of varied chemical functionalities due to specific structures, to which the metal atoms coordinate forming the genuine catalytically active sites (M–N–C) in the catalytic process. Importantly, there is a growing interest in MNCs as electrocatalysts for the CRR and CERs in aqueous-based electrolytes, given their remarkably high selectivity and activities for CO<sub>2</sub> fixation to value-added chemicals and products. More importantly, the versatile MNCs acquired through facile synthesis procedures will hold the promise for large-scale application. In this case, there are several advantages of MNCs in Li–CO<sub>2</sub> batteries: (i) the existence of doped carbon substrates and M–N–C will provide multiple active sites for catalysing the CRR and CER processes; (ii) the atom dispersion achieved in MNCs will maximum the atom utilization; (iii) the chemical surrounding environment of MNC will be easily tuneable; (iv) clear active centres will be beneficial for mechanism investigation and performance regulation [80]. Because of more and more studies showing that the metal centre plays a crucial role in determining the catalytic performance of the material, the metals that can effectively catalyze both CRR and CER procedures will be interesting for Li–CO<sub>2</sub> batteries, such as Ni–Ru MNC, Co–Ru MNC, and Bi–Sn MNC, despite the reaction mechanism and electrochemical performance need to be further investigated.

Except for the non-metallic substrates, alloys, containing two or more metallic elements, have received much more attention because of their highly conductive and intriguing catalytic effects [38]. They will not only integrate the promising properties of each of the different component, but also endow

the alloy with synergistic effects due to the electronic interactions between them. How to select from the massive alloy space suitable as candidates that have at least a chance of being suitable catalysts in Li–CO<sub>2</sub> batteries is still challenging. A hint provided here is that researchers can be inspired by simulation results with regard to the catalysts for efficient CRR and CER processes. Absolutely, subsequent experimental validation may then confirm whether these candidates are advantageous catalyst materials, while the electrochemical process should be further understood.

Also, the fabrication of versatile and effective metal-based catalysts has been the hotspot in Li–CO<sub>2</sub> batteries owing to their unique electrochemical properties. For example, transition-metal-based catalysts own excellent adsorption properties and precious metals own extraordinary catalytic activities toward the formation and decomposition of products. For instance, Chen and co-authors proposed a new bimetallic catalyst, that is, alloyed Ru<sub>82</sub>Co<sub>18</sub> nanoparticles evenly dispersed on carbon nanofibers, which demonstrates a remarkably reduced charge voltage of 3.75 V and maintains a stable cycling performance of over 90 cycles [30]. In addition, the RuRh alloy nanosheets proposed by Guo and co-workers were able to effectively activate CO<sub>2</sub> reduction and evolution reactions. The enhanced electrochemical performance can be attributed to the unique electronic structure because alloying Ru with Rh can impose a high activity in electron transfer of surface Ru [29]. Meanwhile, Ge et al. developed a Co-doped MnO<sub>2</sub> catalyst, which exhibits a low overpotential (~0.73 V) and a cyclability (over 500 cycles at a current density of 100 mA·g<sup>-1</sup>). Based on *in situ* experimental observations in combination with density functional theory calculations, they attributed the excellent performance to the high conductivity, the hierarchical channels, the unique Co interstitial doping, which might be of benefit for the diffusion of CO<sub>2</sub>, the reversibility of Li<sub>2</sub>CO<sub>3</sub> products, and the prohibition of side reactions between the electrolyte and the electrode. This result further highlights that the heteroatom doping effects can be widely used in various catalysts to engineer the electrochemical improvement of performance of Li–CO<sub>2</sub> batteries.

### 3.1.2.2 Defect effects

In terms of modulation of the electronic structures, engineering defects in materials shares a similarity with the strategy of heteroatom doping, which has been realized in various electrode materials for energy storage applications [59, 81–83]. In general, defects are inevitable in materials due to the imperfect materials preparation/synthesis processes, and they can be generally classified into point defects, dislocations, grain boundaries, or voids. Considering the fact that most of defects are correlated with superior properties of materials, different defects have intentionally been introduced into materials through various methodologies, such as thermal treatment or physical irradiation. For example, the introduction of oxygen vacancies has been successfully accomplished to optimize the electronic structure of intrinsic NiO nanosheets in Li–CO<sub>2</sub> batteries. During the CRR process, unpaired electrons delocalized on Ni orbitals can be spontaneously transferred to the carbon 2p orbital in CO<sub>2</sub>, which boost the electrochemical CO<sub>2</sub> reduction with reduced energy barriers. The NiO with O vacancies also promotes the transportation of reactants and/or intermediates, finally demonstrating a Li–CO<sub>2</sub> battery with high capacity, low over-potential, and excellent cycling stability [84]. Indeed, defect engineering is a promising method to modulate materials

to endow them with excellent performance for Li-CO<sub>2</sub> batteries, and the underlying mechanism must be paid more attention to enable us to focus on the specific active sites and identify the true reaction pathways. Notably, previous first-principles calculations reveal that the cation vacancies can serve as active sites to efficiently catalyze the electrochemical process, but the introduction of cation vacancies in transition metal/metal oxides has been rarely reported in Li-CO<sub>2</sub>, which should be emphasized in the following research [85].

