Metal–CO_2 Batteries on the Road: CO_2 from Contamination Gas to Energy Source

*Zhaojun Xie, Xin Zhang, Zhang Zhang, and Zhen Zhou**

Rechargeable nonaqueous metal–air batteries attract much attention for their high theoretical energy density, especially in the last decade. However, most reported metal–air batteries are actually operated in a pure O_2 atmosphere, while CO_2 and moisture in ambient air can significantly impact the electrochemical performance of metal–O_2 batteries. In the study of CO_2 contamination on metal–O_2 batteries, it has been gradually found that CO_2 can be utilized as the reactant gas alone; namely, metal–CO_2 batteries can work. On the other hand, investigations on CO_2 fixation are in focus due to the potential threat of CO_2 on global climate change, especially for its steadily increasing concentration in the atmosphere. The exploitation of CO_2 in energy storage systems represents an alternative approach towards clean recycling and utilization of CO_2. Here, the aim is to provide a timely summary of recent achievements in metal–CO_2 batteries, and inspire new ideas for new energy storage systems. Moreover, critical issues associated with reaction mechanisms and potential directions for future studies are discussed.

1. Introduction

With the rapid development of human society, the global CO_2 emission flux from fossil fuel combustion (coal, natural gas, and petroleum products) is in the order of thousands of tons per year.[1] The increasing concentration of greenhouse gas CO_2 in the atmosphere has caused serious anthropogenic climate changes.[2,3] Reducing the release of CO_2 into the environment is urgently needed. However, energy is an important foundation for economic and social development. Capturing and converting CO_2 into a fuel has opened up the possibility of creating CO_2 emission reduction systems. In the past several years, both photochemical and electrochemical conversion of CO_2 have thus been globally investigated.[4–8]

In order to meet the increasing energy demand of daily life, broad financial efforts are being made to improve the energy and power density of electrochemical energy storage and conversion technologies, such as batteries,[9–11] fuel cells,[12–14] and supercapacitors.[15–17] Compared with the prevailing Li–ion batteries, rechargeable nonaqueous metal–air batteries are generally considered as alternative power systems for both electric vehicles and smart grids. Because their theoretical energy density is especially high, e.g., 3500 Wh kg^{-1} for Li–O_2 batteries and 1600 Wh kg^{-1} for Na–O_2 batteries.[18–20] Metal–air batteries have become the subject of intensive investigations worldwide and enormous progress has been made in the past decade.[21–30] However, this technology is still at an early stage of development, and there still remain many challenges to face.[31–33] The exceptionally high gravimetric energy density primarily originates from the great free energy change of metal–O_2 reactions and the active material in the cathode, O_2, which is available from air rather than being stored within the battery. Remarkably, the term “metal–air batteries” is often optimistically adopted; however, most studies are actually operated in a highly pure O_2 atmosphere instead of ambient air. The presence of moisture and CO_2 leads to new insulating species such as metal hydroxides and metal carbonates at the cathode, which can seriously decrease the rechargeable ability of the batteries.[34] Moisture can be removed by using water-proof films. As for CO_2, in spite of its low concentration in ambient air (400 ppm),[35] its solubility is 50 times larger than O_2 in organic solvents,[36] and CO_2 can react with the active intermediate species $O_2^{\bullet -}$ or the discharge products to form metal carbonates.[37] To develop actual metal–air batteries, it is critical to understand the potential impact of CO_2 contamination on metal–O_2 batteries, and generally a mixture of O_2/CO_2 has been utilized as the reactant gas.[38–42] More interestingly, it has been proved that CO_2 itself can be utilized as the reactant gas, i.e., metal–CO_2 batteries.[43–46] The utilization of CO_2 in electrochemical energy storage devices provides a promising “clean” strategy for reducing fossil fuel consumption and consequently, lessening global warming. In addition, metal–CO_2 batteries are potential energy sources for scientific exploration and future immigration to Mars, for the air there contains 95% of CO_2.[47]

Here, the development of primary metal–O_2/CO_2 batteries to rechargeable metal–CO_2 batteries is summarized, and

---

Dr. Z. Xie, Dr. X. Zhang, Dr. Z. Zhang, Prof. Z. Zhou
Tianjin Key Laboratory of Metal and Molecule Based Material Chemistry
Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education)
Institute of New Energy Material Chemistry
Collaborative Innovation Center of Chemical Science and Engineering (Tianjin)
School of Materials Science and Engineering
National Institute for Advanced Materials
Nankai University
Tianjin 300350, China
E-mail: zhouzhen@nankai.edu.cn

DOI: 10.1002/adma.201605891

the challenges and future directions are discussed regarding rechargeable metal–CO_2 batteries.

