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Progress and Future Perspectives on Li(Na)-CO2 Batteries

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Abstract
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Progress and Future Perspectives on Li(Na)–CO_2 Batteries

Fengshi Cai, Zhe Hu, and Shu-Lei Chou**

Li(Na)–CO_2 batteries are attracting significant research attention due to contemporary energy and environmental issues. Li(Na)–CO_2 batteries make possible the utilization of CO_2 and open up a new avenue for energy conversion and storage. Research on this system is currently in its infancy, and its development is still faced with many challenges in terms of high charge potential, weak rate capability, and poor cyclability. Moreover, the reaction mechanism in the battery is still unclear and hard to determine, due to the generation of carbon along with metal carbonates on the cathode. In this review, the authors present the fundamentals and the latest progress related to Li(Na)–CO_2 research. Detailed discussions are provided on the electrochemical reactions on cathode, cathode materials, and electrolytes. Current challenges and future perspectives on Li(Na)–CO_2 batteries are also proposed.

1. Introduction

With the extensive use of fossil fuels, large quantities of carbon dioxide (CO_2) emitted into the atmosphere have led to the global climate change.[1] Reducing CO_2 emissions and concentration in the atmosphere has become one of today's most important challenges for humanity. To address this problem, it is clearly essential to make carbon resources renewable by using CO_2 capture and recycling approaches.[2–9]

Nowadays, electrical energy storage and conversion devices such as rechargeable batteries[10–13] and fuel cells[14–16] are attracting more interest, considering the need for a low-carbon economy and worldwide sustainable development. Lithium-ion batteries (Li-ion battery) have been playing an important role in our society since their commercialization. The Li-ion battery cannot meet the demands of key markets, however, such as the electric vehicles and smart grids, owing to their insufficient energy density (theoretically, 350–400 Wh kg^{-1}, practically, 100–220 Wh kg^{-1}). Recently, metal–air batteries have attracted much attention as an alternative battery technology due to their high theoretical energy densities (e.g., 3500 Wh kg^{-1} for Li–O_2 batteries and 1600 Wh kg^{-1} for Na–O_2 batteries).[17–28] As a new battery technology, metal–air batteries still face a number of problems, such as poor cycling performance, decomposition of electrolyte, high overpotentials etc.[29–31] It is well known that metal–air batteries with an open cell structure can generate power by the electrochemical reaction between metal and oxygen from the atmosphere. Using ambient air as the cathode for metal–air batteries, however, brings even more problematic molecules into the battery system. For example, moisture and CO_2 from the air easily react with the metal and discharge products to form insulating metal hydroxides and metal carbonates at the cathode, which can induce low energy efficiency and poor cycling stability.[32] Thus, most metal–air batteries in laboratories today run in a pure oxygen environment instead of ambient air.

Although the concentration of CO_2 is low in ambient air (only 0.03 vol%),[33] CO_2 is known to be more soluble in organic electrolytes than O_2 (≈50 times higher than O_2),[34] resulting in the high possibility of CO_2 participation in battery reactions. Considering the influence of CO_2 on the operation of metal–air batteries, researchers have focused on metal–CO_2 batteries that utilize an O_2/CO_2 mixture or pure CO_2 as the reactant gas in the cathode, providing us with a new platform for electrical energy generation and CO_2 conversion and utilization.[35–37] At present, Li(Na)–CO_2 batteries have attracted most attention in relation to the development of primary metal–O_2/CO_2 batteries to achieve rechargeable metal–CO_2 batteries.[38–50] The Li(Na)–CO_2 battery exhibits a high theoretical energy density of 1876 Wh kg^{-1}(1.13 kWh kg^{-1} for Na) based on the reaction of $4Li(Na) + 3CO_2 \leftrightarrow 2Li(Na)_2CO_3 + C$.[36,44] The operation of a rechargeable Li(Na)–CO_2 battery, however, is faced with the critical challenges of the poor round-trip efficiency and the decomposition of electrolyte caused by high charge overpotential, as well as our insufficient understanding of the discharge/charge reaction mechanism, among other factors. This review presents the principles and recent progress made in fields relevant to cathodes, and the selection and optimization of electrolytes for Li(Na)–CO_2 batteries, in order to provide a better understanding of the metal–CO_2 batteries technology for future advances in this field.

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2. Electrochemical Reactions on Cathodes

2.1. Li–O_2/CO_2 Batteries

Takechi et al. first reported a primary Li–CO_2 battery using an O_2/CO_2 mixture as the active cathode gas in 2011.[38] The discharge capacity of the Li–O_2/CO_2 battery with 50% CO_2 in the mixed gas was three times as high as that of a Li–O_2 battery. Moreover, the discharge voltage plateau of a Li–O_2/CO_2 battery was the same as that of a Li-O_2 battery, implying that the reduced species was only O_2. It was also observed that the discharge product Li_2CO_3 almost filled all the overall void volume in the porous cathode, which is not the case for the Li–O_2 battery. Spectrum analysis showed that the main discharge product was Li_2CO_3, and no detectable amount of Li_2O_2 or Li_2O was found. It is known that CO_2 can actively react with $O_2^{\bullet-}$, a reaction which has been widely used in CO_2 sensors or molten-carbonate fuel cells.[51] Therefore, the electrochemical reaction processes on the cathode of a Li-O_2/CO_2 battery were proposed as follows

$$4O_2 + 4e^- \rightarrow 4O_2^{\bullet-} \quad (1)$$

$$O_2^{\bullet-} + CO_2 \rightarrow CO_4^{\bullet-} \quad (2)$$

$$CO_4^{\bullet-} + CO_2 \rightarrow C_2O_6^{\bullet-} \quad (3)$$

$$C_2O_6^{\bullet-} + O_2^{\bullet-} \rightarrow C_2O_6^{2-} + O_2 \quad (4)$$

$$C_2O_6^{2-} + 2O_2^{\bullet-} + 4Li^+ \rightarrow 2Li_2CO_3 + 2O_2 \quad (5)$$

Reaction 1 is common to both Li–O_2 and Li–O_2/CO_2 batteries. The following reactions 2–4 in the Li–O_2/CO_2 battery are believed to be faster than the reaction between the $O_2^{\bullet-}$ radical and Li^+ ions that occurs in a Li–O_2 battery. All of the generated $O_2^{\bullet-}$ species can easily react with CO_2 and follow the Li_2CO_3 precipitation process (Reaction 3–5). Furthermore, it is believed that the intermittent species of peroxydicarbonate ions ($C_2O_6^{2-}$) is relatively stable in the electrolyte and can slow down the Li_2CO_3 precipitation process in the cathode. It is worth noting that carbonate electrolytes used in this study undergo electrochemical decomposition reactions, and CO_2 is not subject to direct reduction in the discharge process.

The reaction mechanisms in Li–O_2/CO_2 batteries with various electrolytes were further investigated using quantum mechanical simulations and experimental verification by Kang and co-workers.[39] Experimental results showed that the $O_2^{\bullet-}$ radical preferentially reacts with CO_2 over Li^+ and forms Li_2CO_3 in electrolytes with high dielectric constants such as carbonates and dimethyl sulfoxide (DMSO). In this case, CO_2 takes part in the reaction. Nevertheless, $O_2^{\bullet-}$ tends to react with Li^+ and form Li_2O_2 as a major discharge product in the low-dielectric-constant electrolytes such as DME. Thus, the reaction mechanism in Li–O_2/CO_2 batteries with low dielectric constant electrolytes is thought to be the same as in the Li–O_2 battery (**Figure 1**). These results are consistent with the density functional theory (DFT) analysis. Moreover, they first demonstrated that the electrochemical activation of CO_2 in DMSO-based electrolytes enables the reversible formation of Li_2CO_3 instead of Li_2O_2. These

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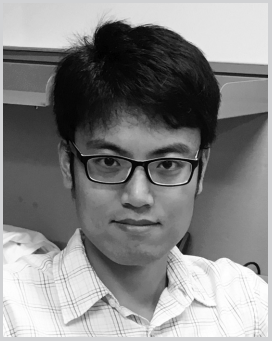

Zhe Hu received his Bachelor's degree (2011) and Master's degree (2013) from Nankai University, China. He is currently a Ph.D. student in the Institute for Superconducting and Electronic Materials (ISEM) at University of Wollongong (UOW) under the supervision of Dr. Shu-Lei Chou and Prof. Shi-Xue Dou. His research focuses on lithium ion batteries and sodium ion batteries.

Shu-Lei Chou is a principal research fellow in ISEM at the University of Wollongong. He obtained his Bachelor's (1999) and Master's degrees (2004) from Nankai University, China. His research focuses on energy storage materials for battery applications, especially on novel composite materials, new binders, and new electrolytes for Li/Na batteries.

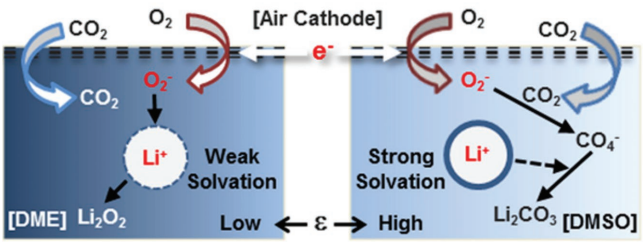

Figure 1. The probable reaction pathways for Li–O_2 batteries using dielectric media discharged in the presence of CO_2. Reproduced with permission.[39] Copyright 2013, American Chemical Society.

findings provide a new possibility for developing rechargeable Li–O_2/CO_2 batteries.