### 3.1.2.3 Framework based engineering

Metal-organic frameworks (MOFs), assembled by the connection of metal ions or clusters by organic ligands, have potential for CO<sub>2</sub> capture, CO<sub>2</sub> separation, and CRR process, owing to their large surface area, high porosity, tuneable pore size, and structural versatility. Previous works identified that the M-MOFs-74 series were able to promptly take up the CO<sub>2</sub> molecules, efficiently reduce the charge overpotential, and regulate the Li<sub>2</sub>CO<sub>3</sub> deposition [86]. In addition, metal phthalocyanines with similar structures to the MOFs can also be employed as a protocol to design cathode catalysts in Li-CO<sub>2</sub> batteries. In addition, MOF and metal phthalocyanines can be served as precursors to produce carbon-based materials, which still hold the potential for Li-CO<sub>2</sub> batteries.

Notably, with diverse connectivity, organic ligands, and metal nodes, more than 20,000 MOFs are currently available, while the development of suitable catalysts toward Li-CO<sub>2</sub> batteries is still ongoing [87]. Because both the metal moieties and the organic ligands greatly contribute to the electrocatalytic activity in MOFs materials, knowledge of how to wisely tailor a MOF for both the CRR and the CER processes is still lacking [88]. The factors influencing the metal, such as the redox activities, and metal-cation exchange, and oxidation states need to be comprehensively considered. Notably, the poor electronic conductivity of MOFs may be one of the factors holding back the design of pristine MOFs with high electroactivity, which should be deliberately improved to fulfil the requirements for Li-CO<sub>2</sub> battery applications. Also, post-mortem analysis of MOF based catalysts will be beneficial to better understanding their structural variation during battery testing, accumulating knowledge for a necessary understanding of how further engineer MOFs with excellent electrocatalytic performance.

### 3.1.2.4 Extrinsic factors

Extrinsic factors of materials, herein defined as their physical geometry, have always been receiving attention in energy storage [89–94]. In terms of Li-CO<sub>2</sub> batteries, the extrinsic factors are mainly indexed to the pores, dimensions, and phases of the aimed catalysts.

As we stated before, the Li-CO<sub>2</sub> batteries are typical electrochemical systems that are relied on three-phase reactions, that is, a gas-liquid-solid integrated system. Electrochemical performance is thus closely related to mass transfer, which includes electrolyte infiltration, product distribution, and CO<sub>2</sub> gas diffusion [95]. Engineering the catalysts with specific structures will be conducive to mass transfer to enable rapid CO<sub>2</sub> and electrolyte diffusion, fast electron transfer, and the accommodation of bulky discharge products, leading to excellent kinetics parameters. For instance, Dai's group developed a series of innovative three-dimensional (3D) holey graphene networks with rapid mass transfer parameters, which highlighted the porous and dimension advantages on performance improvement [22, 38, 96]. In addition, based on the electrochemical

performance shown in Li-CO<sub>2</sub> batteries, Xing and co-workers also identified that the pore shape may be the most influential feature as two-dimensional (2D)/3D mesopores were better than ink-bottle/one-dimensional (1D) mesopores [97]. Upon our understanding, it can be expected that a 3D orderly interconnected porous network will be suitable for enhancing the overall performance.

In addition, the phase of catalysts will affect the electrochemical performance due to the change of accessible active sites. For instance, solid catalysts mostly feature a periodical and fixed arrangement of atoms with plenty of local inhomogeneity, including different crystal facets, lattice defects, and uneven element distribution, while liquid catalysts can greatly homogenize the active sites. The liquid catalyst is believed to also avoid the deterioration of active sites by the accumulation of the solid discharge product during cycling [98]. Nevertheless, the development of liquid catalysts is still in its infancy, so more efforts are required on this concept. The selection criteria should be mainly focused on the room temperature liquid metals, such as Ga based alloys. It should be pointed out that the development of novel synthesis methods to achieve efficient catalysts with specific geometries features still requires in-depth investigation. The advantages of tuning catalyst geometry on the decomposition of the discharge product and controlling the morphology/geometry of discharge products need to be systematically understood.