2. Metal–O_2/CO_2 Batteries

2.1. Li–O_2/CO_2 Batteries

The primary Li–O_2/CO_2 battery was first reported by Takechi et al. in 2011.[38] Compared with pure O_2 as the reactant gas, Li–O_2/CO_2 batteries with a CO_2 ratio from 10 to 80% in the mixed gas showed higher discharge capacity. After the discharge process, no detectable amount of Li_2O_2 or Li_2O was found. The void space in the cathode was fully filled with Li_2CO_3, which is quite different from the morphology of Li_2O_2 in Li–O_2 batteries. As we know, $O_2^{\bullet-}$ can be captured by CO_2, and this reaction has been applied to CO_2 sensors or molten-carbonate fuel cells.[37] Additionally, the discharging plateau of Li–O_2/CO_2 batteries is about 2.7 V, identical to that of Li–O_2 batteries. Therefore, the discharge processes of Li–O_2/CO_2 batteries were proposed as follows:

$$4O_2 + 4e^- \rightarrow 4O_2^{\bullet-} \tag{1}$$

$$O_2^{\bullet-} + CO_2 \rightarrow CO_4^{\bullet-} \tag{2}$$

$$CO_4^{\bullet-} + CO_2 \rightarrow C_2O_6^{\bullet-} \tag{3}$$

$$C_2O_6^{\bullet-} + O_2^{\bullet-} \rightarrow C_2O_6^{2-} + O_2 \tag{4}$$

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

Takechi et al.[38] suggested that good electrochemical performances result from the rapid consumption of superoxide anion radicals by CO_2 (Reaction 2) as well as the slow filling property of the final discharge product Li_2CO_3 in the cathode (Reaction 3–5). However, carbonate electrolytes used in this study are now known to undergo decomposition reactions in the discharge process of Li–O_2 batteries. Hence, such conclusions about Li–O_2/CO_2 batteries are not mature, but it is clear that the higher discharge capacity in Li–O_2/CO_2 batteries has no relation to CO_2 redox reactions.

Later, as reported by McCloskey et al.,[39] CO_2 was mainly considered as a contamination gas for rechargeable Li–O_2 batteries. In their study, a cell with a CO_2/O_2 mixture of 10:90 exhibited a larger discharge capacity than that with pure O_2 (**Figure 1**a). However, the presence of Li_2CO_3 in the discharge products led to an increase in the overpotential during the subsequent charge process, and dramatically reduced the voltaic efficiency of the cell (Figure 1c). It was postulated that the higher capacity resulted from changes of the deposit morphology where CO_2 spontaneously reacted with the primary discharge product Li_2O_2 to form Li_2CO_3 (Figure 1b). The formation of Li_2CO_3 was simply due to chemical reactions, and no active Li–CO_2 electrochemistry was observed as the cell was discharged under pure CO_2. In order to understand the decomposition mechanism of Li_2CO_3, isotopic labeling measurements ($^{18}O_2$ and $C^{18}O_2$) were used. Nevertheless, no isotopic oxygen scrambling was observed during the charging process, indicating that the oxidation reaction cannot be $Li_2CO_3 \rightarrow 2Li^+ + 2e + 1/2O_2 + CO_2$. The decomposition of Li_2CO_3 was finally ascribed to the mediation of the dimethyl ether (DME)-based electrolyte. They suggested to not only completely remove CO_2 from the gas fed to a Li–O_2 battery, but also develop stable cathodes and electrolytes to avoid the formation of carbonate deposits.

The above conclusion was also agreed by Vegge et al.[41] In their investigations, the reactions between CO_2 and Li_2O_2 at the cathode were studied via density functional theory (DFT) computations and galvanostatic charge–discharge measurements. From DFT computations, they suggested that CO_2 would block the surface-active nucleation sites and alter the shape and growth directions of Li_2O_2 on the surface. Meanwhile, their experimental results indicated that the recharging process was strongly influenced by CO_2 contamination. The increased overpotentials for both the discharging and charging processes could be observed even with 1% CO_2 contamination. When 50% CO_2 was used, the battery showed almost no capacity.

The reaction mechanisms in Li–O_2/CO_2 cells under various electrolytes were further investigated by the Kang group,[42] with both quantum mechanical calculations and experimental verifications. On the basis of quantum mechanical calculations, they found that the electrolyte solvation effect can influence the reaction pathway by altering the potential energy surface, and thereby the final discharge product of Li–O_2/CO_2 batteries can be modified. It is believed that the high dielectric dimethyl sulfoxide (DMSO) favors the reaction between the $O_2^{\bullet-}$ radical and CO_2 instead of Li_2O_2, while the low dielectric DME tends to form Li_2O_2 as a major discharge product, consistent with former studies. By using DMSO-based electrolytes, they discovered for the first time that a reversible Li–O_2/CO_2 (50% CO_2) battery can run over 20 cycles with controlled capacity of 1000 mAh g^{-1} at 0.4 mA cm^{-2}. However, both the Aurbach group[48] and the Yang group[49] have revealed that sulfoxide is susceptible to nucleophilic attacks by reduced oxygen species. As a consequence, more attention should be paid to the chemical stability of electrolytes.

After that, the Li group also reported a rechargeable Li–O_2/CO_2 battery (O_2/CO_2 = 1:2, volume ratio) with tetraethylene glycol dimethyl ether (TEGDME)-based electrolytes.[43] X-Ray diffraction (XRD) patterns show that Li_2CO_3 is the main discharge product in the cell, and does not disappear completely after the fifth charge. This fact explains the rapid increase in overpotentials during the subsequent cycling. Note that the electrochemical reduction of CO_2 is a key factor for the utilization of CO_2 in energy storage systems. Among all the above Li–O_2/CO_2 batteries, CO_2 does not participate in redox reactions.