Recently, Yin et al. also studied the effects of two solvents (DMSO and DME) on the discharge process of Li–O_2/CO_2 batteries.[40] Oxygen is first observed to be reduced to superoxide. Afterward, the reaction between superoxide and CO_2 in DMSO is favorable to form Li_2CO_3 due to the strong solvation of Li^+ by DMSO, while superoxide reacts with Li^+ in the low donor number solvent DME to first form lithium superoxide, and then chemically reacts with CO_2 to form carbonate. Despite the different intermediate processes, Li_2CO_3 is the final discharge product in both solvents, but the morphology of Li_2CO_3 formed in DMSO differs from that formed in DME. Moreover, they observed that CO_2 cannot be reduced within the electrochemical stability window of DMSO and DME.

McCloskey and co-workers investigated the effect of CO_2 on the rechargeability of Li–O_2 batteries with DME-based electrolyte.[41] They claimed that Li_2O_2 formed via a $2e^-/O_2$ process is the main discharge product in more stable solvents such as DME, regardless of whether CO_2 is present or not. However, results indicated that CO_2 in the feed gas can spontaneously react with Li_2O_2 to form the discharge product Li_2CO_3, which results in an increase in charging potential, thereby dramatically reducing the rechargeability of the Li–O_2 battery (**Figure 2**). To understand the decomposition mechanism of Li_2CO_3, isotopic labeling measurements ($^{18}O_2$ and $C^{18}O_2$) were used. The Li_2CO_3 oxidative reaction, however, namely, $Li_2CO_3 \rightarrow 2(Li^+ + e^-) + 1/2O_2 + CO_2$, did not show activity in their experiments. Thus, the decomposition of Li_2CO_3 was finally ascribed to the mediation of the DME-based electrolyte.

Vegge and co-workers also studied the influence of CO_2 on nonaqueous Li–air batteries by DFT calculations and galvanostatic measurements.[42] DFT calculations results showed that CO_2 adsorption on the stepped $(1\bar{1}00)$ Li_2O_2 surface is most favorable and changes the Li_2O_2 surface shape and growth directions. Experimental results show that CO_2 strongly influences the recharging process. It is observed that the charging overvoltage is significantly increased with 1% CO_2 contamination, while there is almost no capacity in the case of 50% CO_2 batteries.

Previous research has shown that discharge products (Li_2CO_3) with low electron conductivity tend to accumulate in the cathode during cycling, severely influencing the electrochemical performances of metal–air batteries.[46–49] Therefore, it is important to have a profound understanding of the decomposition

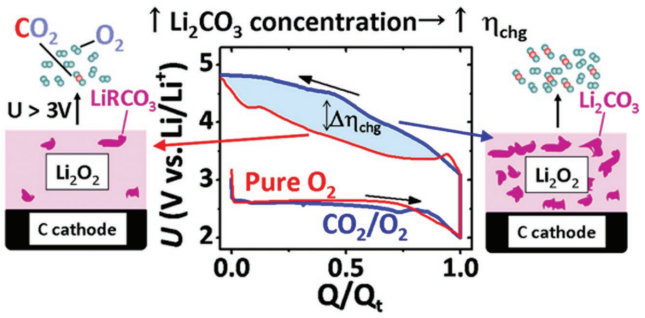

Figure 2. The discharge and charge cycle for batteries under pure O_2 and a 10:90 CO_2:O_2 mixture. Reproduced with permission.[41] Copyright 2013, American Chemical Society.

mechanism of Li_2CO_3. Zhou and co-workers investigated the electrochemical oxidation of Li_2CO_3 in the Li–air/CO_2 battery by using isotopic tracing and gas chromatography-mass spectrometry.[43] Their results show that Li_2CO_3 decomposes into CO_2 and superoxide radicals during charging, and the latter are finally consumed by the tetraglyme electrolyte solvent (**Figure 3**). Meanwhile, electrolyte solvent decomposition caused by superoxide radicals was also detected. Much effort is still needed to understand and improve the kinetics of the electrochemical formation and decomposition of Li_2CO_3 in Li–CO_2 batteries.

2.2. Na–O_2/CO_2 Batteries

The state-of-art advances in Li–O_2/CO_2 batteries may be extended to the development of Na–O_2/CO_2 batteries owing to the similar electrochemical behavior of Li and Na and the abundance of sodium compared with lithium. The Archer group first reported a primary nonaqueous Na–O_2/CO_2 battery for CO_2 capture and generation of electrical energy.[44] This battery exhibited higher discharge capacity than the corresponding Na–O_2 cell. Experimental analysis indicated that $Na_2C_2O_4$ is the main discharge product in ionic liquid electrolytes, whereas both Na_2CO_3 and $Na_2C_2O_4$ coexist in tetraglyme-based electrolytes. Therefore, they proposed the following reaction mechanisms. For the formation of Na_2CO_3 in tetraethylene glycol dimethyl ether (TEGDME) based cells, the reaction is analogous to Reaction 1–5 in a Li-O_2/CO_2 battery. Since $Na_2C_2O_4$ is a discharge product, the possible reactions are summarized as follows

$$O_2 + 2e^- \rightarrow O_2^{\bullet -} \tag{6}$$

$$O_2^{\bullet -} + CO_2 \rightarrow CO_4^{\bullet -} \tag{7}$$

$$CO_4^{2-} + CO_2 + 2Na^+ \rightarrow Na_2C_2O_4 + O_2 \tag{8}$$

Archer and co-workers have further reported a rechargeable Na–O_2/CO_2 battery with the electrolyte stabilized by the addition of 10% ionic-liquid-tethered silica nanoparticles.[45] The cathodic stability of the propylene carbonate-based electrolyte was extended by at least 1 V. Therefore, the Na–O_2/CO_2 battery could be recharged for over 20 cycles, even at charge potentials as high as 5 V, without electrolyte decomposition. Their results indicated that the principal discharge product was $NaHCO_3$, and the decomposition of $NaHCO_3$ was accompanied by emission of CO_2 and O_2 during charging (**Figure 4**).

2.3. Li–CO_2 Batteries

The earlier Li–O_2/CO_2 batteries with pure CO_2 as the cathode gas exhibited small capacities. Nevertheless, Archer and coworkers reported a primary Li-CO_2 battery (pure CO_2 gas) with high discharge capacities working at high temperatures.[46] They believed that increasing the cell operation temperature may limit the thick insulating coating of discharge products and improve the reaction kinetics at the electrolyte–cathode interface. Preliminary ex situ analysis showed that Li_2CO_3 is the

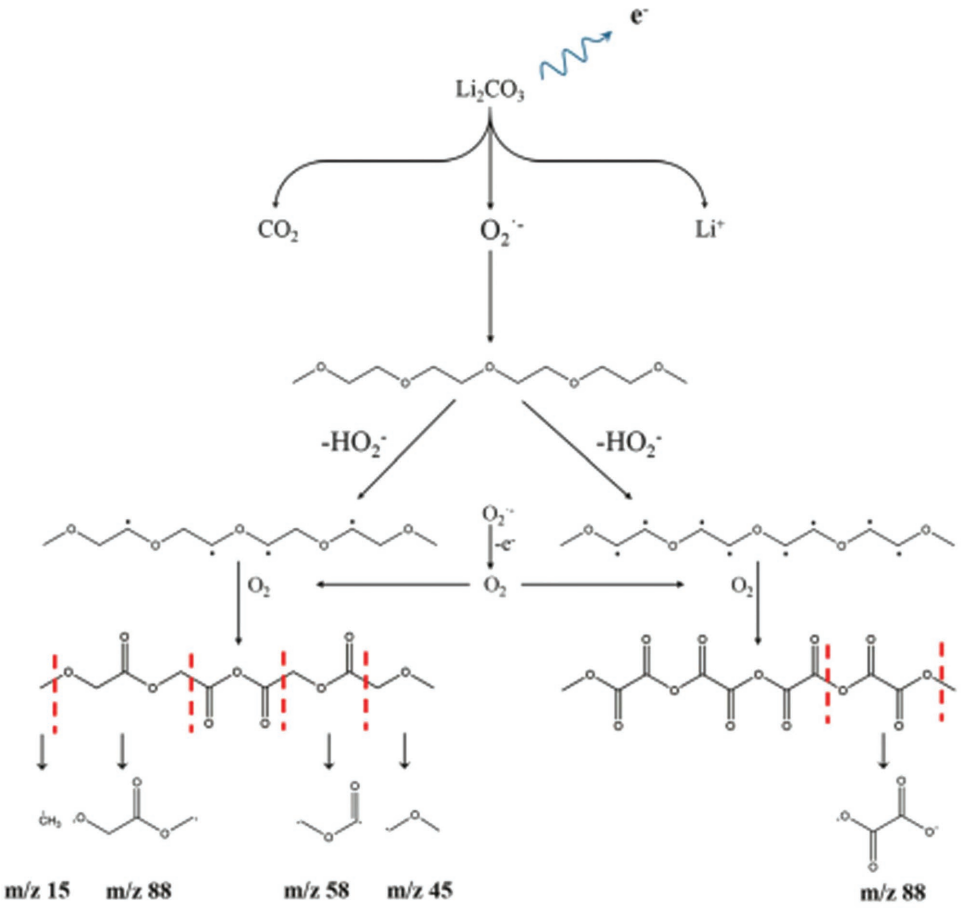

Figure 3. Proposed electrochemical decomposition mechanism of Li_2CO_3. Reproduced with permission.[43] Copyright 2016, Royal Society of Chemistry.

principal solid discharge product and CO is the gas product. It was only deduced that the formation of carbon is by the exothermic reaction of $2CO \rightarrow CO_2 + C$, which is hard to detect due to the use of carbon cathode. Thus, the overall reaction is concluded as $4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$ (9).