### 3.1.3 The *in situ* characterization of the catalytic process

Detailed characterization of the Li-CO<sub>2</sub> batteries, especially the chemical processes of catalysts and electrochemical procedures at the solid-liquid-gas interfaces, will provide sufficient information to reveal the underlying mechanism, and in turn, give feedback to the design of functional catalysts in cathode electrodes. Thanks to the development and application of various *in situ* or *operando* characterizations, advances in understanding these technics in characterizing the electrochemical procedure have been made [53, 54, 99]. Unlike the *ex situ* characterization techniques, which only focus on the components from the disassembled cell, *in situ* and *operando* observations will allow elaborate characterization of the reactions in the assembled state without interference damaged by exposure to a new atmosphere. Considering the complexity of interfacial reactions in Li-CO<sub>2</sub> batteries, *in situ* characterizations should be mainly focused on techniques that are sensitive to the interface changes and offer high spatial and temporal resolution, as well as compatible with the electrochemical reactions. Potential techniques, such as *in situ* X-ray absorption spectroscopy, surface enhanced Raman spectroscopy, ultraviolet-visible spectroscopy, electron paramagnetic resonance spectroscopy, ambient-pressure XPS, and microscopy techniques will be valuable to detect the local change of cathode, catalysts, and interface in various research projects [100]. Notably, these techniques may be affected by different experimental conditions, and complementary or corroborative information cannot be obtained. Developing innovative reactors or holders for synergetic and synchronous coupling of these techniques will be more promising.

## 3.2 New electrolyte chemistry

As we are all aware, a great many electrolytes with different states, such as liquids, solids, quasi-solids have been studied and developed, and some excellent review papers have contributed to more comprehensive understanding and discussion [6, 10].

In this section, we purposely focus on the general liquid state electrolyte and a brief guideline for electrolyte selection will be provided. In terms of liquid electrolytes, the solvents or salts alone have an impact on the performance of Li-CO<sub>2</sub> batteries; however, the design of suitable electrolytes needs to consider the electrolyte as a whole system. Here, the design of new electrolyte formulas will be mainly focused on two directions: changing the reaction pathway of Li-CO<sub>2</sub> batteries and avoiding the continuous decomposition of electrolyte.

### 3.2.1 Changing the reaction pathway of Li-CO<sub>2</sub> batteries

As previous work introduced, there will be two main mechanisms for Li<sub>2</sub>CO<sub>3</sub> (discharge product) formation in O<sub>2</sub>-assisted Li-CO<sub>2</sub> batteries, one is the *electrochemical solution route*, and another is the *chemical surface route*. In our opinion, changing the formation mechanism from *chemical surface route* to *electrochemical solution route* could decrease the direct contact of discharge products with the cathode electrode and probably reduce the parasitic reactions, especially for the reaction between intermediate superoxide radicals and catalysts. To this end, manipulating the DN numbers of solvents/additives will affect the solubility of Li<sub>2</sub>CO<sub>3</sub> formation and dictate the growth of Li<sub>2</sub>CO<sub>3</sub> either in electrolyte solution or on the electrode surface. Many solvents or additives with high DN number will be promising, such as 1-ethylimidazole and alcohols. Amines are broadly recognized as another kind of good scrubbing agents in CO<sub>2</sub> capturing facilities, which could be served as a potential candidate in Li-CO<sub>2</sub> batteries [101]. In addition, new types of RMs that can convert the solid Li<sub>2</sub>CO<sub>3</sub> to be a soluble state are also welcome [46]. It should be pointed out that, whatever new solvents or additives will be selected for the Li-CO<sub>2</sub> batteries, their influence on the lithium metal anode should be firstly understood and characterized, in order to minimize the potential side reactions and achieve stable and reversible Li-CO<sub>2</sub> batteries.

### 3.2.2 Avoiding the continuous decomposition of electrolyte

The decomposition of electrolytes is mainly induced due to attack by the discharge products and intermediates as well as the active Li metal, in which the decomposition will be severer if the charging process is highly voltage-demanding. Among the strategies discovered to stabilize electrolytes, highly concentrated electrolytes (HCEs) would be more promising for avoiding attack by Lewis bases and electron-transfer agents, owing to a shortage of sacrificial anions and available reactive solvents [102]. The HCEs can provide a superior electrochemical performance, which is mainly attributed to the increment of the high Li<sup>+</sup> on the surface of anode side and enhancing the reductive stability of electrolytes. Unfortunately, their practical applications are still obstructed by their high viscosity, high material expense, and poor wettability on electrodes and separators. Although many efforts have been undertaken to develop a new class of localized high-concentration electrolytes (LHCEs) by introducing additives to dilute the HCEs, such as hydrofluoroether to overcome the aforementioned issues associated with HCEs, it is still questioned to be used in Li-CO<sub>2</sub> batteries with a high CE behaviour.