2.2. Na–O_2/CO_2 Batteries

In contrast to Li–O_2/CO_2 batteries, the Archer group focused on Na–O_2/CO_2 batteries as a platform for CO_2 capture from an effluent gas mixture and a technology for electricity supply in the form of "primary" batteries.[40] This strategy seems appropriate because of its high theoretical capacity and the abundance of sodium compared with lithium. When CO_2/O_2 mixtures with different ratios were used as cathode gas streams, Na–O_2/CO_2 batteries also exhibited higher discharge capacity than Na–O_2 cells (**Figure 2**a–c). Through ex situ XRD and fourier transform

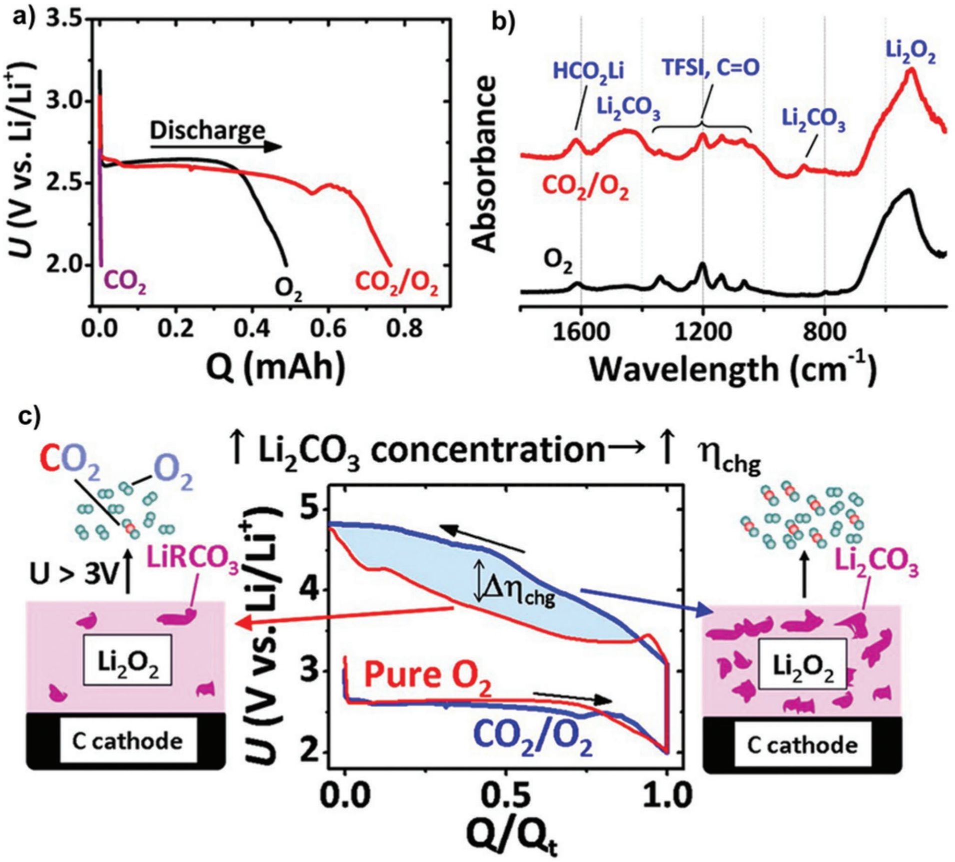

Figure 1. a) Galvanostatic discharge profiles (0.47 mA cm^{-2}) of Li cells discharged under three atmospheres: pure CO$_2$, pure O$_2$, and a 10:90 CO$_2$:O$_2$ mixture. XC72-based cathodes were used. b) FTIR of cathodes extracted from cells discharged under pure O$_2$ and a 10:90 CO$_2$:O$_2$ mixture. c) The voltaic efficiency of the discharge-charge cycle for cells under pure O$_2$ and a 10:90 CO$_2$:O$_2$ mixture. Reproduced with permission.[39] Copyright 2013, American Chemical Society.

infrared spectroscopy (FTIR) techniques, the authors found that Na$_2$C$_2$O$_4$ was the dominant discharge product for cells with ionic liquid electrolytes, while Na$_2$CO$_3$ and Na$_2$C$_2$O$_4$ coexisted for Na–O$_2$/CO$_2$ cells with TEGDME electrolytes. No Na$_2$O$_2$ was detected in the electrodes with the O$_2$/CO$_2$ mixed gas. For the formation of Na$_2$CO$_3$ in the TEGDME based cells, they believed that the reaction processes were quite similar to the series of Reaction 1–5. In the case of Na$_2$C$_2$O$_4$, the possible reactions are summarized as follows:

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

$$O_2^- + CO_2 \rightarrow CO_4^{2-} \tag{7}$$

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

In this case, CO$_2$ is involved in the electrochemical reactions due to the formation of Na$_2$C$_2$O$_4$. However, this system is not rechargeable.