After that, Li and co-workers reported a rechargeable Li–CO_2 battery with $LiCF_3SO_3$ in TEGDME electrolyte that could operate at room temperature.[47] To confirm the presence of carbon, both Li and co-workers and Zhou and co-workers studied the rechargeable Li–CO_2 batteries using a porous gold[47] and a platinum net cathode,[48] respectively. They detected the formation of amorphous carbon and the reversible formation and decomposition of Li_2CO_3, consistent with Reaction 9. According to the reaction, the theoretical voltage is about 2.8 V, consistent with the experimental value. Rechargeable room-temperature Li–CO_2 batteries will open new paths for both CO_2 capture and energy storage.

2.4. Na–CO_2 Batteries

Recently, Chen and co-workers developed rechargeable room-temperature Na-CO_2 batteries.[50] The reversible formation and decomposition of Na_2CO_3 was detected by in situ Raman, ex situ X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Meanwhile, the reversibility of CO_2 was also verified by measuring the evolved gas during the charging process. The presence of carbon in the discharge products was verified using Ag nanowire cathode in Na–CO_2 batteries. The reversibility of the carbon product was also detected. Based on various characterizations and analysis, the reversible battery reaction of $3CO_2 + 4Na \leftrightarrow 2Na_2CO_3 + C$ was first demonstrated. Their study further provides an opportunity for the clean recycling/utilization of CO_2.

3. Cathode Materials for Li(Na)–CO_2 Batteries

Carbon materials are generally utilized as the cathode materials in metal–CO_2 batteries owing to their adequate electrical conductivity, large surface area and relative chemical stability. Among the carbon materials, commercially available carbon materials, such as Ketjen black (KB) and Super P, have been explored as porous cathode materials for Li(Na)–CO_2 batteries. Takechi et al. first reported primary Li–O_2/CO_2 batteries using KB as the cathode.[38] The Li–O_2/CO_2 battery with 50% CO_2 exhibited

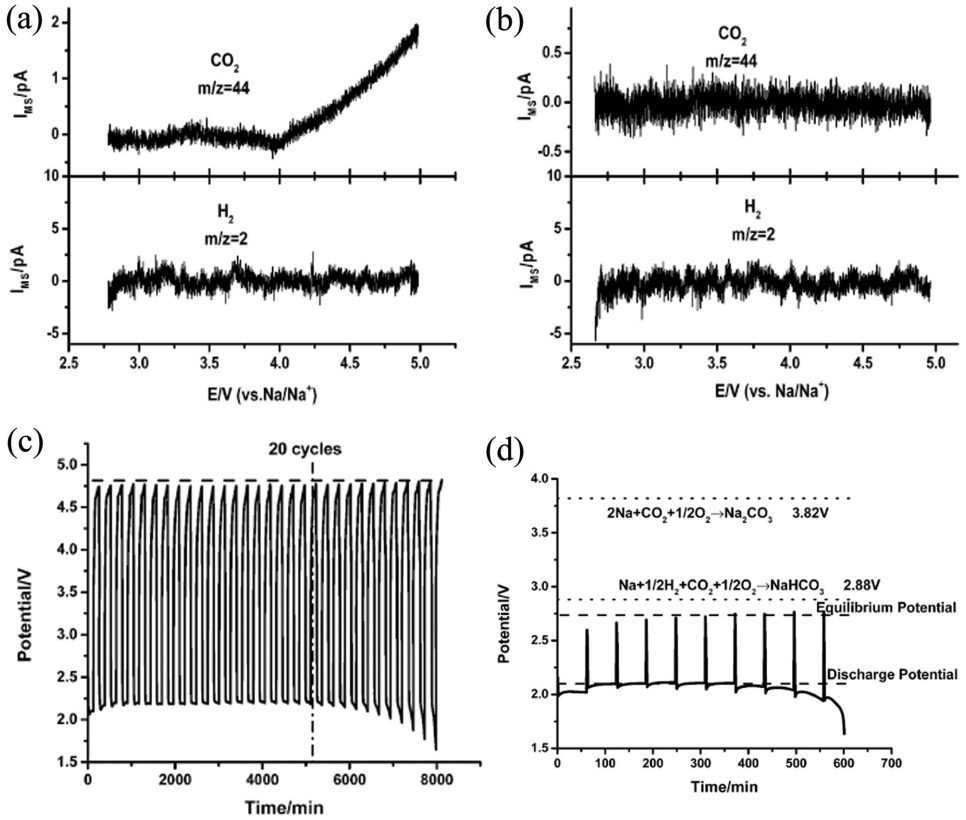

Figure 4. DEMS result of the positive potential scan of PC electrolyte a) and SiO_2–IL–TFSI/PC electrolyte b). Cycling profiles c) and galvanostatic intermittent titration technique discharge profile d) of the Na–CO_2/O_2 cell. Reproduced with permission.[45] Copyright 2014, Royal Society of Chemistry.

the high discharge capacity of 5860 mA h g^{-1} as compared with that of the Li–O_2 battery with 0% CO_2, but the capacity of the pure CO_2 battery was very small (only 66 mA h g^{-1}). The discharging plateau of Li–O_2/CO_2 batteries is about 2.7 V, the same as that of Li–O_2 batteries. The higher discharge capacities are mainly due to the benefits of the porous structure and high surface areas of carbon materials. Kang and co-workers first discovered that a reversible Li–O_2/CO_2 (50% CO_2) battery with KB as air cathodes could run over 20 cycles with controlled capacity of 1000 mAh g^{-1} by using DMSO-based electrolytes.[39] Later, Liu et al. reported rechargeable Li–O_2/CO_2 (2:1) and Li–CO_2 batteries using KB as the cathode that operated at room temperature.[47] The discharging capacities of the Li–O_2/CO_2 battery and the Li–CO_2 battery were 1808 mA h g^{-1} and 1032 mA h g^{-1}, respectively, and both batteries can work reversibly over tens of cycles at high CO_2 concentrations. In another study, Archer and co-workers reported that a primary Li–CO_2 battery with Super P based cathodes could deliver a discharge capacity of 2500 mA h g^{-1} at moderate temperatures.[46] Later on, they reported that a Na–O_2/CO_2 battery using a Super P cathodes was rechargeable over 20 cycles.[45] In these studies, commercial KB and Super P materials were generally used as conductive agents or for catalyst support.

Benefitting from their unique structures and greater number of defects/vacancies, functional carbon materials, such as graphene, carbon nanotubes (CNTs), B, N-codoped holey graphene (BN-hG), etc. have also been reported as cathode materials in Li(Na)–CO_2 batteries.

Graphene has attracted much attention as a catalyst in fuel cells and a cathode material for metal–air batteries.[52–54] Zhang et al. first introduced graphene into rechargeable Li–CO_2 batteries, showing a higher discharge capacity of 14774 mAh g^{-1} as compared with that of the electrodes with KB and Super P (**Figure 5**a,b).[48] The authors proposed that the graphene with its porous structure and excellent electrochemical activity provides efficient diffusion channels, and enough space and active sites for CO_2 utilization and capture. Nevertheless, the kinetic parameters of Li–CO_2 batteries with graphene cathodes still need to be further improved to reach higher efficiency.

Similar to graphene, CNTs have also been considered as cathode candidates for Li–CO_2 batteries. Zhou and co-workers reported that CNT cathodes exhibited an initial discharge capacity of 8379 mA h g^{-1} at a current density of 50 mA g^{-1}, and the cells operated stably over 20 cycles (Figure 5c,d).[49] They proposed that using the 3D networks of CNTs could significantly improve the electrochemical performance and cycling stability of the Li–CO_2 batteries.[55] The formation and decomposition of the main discharged product Li_2CO_3 could be clearly seen from (**Figure 6**). Since Li_2CO_3 has poor electrical conductivity, the Li–CO_2 batteries still suffered from high charge potential (≈4.5 V), which not only led to low energy efficiency, but also limited the cycling and rate capability of Li–CO_2 batteries. Thus, more efficient CO_2 cathodes should be developed.

It is well known that the introduction of nonmetallic elements, such as boron (B) or nitrogen(N), into carbon materials

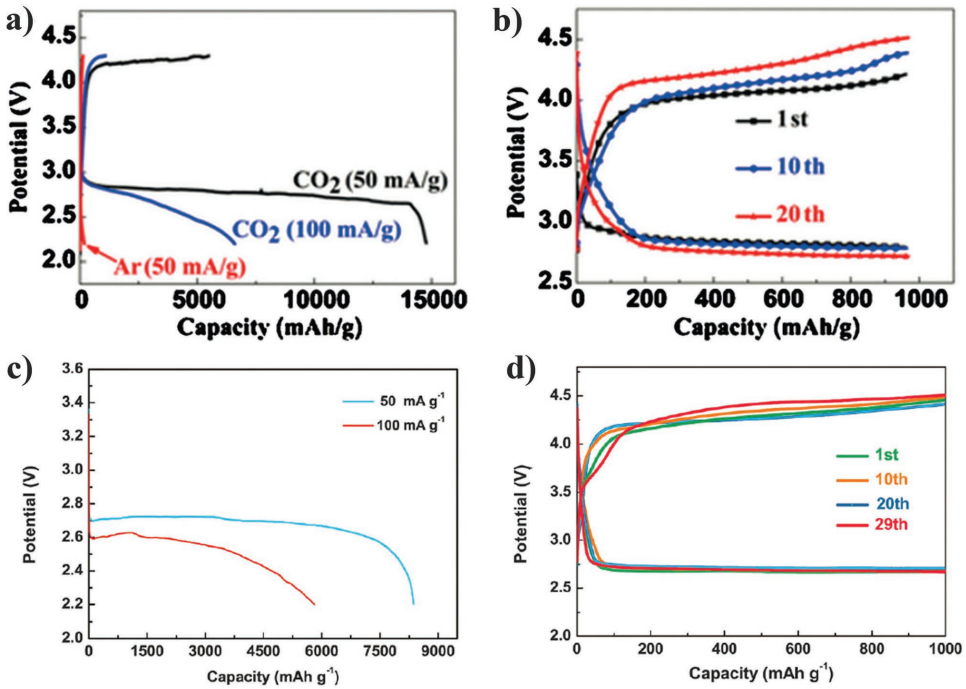

Figure 5. Initial discharge curves of the batteries with a) graphene, and c) CNT cathodes; Cycling performance of Li–CO_2 batteries with b) graphene and d) CNT cathodes. a,b) Reproduced with permission.[48] Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. c,d) Reproduced with permission.[49] Copyright 2015, Royal Society of Chemistry.