Besides, optimizing the electrolyte by introducing different functional groups has been recently received much attention to produce a stabilized SEI layer on Li metal or regulate the high voltage stability of electrolyte, as in the case of all-fluorinated electrolyte or F functionalized ethers [103, 104]. These interesting concepts have expanded our views on electrolyte behaviour,

which will promote the development of strategies for safe and long-lifespan Li-CO<sub>2</sub> batteries in turn.

### 3.3 Stabilizing the Li metal anode

As an indispensable component in Li-CO<sub>2</sub> batteries, the lithium metal anode suffers from tremendous disadvantages related to the continuous growth of the SEI layer, Li dendrite formation, and corrosion by intermediates/products, which increase the CRR/CER polarization and result in cell death eventually. Therefore, building a robust Li metal anode is a key to opening up stabilized metal-CO<sub>2</sub> batteries. The study of Li metal anode in Li-CO<sub>2</sub> batteries is still in its early stage, however, and only several studies have paid attention to the intentional protection of Li metal. For instance, a commercially available Li-ion conductive ceramic membrane (Li<sub>1+x+y</sub>Al<sub>x</sub>Ti<sub>2-x</sub>Si<sub>y</sub>P<sub>3-y</sub>O<sub>12</sub>) was inserted into the battery devices during assembly to protect Li anode from attack by quinones additives and aggressive cathode [15]. Considerable efforts have been devoted to alleviating the dendritic growth issue in metal anode [105]. Along with the concept of electrolyte optimization that we discussed above, most of the strategies can be classified as construction of an artificial SEI, current collector modification, and separator film improvement [58, 106–108]. Apart from these approaches, the concept of a dendrite-free anode, such as liquid NaK alloy would be an alternative candidate to replace the concept of Li metal to assemble NaK-CO<sub>2</sub> batteries or serve as an artificial liquid SEI layer on Li metal to obtain a composite Li anode. As expected, the protected Li metal would contribute the Li-CO<sub>2</sub> batteries to a long cycle life with enhanced stability.

### 3.4 New concepts toward practical Li-CO<sub>2</sub> batteries

Capturing the CO<sub>2</sub> gas from industrial gas atmosphere or greenhouse gases will promote the practical application of Li-CO<sub>2</sub> batteries. Inspired by the concept in fuel cells and general CO<sub>2</sub> electrolysis, the introduction of gas diffusion layers (GDLs) seems promising to enhance CO<sub>2</sub> gas transport to the electrochemical interface. Unlike the typically GDLs that are formed from polytetrafluoroethylene (PTFE)-treated porous carbon membranes, MOF-based membrane will be more promising for selection as GDLs due to its excellent ability to capture CO<sub>2</sub>, although more work should be done to validate this kind of concept [56]. In addition, the electrochemical testing of Li-CO<sub>2</sub> batteries must employ a small box or a container as a CO<sub>2</sub> gas reservoir, where the coin cells have several holes inside. This kind of design can only be practical in the laboratory research, which is hard to be extended to large-scale application. How to design a novel cell configuration for practical utilization is still perplexing researchers all the time.

In addition, the temperature has a significant impact on the electrochemical performance of Li-CO<sub>2</sub> batteries. Previous works have demonstrated that the electrochemical performance can be boosted under high temperatures because of the quick decomposition kinetics of the solid Li<sub>2</sub>CO<sub>3</sub> at high temperatures, but the safety issues (such as gas leakage due to the less hermetic cell seal) and an additional energy input caused by high temperature should be fully considered [109, 110]. In contrast, low temperature operation condition for Li-CO<sub>2</sub> batteries will inevitably lead to inferior performance due to the sluggish kinetics of CER and CRR processes, a decreased electrolyte conductivity, and poor electrode/electrolyte interfaces

[111]. However, utilizing Li-CO<sub>2</sub> batteries at low temperatures is indeed meaningful in some areas, such as aerospace exploration on the Mars, which is filled with CO<sub>2</sub> concentration of up to 96% in the atmosphere, but with an average temperature of approximately -60 °C. It is necessary to design Li-CO<sub>2</sub> batteries that could efficiently work at either low or high temperature environments for future realistic application, but the corresponding problems must be properly tackled.