As discussed in Section 2.1, one problem for developing a rechargeable M–O$_2$/CO$_2$ battery lies in the stability of electrolytes. The Archer group showed that with the addition of 10% of ionic liquid tethered silica nanoparticles, the stability of the propylene carbonate-based electrolyte was enhanced by nearly 1 V.[50] Even though the charge potential was close to 5 V, no electrolyte decomposition was observed, and their Na–O$_2$/CO$_2$ batteries were stably cycled for over 20 cycles (Figure 2d). The rechargeability of their cells can be further improved with the introduction of a Ni-foam cathode.[51] Most surprisingly, the discharge product in this work was NaHCO$_3$ confirmed by ex situ XRD and FTIR, and no carbonate was found. In addition, CO$_2$ evolution was obvious during the recharge of the battery, and differential electrochemical mass spectrometry (DEMS) based on ^{12}C and ^{13}C confirmed that the decomposition of NaHCO$_3$ is accompanied by the reaction of O$_2$ and the carbon cathode. However, there are still some questions pending in this study. Meanwhile, in the O$_2$-rich atmosphere, the decomposition of the imidazolium group of the ionic liquid was detected from FTIR analysis. The authors explained that the highly active $O_2^{\bullet -}$ is captured by CO$_2$ to form $CO_4^{\bullet -}$ (Reaction 2) instead of the electrolyte when the CO$_2$/O$_2$ mixture was used. Consequently, new types of electrolytes with high-voltage stability need more investigations.

2.3. Al–O$_2$/CO$_2$ Batteries

Compared with lithium and sodium, aluminum is a more attractive anode material for electrochemical capture and

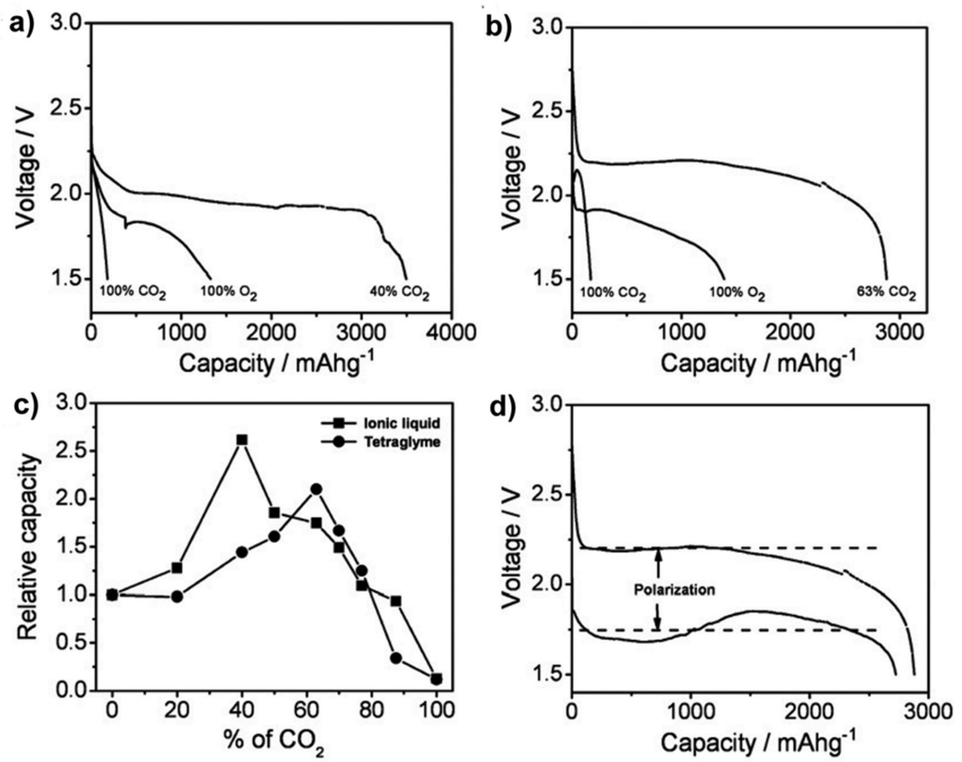

Figure 2. Galvanostatic discharge profiles for Na–O_2/CO_2 cells operated with a mixed O_2/CO_2 feed. a) Ionic liquid (IL) and b) tetraglyme electrolytes; c) variation of capacity with CO_2 concentration. Reproduced with permission.[40] Copyright 2012, Elsevier B.V.; d) Cycling profiles for Na–O_2/CO_2 (1:1) batteries with SiO_2–IL–TFSI/PC electrolytes. The current density employed is 200 mA g^{-1} and the capacity cutoff is 800 mAh g^{-1}. Reproduced with permission.[50] Copyright 2014, Royal Society of Chemistry.