can effectively enhance the electrochemical activity and electronic conductivity by forming defects and functional groups.[56,57] Recently, the first introduction of BN-hG into Li–CO_2 batteries was conducted by Dai and co-workers.[58] They prepared BN-hG by heating the pure hG with H_3BO_4 under Ar gas to achieve B-doping, and then with NH_3 for N-doping. The as-obtained BN-hG- based cathode exhibited low polarization, excellent rate performance, and good reversibility over 200 cycles at 1.0 A g^{-1} (**Figure 7**). As suggested by the researchers, the enhanced performance was attributed to the unique porous holey nanostructure, abundant defects and/or functional groups around hole edges, and high catalytic activity of the BN-hG.

To further improve the reactivity of carbon nanotubes on cathodes for rechargeable Na–CO_2 batteries, Chen and co-workers reported a TEGDME-wettable surface composed of a-activated multiwalled CNTs (a-MCNTs) fabricated by boiling the MCNTs in TEGDME solvent.[50,59] Both DFT calculations and Raman and Fourier transform infrared (FTIR) results suggest that the porous structure and activated surface of the a-MCNTs facilitated the adsorption of CO_2, the storage of discharge product, and the cathode reactions (**Figure 8**). Therefore, a low overpotential of 1.39 V is observed for the cells with a-MCNT cathodes compared with that with nonactivated MCNT cathode (2.04 V) (Figure 8f), which is a preliminary indication of the effectiveness of a-MCNT cathodes.

As discussed above, the cathode materials require not only a porous structure to store discharge products but also high electrochemical catalytic activity toward discharge products. It is difficult, however, to meet the requirement of high catalytic activity toward discharge products such as Li_2CO_3 for many pure carbon materials. Therefore, composite materials as electrodes have been applied to improve the performance of Li(Na)–CO_2 batteries.

Carbon supported metals and/or metal compound catalysts seem to be good choices to reduce the charge potential and improve the electrochemical performance of the cell.[60] Considering the superior catalytic activity of ruthenium (Ru), Yang et al. prepared the uniformly dispersed Ru nanoparticles on Super P carbon (Ru@Super P) cathode by a solvothermal method for Li–CO_2 batteries.[61] The charge potential of the cell was below 4.4 V, and the battery could operate for 80 cycles with a fixed capacity of 1000 mAh g^{-1} at 100, 200, and 300 mA g^{-1} due to the superior catalytic activity and cycling stability of Ru@Super P. Their results showed that Li_2CO_3 and carbon are the main discharge products, and Ru can promote the reaction between Li_2CO_3 and carbon during charge (**Figure 9**). Chen et al. also reported a low charge potential of 4.02 V and a good cycle stability (67 cycles with a fixed capacity of 500 mAh g^{-1}) in the O_2-assisted Li–CO_2 battery with the Ru/graphene nanosheets cathode.[62] That is to say, the presence of Ru helps to reduce the charge potential, which can avoid electrolyte decomposition in the operating potential range, and the Li-CO_2 cells can achieve excellent reversibility. Recently, Zhang et al. indicated that the highly dispersed Ni nanoparticles on N-doped graphene (Ni-NG) could be used as an efficient cathode for Li–CO_2 batteries, with a discharge capacity of 17 625 mAh g^{-1}, and a cycle life of 100 cycles with a cutoff capacity of 1000 mAh g^{-1} at 100 mA g^{-1}.[63] This work is instructive for developing highly efficient nonprecious metal cathodes for Li–CO_2 batteries.

Chen et al. reported a composite cathode with Mo_2C nanoparticles as catalysis sites dispersed on carbon nanotubes as

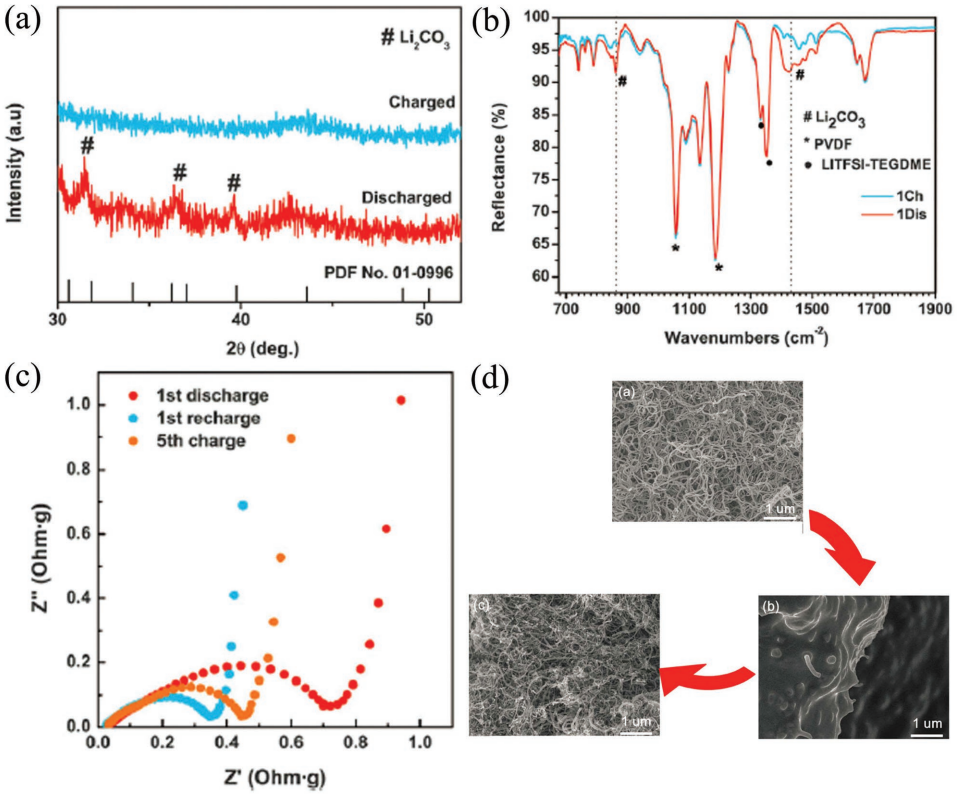

Figure 6. a) XRD patterns, b) FTIR spectra, c) Nyquist plots, and d) SEM images of discharged and charged CNT cathodes. Reproduced with permission.[49] Copyright 2015, Royal Society of Chemistry.

the conductive matrix (Mo_2C/CNTs) prepared by a carbothermal reduction process.[64] They found that the Mo_2C nanoparticles could stabilize the $Li_2C_2O_4$ intermediate reduction product of CO_2 on discharge and prevent its disproportionation to Li_2CO_3. Based on their experimental results, the sequence of proposed possible reaction steps of Mo_2C for the rechargeable Li–CO_2 battery is summarized by the schematic illustration shown in **Figure 10**. The Li–CO_2 batteries with Mo_2C/CNTs cathode could be reversibly discharged and charged at a low charge potential (<3.5 V) for 40 cycles. The introduction of Mo_2C provides a good example of how it is possible to reduce the charge potential plateau and improve the reversibility of Li–CO_2 batteries.

Recently, Tao et al. designed freestanding Co_2MnO_x nanowire-decorated carbon fibers (CMO@CF) cathodes for the Na–CO_2 batteries.[65] They found that CMO@CF can promote the discharge product Na_2CO_3 decomposition at the lower charge voltage. The Na–CO_2 battery with CMO@CF cathode presented a high discharge capacity of 8448 mAh g^{-1}, a low overpotential (1.77 V), and a stable cyclability over 75 cycles at 500 mAh g^{-1}. The superiority was mainly due to the in situ growth of CMO nanowires on the CFs with a sea-urchin-like structure and the hybrid Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+} redox couples.