Most Li-CO<sub>2</sub> batteries operated in a pure CO<sub>2</sub> atmosphere, because the presence of other constituents in ambient air (including H<sub>2</sub>O and O<sub>2</sub>) would alter the reaction pathway. The involvement of oxygen in Li-CO<sub>2</sub> batteries will increase the discharge capacity because O<sub>2</sub> can easily react with Li metal to form the Li<sub>2</sub>O<sub>2</sub>; however, the participation of O<sub>2</sub> in Li-CO<sub>2</sub> batteries will make the discharge mechanism of Li-CO<sub>2</sub> batteries complicated. Especially, the generation of intermediates such as O<sub>2</sub><sup>2-</sup>, O<sub>2</sub><sup>-</sup>, and singlet oxygen (<sup>1</sup>O<sub>2</sub>) may drastically decompose the organic electrolyte, leading to rapid performance fading when compared to the Li-CO<sub>2</sub> batteries in pure CO<sub>2</sub> [112]. It is no doubt that the corrosion of Li metal will be further aggravated in Li-O<sub>2</sub>/CO<sub>2</sub> batteries. To deal with issues related to O<sub>2</sub> introduction, Zhang and co-authors proposed a trifunctional ether-based mediator into the electrolyte to collect reactive O<sub>2</sub><sup>-</sup> and alleviate the demanding oxidative environment of Li-CO<sub>2</sub> batteries, and improved the battery's stability [113]. They also introduced a protective SEI layer on Li metal to provide dendrite-free plating/stripping and anticorrosion behaviours in both ether-based and ester-based electrolytes [114]. All in all, as an integrated system, the realization of high-performance Li-O<sub>2</sub>/CO<sub>2</sub> batteries requires the electrode, electrolyte, and interface components to be optimized simultaneously.

Also, with the rapidly increasing interests on wearable electronics over the past decades, the Li-CO<sub>2</sub> batteries with high energy density will be promising in achieving wearable consumer electronics toward ubiquity [115–117]. However, only very few reports in the literature were related to the development of flexible Li-CO<sub>2</sub> batteries, owing to the lack of flexible cell structure. Currently, most of Li-CO<sub>2</sub> batteries have been produced in a 2D rigid bulk structure with heavy weight, which are obviously not adaptable for flexible and wearable electronics. The development of a binder-free and liquid-free electrode/electrolyte interface with robust feature and interfacial stability is indispensable for the flexible Li-CO<sub>2</sub> batteries. More importantly, the commonly used liquid electrolyte is not appropriate to design a flexible Li-CO<sub>2</sub> battery because of the possible leakage and flammable properties. Therefore, more attention should be paid into the field of durable catalyst electrode with sufficiently mechanical rigidity and sophisticated electrolyte formula.

## 4 Conclusion

Obviously, next-generation metal-CO<sub>2</sub> batteries, represented by the Li-CO<sub>2</sub> batteries, will play a vital role in effective CO<sub>2</sub> fixation and advanced energy storage, not only in daily life, but also in industrial production. Although the development of Li-CO<sub>2</sub> batteries is still in its infancy, a systematic understanding of the critical problems, including high overpotential, poor reversibility, and inferior rate capability, will be an essential step to facilitate their implementation on a large scale. In order to realize highly reversible Li-CO<sub>2</sub> batteries, researchers have made arduous efforts to overcome the challenges

of characterization reaction pathways, sluggish kinetics of redox reactions, development of efficient catalysts, and modification of electrolytes and interfaces. This review exhaustively provides a summary of the problems discovered in Li-CO<sub>2</sub> batteries and concentrates on the current efforts and our understanding directed towards alleviating these issues that have arisen from each of these areas in Li-CO<sub>2</sub> battery research. There is no doubt that there is a long way to go, and more investigation and a better fundamental understanding of high energy density Li-CO<sub>2</sub> batteries require multidisciplinary and cross-field research, ranging from chemical engineering to material science, electrochemistry, and nanotechnology. Despite the challenges, we have to say that, with continuous efforts, practical Li-CO<sub>2</sub> batteries will be eventually obtained with highly efficient CO<sub>2</sub> fixation and high energy storage in the future. We hope that this review will inspire innovative ideas in the fields of batteries and catalysis, and serve to provide guidelines for the development of other important energy storage devices involving metal and gas.

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## Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

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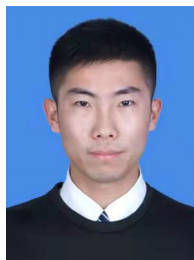
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