conversion of CO_2 because of its lower cost and safer operation. The Archer group have recently reported an Al–O_2/CO_2 battery based on the 1-ethyl-3-methylimidazolium chloride/aluminum chloride ([EMIm]Cl/$AlCl_3$) electrolyte. This cell design provides an effective approach to sequester CO_2 emission by forming the valuable $Al_2(C_2O_4)_3$, and also to generate considerable amounts of electrical energy. When the Al–O_2/CO_2 battery (O_2/CO_2 = 20:80) was discharged at 70 mA/g, it produced a high capacity of ≈13 000 mAh g^{-1} at around 1.4 V. On the other hand, the Al–CO_2 battery showed moderate capacity only at lower potential of about 0.3 V, while the Al–O_2 battery delivered limited capacity but similar potential plateaus. Therefore, electrochemical reduction of CO_2 should be assisted by the superoxide species. The formation of $Al_2(C_2O_4)_3$ involves the reduction of O_2 to form the superoxide radical, which in turn chemically reduces CO_2 to form CO_4^{2-} and then $C_2O_4^{2-}$ radicals. This Al–O_2/CO_2 battery offers an important strategy for electrochemical capture and conversion of CO_2, but it still requires significant efforts to improve, such as the electrolyte which is extremely sensitive particularly to water.[52]

3. Metal–CO_2 Batteries

3.1. Primary High-Temperature Li–CO_2 Batteries

Unlike the control tests with pure CO_2 as the cathode gas in earlier Li–O_2/CO_2 batteries,[38,39] the Archer group reported a primary Li–CO_2 battery with a high discharge capacity of ≈2500 mAh g^{-1} at moderate temperatures.[53] The configuration of the Li–CO_2 battery was similar to their earlier reported Li–air and Na–O_2/CO_2 cells, and the ionic liquid electrolyte, 1 M LiTFSI dissolved in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was used. Based on preliminary ex situ analyzes of the solid products and the absence of CO in the gas products, the overall reaction was concluded as $4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$ (9). Nevertheless, the formation of carbon was only deduced by the exothermic reaction of $2CO \rightarrow CO_2 + C$, and was not further investigated. After all, the produced carbon was hard to detect due to the application of carbon cathodes.

Their study showed that increasing the operation temperature could improve the insulating coating of discharge products, which in turn promotes both the cell potential and discharge capacity.[54] The discharge capacity of Li–CO_2 batteries was enormously enhanced when the operation temperature increased. However, the temperature dependence was considerably weaker for carbon cathodes with higher surface areas. Therefore, it provides a possible approach to realize room-temperature Li–CO_2 batteries by constructing cathode materials with high surface areas and appropriate pore volumes.

3.2. Rechargeable Room-Temperature Li–CO_2 Batteries

With a conventional electrolyte of $LiCF_3SO_3$ in TEGDME and a normal Ketjen black (KB) cathode, the Li group revealed that

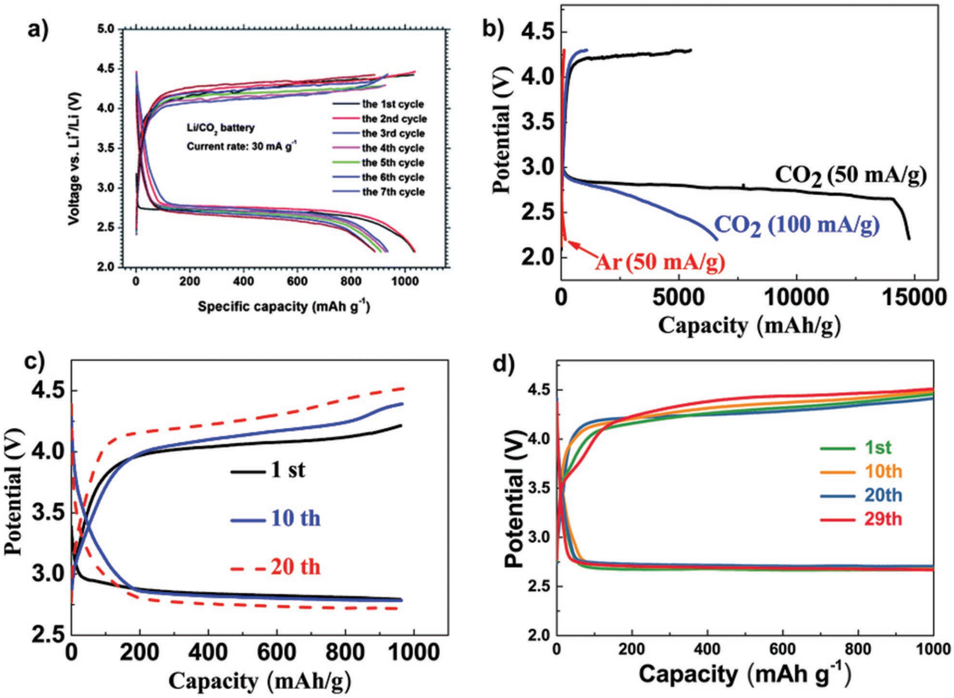

Figure 3. a) Charge–discharge voltage profiles of Li/CO_2 batteries with a cut-off voltage of 2.2 V at 30 mA g^{-1}. Reproduced with permission.[43] Copyright 2013, Royal Society of Chemistry. b) The initial discharge curves of the batteries with graphene cathodes in different atmospheres; Cycling performance of Li–CO_2 batteries under a cutoff capacity of 1000 mAh g^{-1} at 50 mA g^{-1} with c) graphene and d) CNT cathodes. b,c) Reproduced with permission.[44] Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Reproduced with permission.[45] Copyright 2015, Royal Society of Chemistry.