To improve reversible conversion between CO_2 and Li_2CO_3, Wang and co-workers reported metal-organic frameworks (MOFs) as porous catalysts for high-performance CO_2

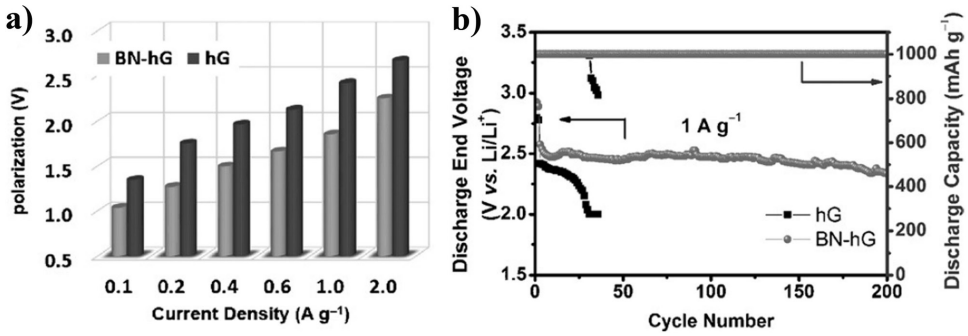

Figure 7. a) Polarization, and b) long-term cycling performance of Li-CO_2 cells with hG and BN-hG cathodes. Reproduced with permission.[58] Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

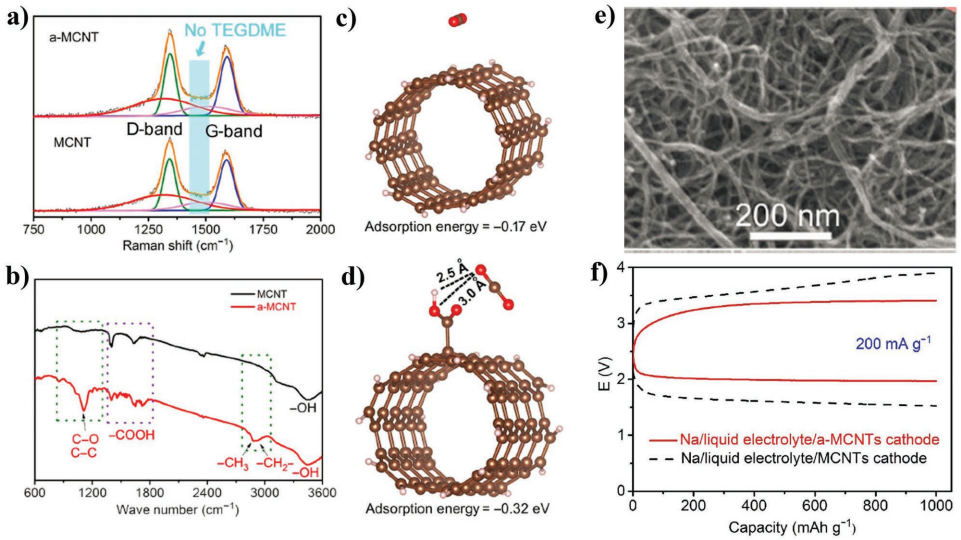

Figure 8. a) Raman and b) FTIR spectra. The optimized geometries and corresponding adsorption energies of CO_2 adsorbed on c) MCNTs and d) a-MCNTs. e) SEM images of a-MCNT cathodes. f) Initial discharge and charge profiles of Na–CO_2 batteries. Reproduced with permission.[59] Copyright 2017, American Association for the Advancement of Science.

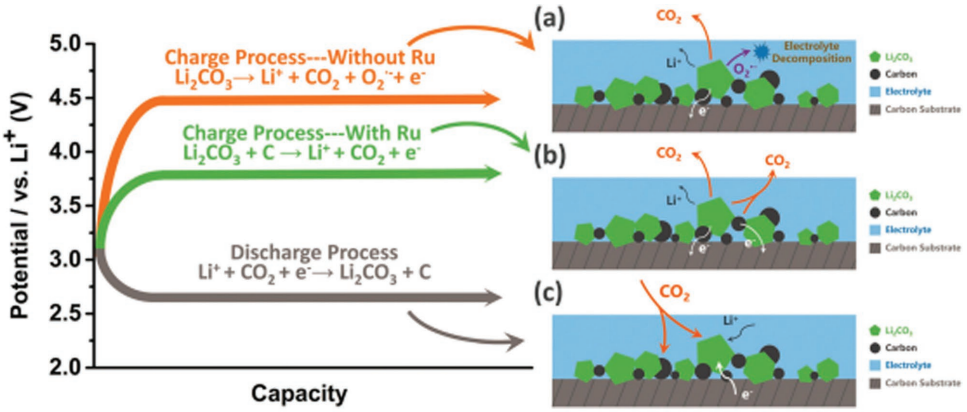

Figure 9. Schematic diagram of a) the reaction mechanism of the charging process of the Li–CO_2 battery without the Ru catalyst and b) with the Ru catalyst. c) Discharging process of the Li–CO_2 battery. Reproduced with permission.[61] Copyright 2017, Royal Society of Chemistry.

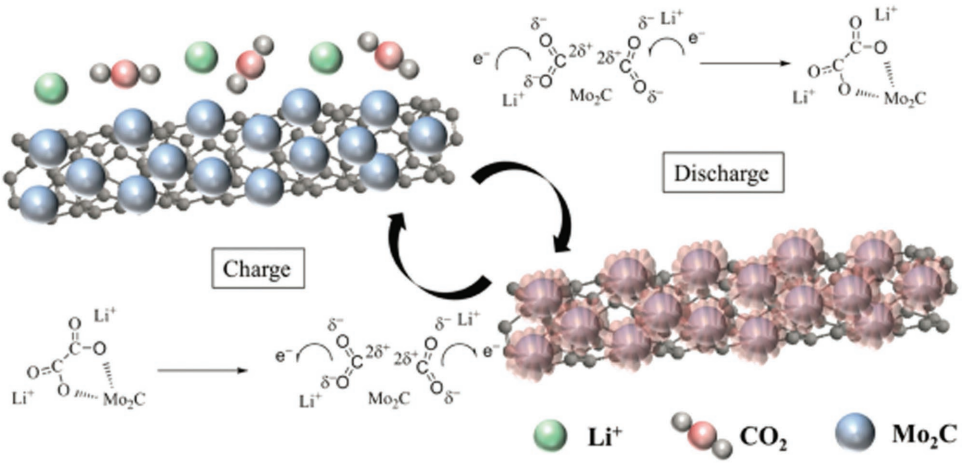

Figure 10. Schematic illustration of reactions during discharge and charge of Mo_2C/CNTs in the Li–CO_2 battery. Reproduced with permission.[64] Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

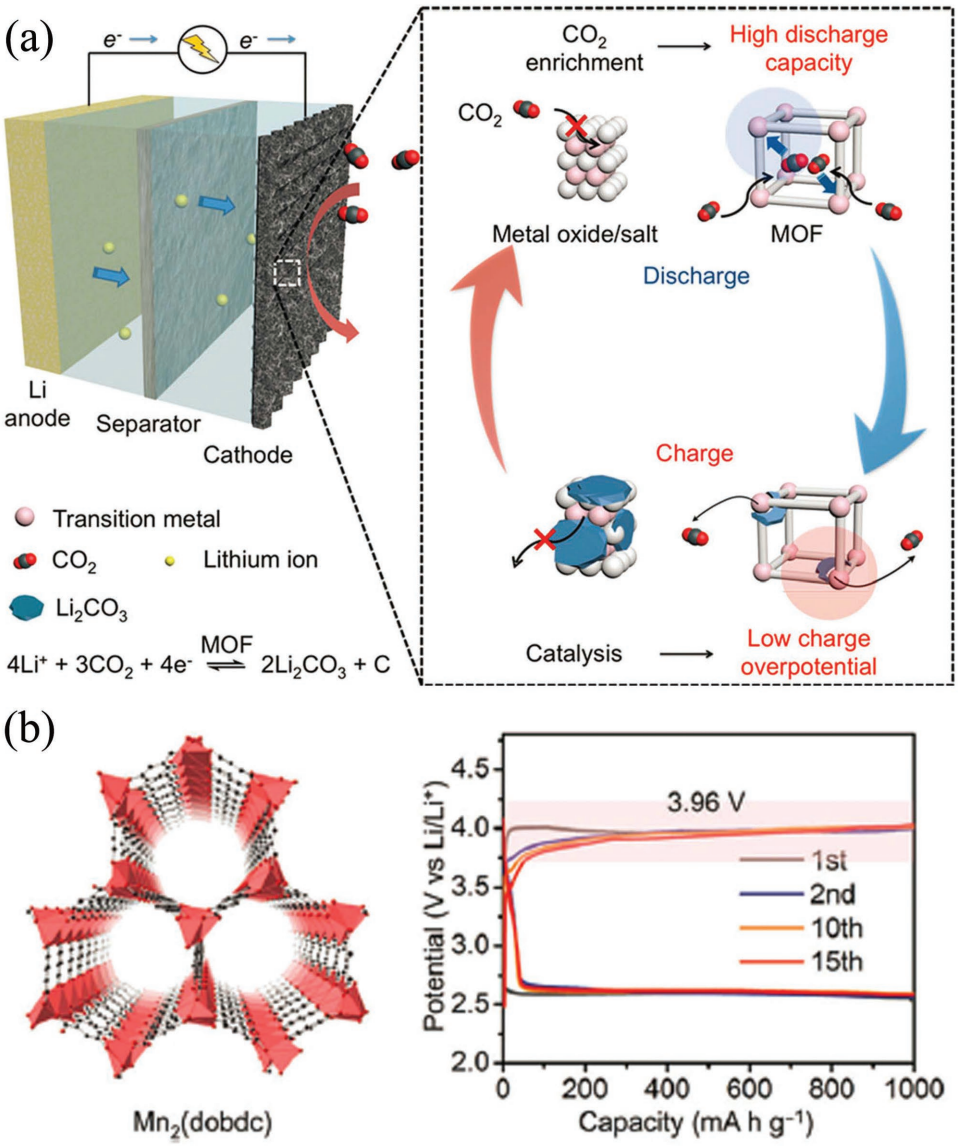

Figure 11. a) Schematic illustration of a Li–CO_2 battery equipped with an MOF-based CO_2 electrode. b) Crystal structures presenting 1D porous channels and corresponding discharge-charge voltage curves of Mn_2(dobdc). Reproduced with permission.[66] Copyright 2018, Royal Society of Chemistry.

electrodes.[66] The Li–CO_2 battery with porous Mn_2(dobdc) exhibited a high discharge capacity of 18 022 mAh g^{-1} and low charge potential of 3.96 V at 50 mA g^{-1}. This can be ascribed to the porous nature of MOFs with monodispersed Mn(II) centers and their capability in CO_2 capture (**Figure 11**). Their works provided useful ways for designing novel electrode materials of Li–CO_2 battery.

4. Electrolyte

From research on the effects of CO_2 contamination on the metal–O_2 battery, it was found that metal–CO_2 batteries are also possible. Hence, the conventional electrolyte for metal–CO_2 batteries in the present study (for example, lithium salt/tetraglyme) is similar to that for previously reported Li–O_2 batteries. Three types of nonaqueous, hybrid, and solid-state electrolytes have been developed for metal–CO_2 batteries.

A Li–O_2/CO_2 primary battery with an organic carbonate-based electrolyte, ethylene carbonate/diethyl carbonate (EC/DEC), was first reported by Takechi and co-workers.[38] It is now agreed based on both theoretical and experimental findings that carbonate electrolytes are highly susceptible to nucleophilic attack by superoxide or peroxide species. Subsequently, based on quantum mechanical simulations and experimental verification, Kang and co-workers investigated the effects of various types of electrolyte solvation on the Li–O_2/CO_2 battery.[39] **Figure 12** shows the possible reaction pathways at the initial complex formation step from DFT calculations. It can be found that the electrolyte decomposition reaction in EC is more favored compared with that for reaction in DMSO (Figure 12b) or DME (Figure 12c), leading to large overpotentials and

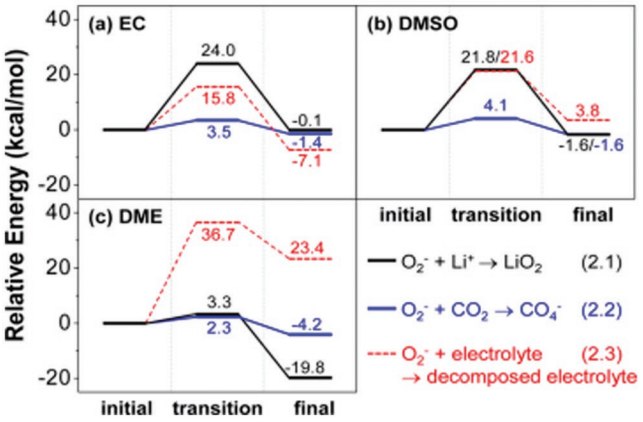

Figure 12. Activation barrier and binding reaction energy from DFT calculations at the initial complex formation (ICF) step with a) EC b) DMSO, and c) DME electrolytes. Reproduced with permission.[39] Copyright 2013, American Chemical Society.

termination of the battery, consistent with previous experimental results in Li–O_2 cells with carbonate electrolytes.[67] The reaction of O_2^- with Li^+ in DME is much more likely compared with the other solvents, indicating the dominant role of LiO_2 formation. In contrast, O_2^- preferentially reacts with CO_2 over Li^+ in DMSO. High dielectric electrolytes in general can effectively shield and stabilize charged ionic species. Therefore, O_2^- was more likely to react with CO_2 in a high dielectric solvent and with Li^+ in a low dielectric solvent. Indeed, their experimental results from a Li–O_2/CO_2 cell showed that the main discharge product was Li_2CO_3 in the high dielectric DMSO, while Li_2O_2 discharge product tended to form in the low dielectric DME, consistent with the theoretical investigations. Moreover, they further discovered that the reversible reaction of Li_2CO_3 can be realized in a high dielectric solvent such as DMSO. The same results were also proven by Grimaud et al.[40]

Currently, longer chain ethers (such as TEGDME) have been the most common solvents used in metal–CO_2 batteries, due to their high thermal stability and oxidation potentials (>4.5 V vs Li/Li^+), and low volatility. Rechargeable Li–CO_2 batteries were first developed with a liquid electrolyte consisting of lithium salt/TEGDME by Li and co-workers.[47] The main discharge product is Li_2CO_3, and the reversible formation and decomposition of Li_2CO_3 can be observed during discharge and charge. Moreover, rechargeable Na–CO_2 batteries were also realized using $NaClO_4$–TEGDME as electrolyte.[50]

Adding redox mediators to the electrolyte has proved to be an efficient method to enhance the performance of Li–O_2 batteries.[68–70] LiBr as an electrolyte redox mediator was first applied in rechargeable Li–CO_2 batteries with TEGDME/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte by Zhou and co-workers.[71] Their results showed that Br_2 could promptly chemically oxidize the discharge products of Li_2CO_3 and C and leave Br_3^- as the reduction product. Hence, the cycling stability and rate capability of the cell with LiBr were improved compared to that without LiBr, supporting the feasibility of applying LiBr as a redox mediator. Recently, Yin et al. used quinones to mediate CO_2 reduction in Li-CO_2 battery.[72] It was found that 2,5-ditert-butyl-1,4-benzoquinone (DBBQ) and CO_2 had an intimate chemical interaction in acetonitrile (MeCN) electrolytes, and using quinones as chemical catalysts could reduce CO_2 with lower activation energy to form stable quinone-CO_2 adducts. This provided new strategies for promoting CO_2 reduction in Li–CO_2 battery.

The aforementioned findings indicated that the electrochemical inactivity of the discharge product Li_2CO_3 resulted in poor performance of a rechargeable Li–CO_2 battery. To address this problem, Zhou and co-workers introduced a super-concentrated electrolyte composed of DMSO-solvated contacted ion-pair (CIP).[73] The electrolyte could efficiently stabilize and restrain peroxodicarbonate species further reduction into Li_2CO_3 (**Figure 13**). Their results showed that the Li–O_2/CO_2 battery with CIP-composed electrolyte operates via pure peroxodicarbonate formation/decomposition, which could realize a very low charge potential (3.5 V) and considerable cycle life. These findings opened a new route toward more practical Li–CO_2 battery system.

Ionic liquids (ILs) have been developed as alternative electrolytes due to their negligible volatility, low flammability, high thermal stability, acceptable conductivity, and wide electrochemical potential window.[74] Nevertheless, until now, the application of ILs in metal–CO_2 batteries has been very rare. A high-temperature Li–CO_2 primary battery with LiTFSI-IL electrolyte was first reported by Archer and co-workers.[46] It was found that the discharge capacity of the battery could be made to rise rapidly by increasing the operating temperature, and the battery using IL-based electrolyte could operate at high temperature. In addition, Archer and co-workers first reported a room temperature Na–O_2/CO_2 battery with tetraglyme and an ionic liquid as electrolyte.[44] It was found that the discharge product is only $Na_2C_2O_4$ in IL-based electrolytes, whereas both Na_2CO_3 and $Na_2C_2O_4$ coexist in tetraglyme-based electrolyte. Moreover, Archer and co-workers utilized ionic liquid tethered to SiO_2 nanoparticles (SiO_2-IL-TFSI) as an additive in propylene carbonate-based electrolytes for rechargeable Na–O_2/CO_2 batteries.[45] The tethered ILs gave rises to the formation of a more stable and conductive solid electrolyte interphase (SEI) on the sodium anode, which prevented the occurrence of side reactions with the electrolyte.[75]

Currently, liquid electrolyte-based Li(Na)–CO_2 batteries face safety risks, including liquid electrolyte leakage, volatilization, electrochemical instability, etc. One of the methods to solve these problems is using quasi-solid-state electrolytes.[76–78] Chen and co-workers prepared a quasi-solid state polymer electrolyte (QPE) by integrating a polymer matrix of polyvinylidene fluoride–cohexafluoropropylene (PVDF-HFP), nanosized SiO_2, and a $NaClO_4$/TEGDME solution, and applied it in Na–CO_2 batteries.[59] The batteries delivered an energy density of 232 Wh kg^{-1} and a working voltage of around 2.2 V.

Inspired by Chen's report, Wang et al. also believed that gel polymer electrolyte (GPE) should be a good choice for rechargeable Li–CO_2 batteries.[79] The GPE is composed of a polymer matrix filled with a liquid electrolyte that has high ionic conductivity of liquid electrolyte. A GPE based on a (PVDF-HFP) matrix and plasticized with LiTFSI/TEGDME was investigated, and it exhibited a large operating window (up to 4.5 V) and acceptable ionic conductivity (0.5 mS cm^{-1}). The GPE-based Li–CO_2 batteries showed outstanding cycling performance (60 cycles), while the one with a liquid electrolyte faded from the 20th cycle. The polarization in liquid electrolyte is more