both the Li–O_2/CO_2 battery (Section 2.1) and Li–CO_2 battery can discharge and charge reversibly at room temperature.[43] Their Li–CO_2 batteries could discharge and charge reversibly for 7 cycles with a capacity cutoff of 1000 mAh g^{-1} at 30 mA g^{-1} (**Figure 3**a). In the process of pursuing the utilization of transition metal carbonates as anode materials for Li ion batteries, the Zhou group found that CO_2 can be probably utilized through electrochemical catalytic conversion reactions.[55] In addition to the Li group's work, they introduced both graphene[44] and carbon nanotubes (CNTs)[45] as air cathodes. The full discharge capacity of room-temperature Li–CO_2 batteries was tremendously enhanced to be over 14 000 mAh g^{-1} (Figure 3b) and the cells were stably cycled for 20 (Figure 3c) or 29 (Figure 3d) cycles with controlled capacity of 1000 mAh g^{-1} at 50 mA g^{-1}. They proposed that the higher electrochemical performance and cycling stability can be ascribed to the excellent electrical conductivity, large surface area, and high electrochemical stability of graphene and CNT cathodes.

In addition, both the Li and Zhou group confirmed the formation of amorphous carbon by using a porous gold[43] and a platinum net cathode,[44] respectively. Along with the reversible formation and decomposition of Li_2CO_3 detected by XRD and FTIR, the proposed discharge process was $4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$. Based on such a reaction, the theoretical voltage is about 2.8 V, which is roughly consistent with the experimental value. Compared with other cathodes, the Zhou group found that Li–CO_2 batteries with CNT cathodes demonstrate better cycling performance.[45] They considered that the design of carbon or other highly active catalysts with connected 3D space is a promising strategy, since 3D networks not only benefit the immersion of electrolytes and the transport of electrons, CO_2, and lithium ions, but also have more space to deposit discharged products without clogging the cathode surface. Although the reported Li–CO_2 batteries were investigated only at low current density (30–100 mAh g^{-1}) and with high overpotential, a growing consensus is that rechargeable room-temperature Li–CO_2 batteries will open new paths for both CO_2 capture and energy storage.

3.3. Rechargeable Room-Temperature Na–CO_2 Batteries

More recently, Hu et al. have reported a rechargeable room-temperature Na–CO_2 battery consisting of a Na anode, an ether-based electrolyte, and a designed cathode with electrolyte-treated multiwall carbon nanotubes (**Figure 4**).[46] The battery showed a high capacity of over 60 000 mAh g^{-1} at 1 A g^{-1}, and can be stably cycled for 200 cycles with a cutoff capacity of 2000 mAh g^{-1} at charge voltages below 3.7 V. It is believed that the 3D tri-continuous porous structure, high electrical conductivity, and good wettability of electrolytes to cathodes lead to the ultrahigh performance. The triple-phase boundary interface reaction of the cathode is greatly improved and large amounts of discharge products can be stored without blocking the air channels. It is not surprising that CNT-based air cathodes presented more excellent general performance according to the Zhou group's previous report.[45]

The reaction in Na–CO_2 batteries was also demonstrated as $4Na + 3CO_2 \leftrightarrow 2Na_2CO_3 + C$ (10). The reversible formation and decomposition of Na_2CO_3 in the battery was confirmed

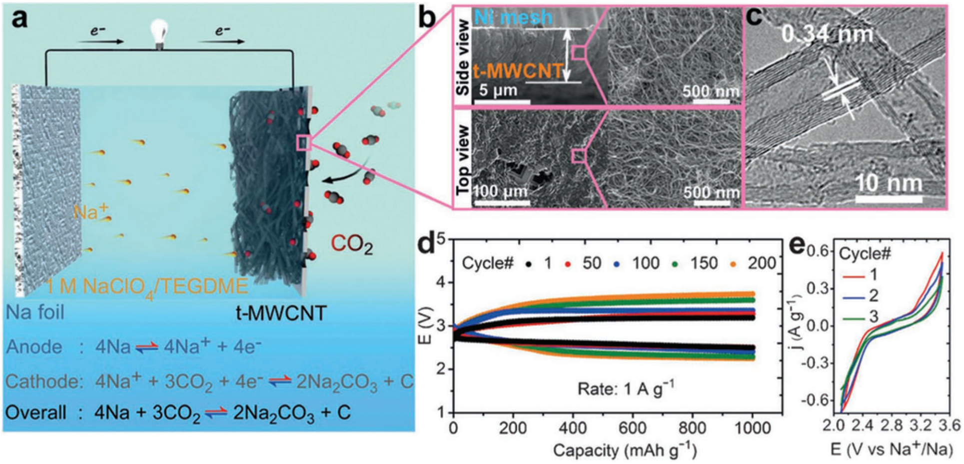

Figure 4. The structure and rechargeability of room-temperature Na–CO_2 batteries. a) Structure of Na–CO_2 batteries with metal Na foil anode, ether-based electrolyte, and t-MWCNT cathode. b) SEM images of cathode from top and side views. c) HRTEM image of t-MWCNT. d) Discharge and charge profiles of Na–CO_2 batteries at 1 A g^{-1}. e) Cyclic voltammetric curves of Na–CO_2 batteries with scan rate of 0.1 mV s^{-1}. Reproduced with permission.[46] Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