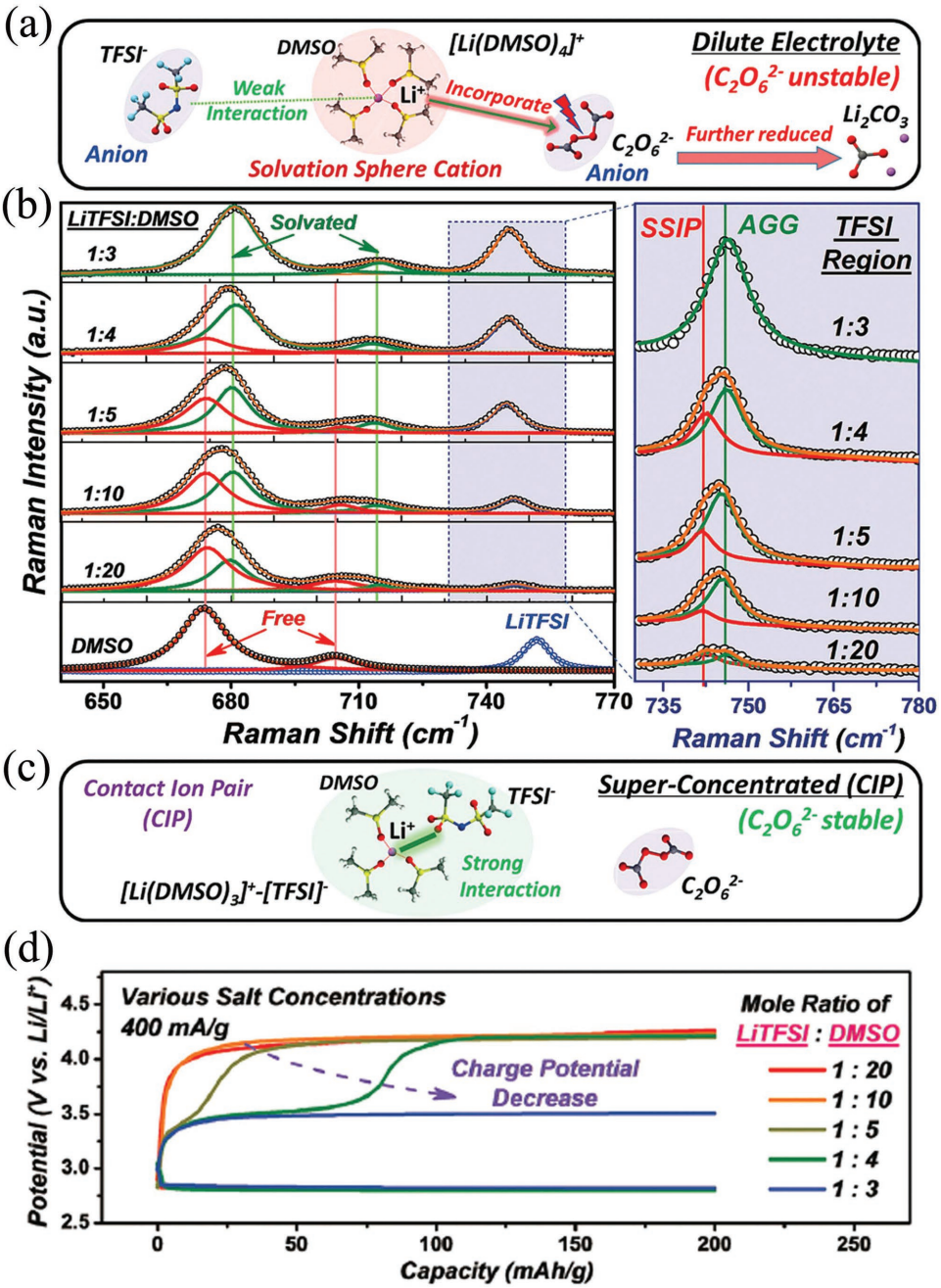

Figure 13. Schematic illustrations of electrolyte structure in dilute LiTFSI/DMSO a) and the superconcentrated fluid network electrolyte composed of $[Li(DMSO)_3]^+$-$[TFSI^-]$ c) based Li–O_2/CO_2 cell, and relevant discharged components. b) Raman spectra and d) Voltage profiles of LiTFSI/DMSO solutions with various mole ratios. Reproduced with permission.[73] Copyright 2018, Royal Society of Chemistry.

serious than in the cells operated in GPE at high current density (250 mA g^{-1}). Compared with a conventional liquid electrolyte, the quasi-solid-state GPE can alleviate dissolution of CO_2 in the bulk of the electrolyte and prevent the unwanted contact reaction between Li anode and CO_2.[46,80]

To meet the required standards for safety and flexibility, further developing high performance flexible solid-state electrolytes as well as achieving high energy density to produce all-solid-state Li-CO_2 batteries is important. Chen and co-workers reported flexible liquid-free Li–CO_2 batteries based on poly(methacrylate)/poly(ethylene glycol)-$LiClO_4$-3wt%SiO_2 composite polymer electrolyte (CPE).[81] The CPE showed ionic conductivity of 7.14×10^{-2} mS cm^{-1} at 55 °C. The Li–CO_2 batteries using the as-prepared CPE can run for 100 cycles with fixed capacity of 1000 mAh g^{-1}. Furthermore, pouch-type flexible batteries exhibited a large reversible capacity of 993.3 mAh, high energy density of 521 Wh kg^{-1}, and long operation time of 220 h at different degrees of bending (0–360°) at 55 °C

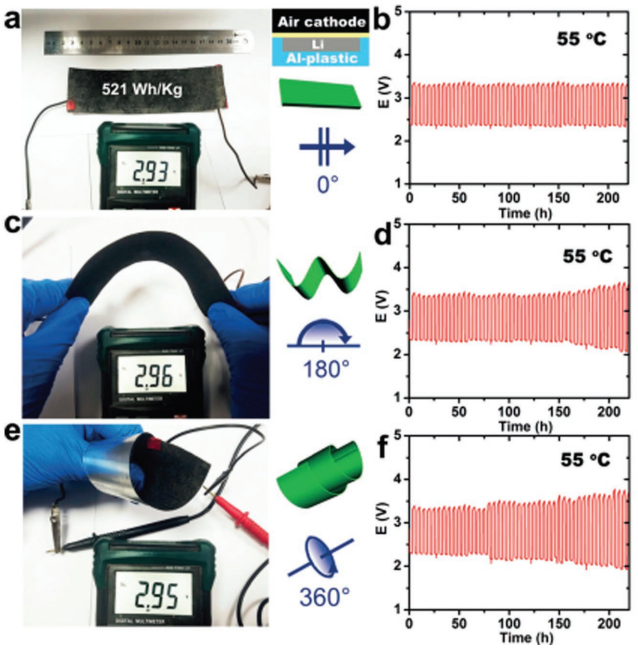

Figure 14. The bending and twisting properties and corresponding cycle numbers of Li–CO_2 batteries at 2.5 mA. a,b) No bending or twisting. c,d) Bent to 180°. e,f) Twisted to 360°. Reproduced with permission.[81] Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(**Figure 14**). The initial feasibility study offers a promising direction to develop practical Li–CO_2 batteries with satisfactory flexibility and high energy density.

5. Anodes

Currently, almost all the research of Li(Na)–CO_2 batteries has used pure Li (Na) metal as anode, which possesses an extremely high theoretical capacity and low redox potential. It is well known that the chief problem with using Li (Na) metal anode in liquid electrolytes is the dendrite formation or surface cracks during cycling, resulting in short-circuiting of the battery.[82,83] Therefore, it is vitally important to seek effective methods to stabilize Li (Na) metal anode and new alternatives for the pure Li (Na) anode. Strategies such as electrolyte modification, interface protection, and electrode framework construction etc. are beneficial to improve the Li (Na) metal anode.[82–85] Recently, Chen and co-workers reported a reduced graphene oxide (rGO)–Na anode for quasi-solid-state Na–CO_2 batteries.[59]

Figure 16. Summary of the challenges and the opportunities for Li(Na)–CO_2 batteries.

Their electrochemical performance showed a higher cyclic voltammetry (CV) current density (5.7–16.5 mA cm^{-2}) with rGO–Na anode than with pure Na anode. The rGO–Na anode surface was smooth after 450 cycles, whereas the pure Na anode was seriously cracked, indicating that the addition of rGO foam helps Na^+ to achieve dendrite-free plating/stripping of Na^+ on the rGO–Na anode (**Figure 15**). Therefore, significant future developments of the Li (Na) metal anode will be necessary for high safety and high energy-density Li(Na)–CO_2 batteries.

6. Conclusions and Perspectives

To solve contemporary energy and environmental issues, Li(Na)–CO_2 batteries provide a new pathway for CO_2 capture and utilization. The development of Li(Na)–CO_2 batteries in its infancy, however, and still faces many challenges. These challenges include low discharge capacity, weak rate capability, high charge overpotential, poor cyclability, and many other problems (**Figure 16**). These problems seem to be caused by the sluggish electrochemical reactions at the air cathodes. Stable and efficient Li(Na)–CO_2 batteries require stable electrolytes and effective catalysts to reduce the discharge/charge overpotential and improve their electrochemical performance. Therefore, developing a high-performing air cathode with high catalytic activity and unique structure, and highly stable electrolytes are the primary future tasks. Some of the achievements of Li(Na)–CO_2 batteries are summarized in **Table 1**.

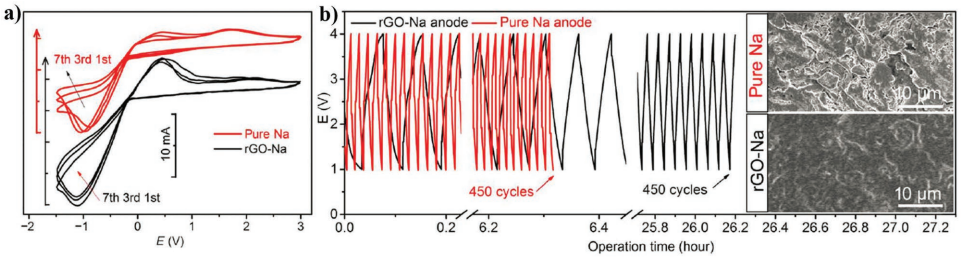

Figure 15. a) Cyclic voltammograms and b) fast discharge/charge profiles of quasi-solid-state Na-CO_2 batteries. Inset: SEM images of rGO-Na and pure Na anode surfaces after 450 cycles. Reproduced with permission.[59] Copyright 2017, American Association for the Advancement of Science.

Table 1. Summary of Li(Na)–CO_2 batteries and their performances.

Cathode	Electrolyte	Working gas (ratio by volume)	Working temperature [°C]	Initial capacity, current density	Cycle current/capacity [mA g^{-1}/mA h g^{-1}]	Cycle number	Refs.
Li–CO_2							
Ketjen black	LiTFSI dissolved in EC/DEC	CO_2:O_2 = 2:1	25	≈5800 mAh g^{-1}, 0.2 mA cm^{-2}	–	–	[38]
	LiTFSI dissolved in EC/DEC	Pure CO_2	25	66 mAh g^{-1}, 0.2 mA cm^{-2}	–	–	[38]
	TBAPF6 dissolved in DMSO	CO_2:O_2 = 1:1	25	≈2400 mAh g^{-1}, 0.4 mA cm^{-2}	0.4/1000	20	[39]
	TBAPF6 dissolved in DMSO	CO_2:O_2 = 9:1	25	≈2200 mAh g^{-1}, 0.4 mA cm^{-2}	–	–	[39]
	TBAPF6 dissolved in DME	CO_2:O_2 = 1:1	25	≈2050 mAh g^{-1}, 0.4 mA cm^{-2}	–	–	[39]
	TBAPF6 dissolved in DME	CO_2:O_2 = 9:1	25	≈3800 mAh g^{-1}, 0.4 mA cm^{-2}	–	–	[39]
	$LiCF_3SO_3$ dissolved in TEGDME	CO_2:O_2 = 2:1	25	1880 mAh g^{-1}, 30 mA g^{-1}	30/≈1000	10	[47]
	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25	1032 mAh g^{-1}, 30 mA g^{-1}	30/≈1000	7	[47]
	LiBr and LiTFSI dissolved in TEGDME	Pure CO_2	25	11500 mAh g^{-1}, 50 mA g^{-1}	100/500	38	[71]
	LiBr and LiTFSI dissolved in TEGDME	Pure CO_2	25		200/500	16	[71]
Super P	LiTFSI dissolved in [BMIM][Tf_2N]	Pure CO_2	25	0 mAh g^{-1}, 0.05 mA cm^{-2}	–	–	[46]
High surface area carbon	LiTFSI dissolved in [BMIM][Tf_2N]	Pure CO_2	25	≈750 mAh g^{-1}, 0.05 mA cm^{-2}	–	–	[46]
Conductive carbon	LiTFSI dissolved in [BMIM][Tf_2N]	Pure CO_2	60	≈2000 mAh g^{-1}, 0.05 mA cm^{-2}	–	–	[46]
	LiTFSI dissolved in [BMIM][Tf_2N]	Pure CO_2	80	≈2800 mAh g^{-1}, 0.05 mA cm^{-2}	–	–	[46]
	LiTFSI dissolved in [BMIM][Tf_2N]	Pure CO_2	100	≈3800 mAh g^{-1}, 0.05 mA cm^{-2}	–	–	[46]
Graphene	LiTFSI dissolved in TEGDME	Pure CO_2	25	14774 mAh g^{-1}, 50 mA g^{-1}	50/1000	20	[48]
	LiTFSI dissolved in TEGDME	Pure CO_2	25	6600 mAh g^{-1}, 100 mA g^{-1}	100/1000	10	[48]
B,N-codoped holey graphene	LiTFSI dissolved in TEGDME	Pure CO_2	25	16033 mAh g^{-1}, 300 mA g^{-1}	1000/1000	200	[58]
CNTs	LiTFSI dissolved in TEGDME	Pure CO_2	25	8379 mAh g^{-1}, 50 mA g^{-1}	50/1000	29	[49]
	LiTFSI dissolved in TEGDME	Pure CO_2	25	5786 mAh g^{-1}, 100 mA g^{-1}	100/1000	22	[49]
	PMA/PEG–$LiClO_4$–3 wt%SiO_2	Pure CO_2	55	950 mAh g^{-1}, 100 mA g^{-1}	100/1000	16	[81]
	LiTFSI/TEGDME–GPE	Pure CO_2	25	8536 mAh g^{-1}, 50 mA g^{-1}	100/1000	60	[79]
	LiTFSI dissolved in TEGDME	Pure CO_2	25	5000 mAh g^{-1}, 50 mA g^{-1}	100/1000	20	[79]
Ru@Super P	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25	8229 mAh g^{-1}, 100 mA g^{-1}	100/1000	70	[61]
	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25		200/1000	70	[61]
	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25		300/1000	70	[61]
Ru/graphene nanosheets	$LiClO_4$ dissolved in DMSO	CO_2 with 2% O_2	25	4742 mAh g^{-1}, 0.08 mA cm^{-2}	0.16 mA cm^{-2} /500	67	[62]
Ni/N-doped graphene	LiTFSI dissolved in TEGDME	Pure CO_2	25	17625 mAh g^{-1}, 100 mA g^{-1}	100/1000	101	[63]
Mo_2C/CNT	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25	1150 µAh, 20 µA	20 µA/100 µAh	40	[64]
Porous Au	$LiCF_3SO_3$ dissolved in TEGDME	Pure CO_2	25	≈220 mAh g^{-1}, 30 mA g^{-1}	–	–	[47]
Mn_2(dobdc)/CNT	LiTFSI dissolved in TEGDME	Pure CO_2	25	18022 mAh g^{-1}, 50 mA g^{-1}	200/1000	50	[66]
Na–CO_2							
Super P	$NaCF_3SO_3$/IL	CO_2:O_2 = 2:3	25	3500 mAh g^{-1}, 70 mA g^{-1}	–	–	[44]
	$NaCF_3SO_3$/IL	Pure CO_2	25	183 mAh g^{-1}, 70 mA g^{-1}	–	–	[44]
	$NaClO_4$ dissolved in TEGDME	CO_2:O_2 = 3:2	25	2882 mAh g^{-1}, 70 mA g^{-1}	–	–	[44]
	$NaClO_4$ dissolved in TEGDME	Pure CO_2	25	173 mAh g^{-1}, 70 mA g^{-1}	–	–	[44]
Porous carbon	SiO_2–IL–TFSI/PC–NaTFSI	CO_2:O_2 = 1:1	25	–	200/800	20	[45]
t-MWCNTs	$NaClO_4$ dissolved in TEGDME	Pure CO_2	25	60000 mAh g^{-1}, 1000 mA g^{-1}	1000/2000	200	[50]

Table 1. Continued.

Cathode	Electrolyte	Working gas (ratio by volume)	Working temperature [°C]	Initial capacity, current density	Cycle current/capacity [mA g^{-1}/mA h g^{-1}]	Cycle number	Refs.
a-MCNTs	PVDF-HFP -4% SiO_2/$NaClO_4$ –TEGDME	Pure CO_2	25	5000 mAh g^{-1}, 50 mA g^{-1}	500/1000	400	[59]
Co_2MnO_x @ carbon fibers	$NaClO_4$ dissolved in TEGDM	Pure CO_2	25	8448 mAh g^{-1}, 200 mA g^{-1}	200/500	75	[65]

$LiCF_3SO_3$, lithium triflate; LiTFSI, lithium bis(trifluoromethanesulfonyl)imide; NaTFSI, sodium bis(trifluoromethanesulfonyl)imide; $NaCF_3SO_3$, sodium triflate; $NaClO_4$, sodium perchlorate; TEGDME, tetraethylene glycol dimethyl ether; DME, dimethoxyethane; EC, ethylene carbonate; DEC, diethyl carbonate; PC, propylene carbonate; PMA/PEG, poly(methacrylate)/poly(ethylene glycol); PVDF-HFP, poly(vinylidene fluoride co-hexafluoropropylene); t-MWCNT, tetraethylene glycol dimethyl-treated multiwall carbon nanotube; TBAPF6; tetrabutylammonium hexafluorophosphate, DMSO, dimethyl sulfoxide, [BMIM][Tf_2N], 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide; GPE, gel polymer electrolyte; IL, 1-ethyl-3-methyl imidazolium trifluromethanesulfonate; Mn_2(dobdc), Mn_2(2,5-dioxido-1,4-benzenedicarboxylate).

So far, apart from several pure carbon materials, efforts have also devoted to developing other highly active and stable catalysts, including B and N-codoped holey graphene, Ru@Super P, and Mo_2C/CNTs, to expedite the reversible decomposition of metal carbonates. Meanwhile, the developed catalysts should have insignificant effects on the electrolyte decomposition. Therefore, the carbon supported composite catalysts and carbon-free catalysts should receive more attention in the future. Building the electrode with 3D porous structure could be a good choice for improving the triple-phase boundary interface reaction of the cathode and storing discharge product without blocking air channels. As one of the key factors, the electrochemical stability of electrolytes is playing a crucial role in the development of long-life Li(Na)–CO_2 batteries. Due to the stability of metal carbonates, the charge potentials of Li(Na)–CO_2 batteries are usually beyond the stability window of most electrolytes. Suitable electrolytes that are stable and do not react with the discharge products are yet to be identified. In addition, it is necessary to develop more stable alternatives such as ionic liquids and solid-state electrolytes with high ionic conductivity. At the air cathode, this reaction mainly takes place at the triple-phase boundary where the solid electrode is simultaneously interfaced with the electrolyte and gaseous CO_2. Thus, integral optimization of the electrolyte–cathode couple would greatly benefit the battery charge–discharge performance. Moreover, understanding the effects of the gas atmosphere, gas pressure, catalyst, and architecture of the electrode on the distribution and morphology of the discharge products is also very important. Apparently, the electrochemistry of the air electrode in Li(Na)–CO_2 batteries is complex and requires further investigation. In addition, efforts should be made toward exploring safe anode materials to build safer Li(Na)–CO_2 batteries.

Although Li(Na)–CO_2 batteries have made great progress since 2011, the research on Li(Na)–CO_2 batteries is still in its infancy, and the challenges remain. Considering the great practical significance of alleviating the energy shortage and global warming issues, it is worth applying great effort to developing rechargeable Li(Na)–CO_2 batteries.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathode materials, electrolytes, energy conversion and storage, lithium–carbon dioxide batteries, sodium–carbon dioxide batteries

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