by in situ Raman, ex situ XRD and X-Ray photoelectron spectroscopy (XPS). Meanwhile, by measuring the evolved gas in the charging process, they verified that CO_2 actually reversibly formed. In order to illustrate carbon involved in the battery reaction, a silver nanowire cathode was used, since carbon nanotubes would cover the signals of the carbon products. The superior reversibility of the carbon product was indeed detected by electron energy loss spectroscopy (EELS) in transmission electron microscopy (TEM), but still needs to be verified via in situ detection. Their studies further strengthen the idea that rechargeable M–CO_2 batteries offer a practical opportunity in clean conversion/utilization of CO_2 and advanced electrochemical energy storage systems. By rational design of air cathodes, M–CO_2 batteries with excellent electrochemical performances can be achieved.

4. Mechanism: Electrocatalytic Conversion of CO_3^{2-} and CO_2

4.1. Electrochemical Redox Reactions of Metal Carbonates

In addition to CO_2 contamination, there are trace amounts of metal carbonates and carboxylates resulting from the degradation of the electrolyte and/or carbon cathode surface in pure metal–O_2 cells.[56–58] The accumulation of metal carbonates during cycling can severely influence the electrochemical performances of metal–air batteries. Therefore, studies on the decomposition of metal carbonates are quite significant for metal–CO_2 batteries, as well as for the development of true metal–air batteries. So far, the electrochemical decomposition of Li_2CO_3 has been studied by several research groups by constructing model cathodes pre-filled with Li_2CO_3.[59–62] Although a thorough understanding of the electrochemical reaction of Li_2CO_3 is not obtained, some identical phenomena have been observed. The decomposition of Li_2CO_3 only occurs at charging potentials over 4 V, and CO_2 is released during the electrochemical oxidation process. Consistent with the previous discussion in Section 2.1, no O_2 is detected through the whole charging process in each case, indicating that the decomposition reaction cannot be $Li_2CO_3 \rightarrow 2Li^+ + 2e + 1/2O_2 + CO_2$. By using the isotopic tracing and gas chromatography-mass spectrometry (GC-MS) method, Yang et al. suggested that Li_2CO_3 decomposes into CO_2 and superoxide radicals,[62] and the latter are finally consumed by the tetraglyme electrolyte solvent instead of the additional carbon. On the contrary, the Chen group found that cathodes prefilled with only Na_2CO_3 showed higher charging voltage by 0.5 V than that with Na_2CO_3/carbon hybrids, indicating a reaction between Na_2CO_3 and carbon.[46] However, carbon in both cases was not originally generated, and the chemical activity might be quite different; therefore, in situ measurements are needed for metal–CO_2 batteries to clarify these issues. Combined with the studies in rechargeable metal–CO_2 batteries,[43–45] the decomposition of metal carbonates is most likely accompanied by the degradation of carbon materials. Notably, when catalysts such as NiO[59] or Pt[60] were used, the electrochemical oxidation potentials for Li_2CO_3 dropped dramatically. In order to pursue lower charging potentials, better cyclability and energy efficiency of metal–CO_2 batteries, investigations should be focused on the development of highly effective catalysts.

On the other side, the electrochemical properties of metal carbonates are also meaningful for CO_2 recycling and utilization in energy storage devices. The Zhou group[55] first proposed that metal carbonates could be reduced to low-valence carbon, owing to the excellent catalytic activity of newly generated transition-metal nanoparticles. Based on this electrochemical catalytic conversion mechanism, a series of metal carbonates were explored and applied to many energy storage systems.[10,63–65] By using spectroscopic and transmission electron microscopic analyzes, the Wang group clarified that Li_2CO_3 could be reversibly converted to lithium carbide (Li_2C_2) and lithium oxide (Li_2O).[66] These findings promote the utilization of metal carbonates as well as the understanding of the reaction mechanisms about metal–CO_2 batteries.

4.2. Decomposition of Li_2CO_3 in Li–Air Batteries

Although the discharge products for Li–air batteries with ambient air are a mixture of Li_2O_2, LiOH, and Li_2CO_3, the decomposition of the whole products during recharge is achievable. Zhang et al. reported a rechargeable lithium–air battery working in ambient air for 100 cycles (about 78 days), with a discharge capacity of 2000 mAh g^{-1}.[67] The superiority was mainly derived from the unique hybrid system: a solid catholyte was used to prevent electrolyte degradation and the usual air cathodes were replaced by a gel cathode, forming a closed and sustainable gel/solid interface. They concluded that the high recharging overpotential is largely caused by the decomposition of the Li_2CO_3 product, and it can be reduced by raising the operation temperature. Meanwhile, transition metal oxides and precious metals employed in Li–O_2 batteries are recommended to test the decomposition of Li_2CO_3.

After the Li group reported that NiO can act as a catalyst to decompose Li_2CO_3,[59] several other studies have also demonstrated that the catalytic oxidation of carbonate/carboxylate species can be realized by using NiO catalysts in Li–O_2 cells.[68,69] Very recently, Tan et al. fabricated a cathode composed of RuO_2 nanoparticle-decorated NiO nanosheets for a non-aqueous Li–air battery.[70] The battery could be truly operated in ambient air at 500 mAh g^{-1} for 200 cycles (800 h), with nearly 100% Coulombic efficiency and ≈75% energy efficiency. The wonderful electrochemical performance can be attributed to the favorable combination: NiO nanosheets act as both support matrix and the catalyst for the decomposition of carbonates and carboxylates, while RuO_2 nanoparticles facilitate the oxygen reduction and evolution reactions, as well as the decomposition of LiOH. Obviously, metal–air batteries and metal–CO_2 batteries share the same objective of obtaining efficient catalysts for the decomposition of carbonates.

4.3. Potential Industrial Advantages of Metal–CO_2 Batteries

For metal–CO_2 batteries, pure CO_2 needs to be supplied from a tank stored on board in a vehicle. However, as questioned by Scrosati et al.,[32] it is hard for an electric vehicle to run with a Li-air battery operating in the "breathing mode". Taking a 500 km range as an example, the total consumption of O_2 is 967 mol, corresponding to an O_2 flow of ≈1.2 L s^{-1} if all O_2 was consumed. Considering that oxygen only takes up about one fifth of the earth's atmosphere, much higher flows are expected to be needed. In addition, the deposition of the discharge products would make the triple-phase interface reaction even more sluggish. Both the extra devices for feeding O_2 to the cathode substrates and the electrode surface area must be settled within a limited weight range. When compressed to a relatively safe and practical 120 bar pressure at 30°C, the density of O_2 is only 0.160 kg L^{-1}, while that of CO_2 is up to 0.802 kg L^{-1}.[71] Potentially even the economically available solid CO_2, "dry ice", could be stored with a high density of 1.6 kg L^{-1}. Obviously, CO_2 appears far more advantageous for on-board storage than O_2 due to its far better compressibility and greater density. Moreover, CO_2 can be supplied as a supercritical fluid when taken from the storage tank. In that case, it can serve as both the electroactive species and the solvent. The solubility for salts and the ionic conductivity could be enhanced by adding polar modifiers[72] and supporting electrolytes,[73] thus very fast ion transport and high charge/discharge rates could be achieved. Based on the CO_2/oxalate reversible electrochemical conversion in ionic liquid electrolytes[40] with special catalysts,[74] Németh et al. further proposed the use of CO_2/oxalate electrodes in metal–air type batteries and offered a rechargeable Li–CO_2/oxalate flow battery (**Figure 5**).[71] Compared with metal peroxides and superoxides, metal carbonates and oxalates are much safer discharge products than peroxides. Hence, the potential industrial advantages of metal–CO_2 batteries may be realized in terms of significantly improved safety, environmental friendliness, high energy and power density, and efficient on-board storage.

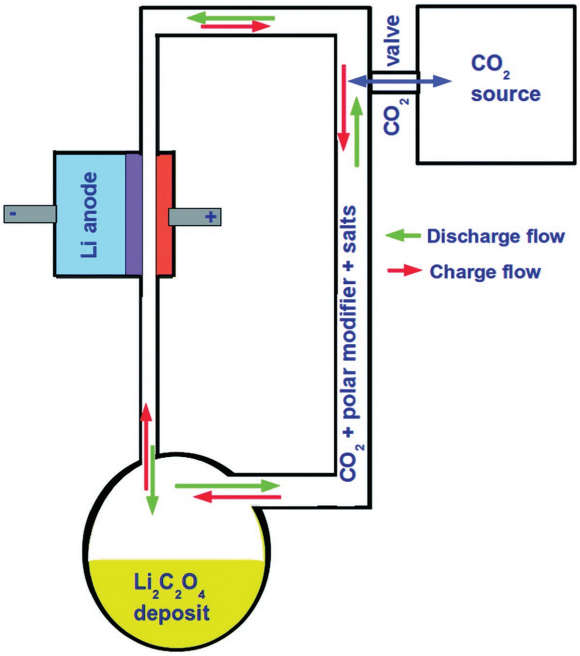

Figure 5. Schematic view of a rechargeable Li–CO_2/oxalate flow battery. Reproduced with permission.[71] Copyright 2013, Royal Society of Chemistry.

5. Summary and Prospective

CO_2 exploitation, especially coupled with energy storage devices, has great practical significance in alleviating energy shortage and global warming issues. Recent development of primary metal–O_2/CO_2 batteries to rechargeable metal–CO_2 batteries is summarized in this review. Encouragingly, rechargeable room-temperature metal–CO_2 batteries are gradually realized. However, the whole discharge–charge reaction mechanism is still ambiguous. Additionally, there are considerable obstacles and difficulties to be overcome, including low discharge capacity, weak rate capability, high charge overpotential, poor cyclability, and many other problems. All the above challenges seem to be caused by the sluggish electrochemical reactions at air cathodes. To overcome these challenges, the following research directions may present new opportunities to break through the technology bottleneck of metal–CO_2 batteries.

Better understanding of discharge–charge reaction mechanism. Although the metal–CO_2 battery reaction has been demonstrated as $4M + 3CO_2 \leftrightarrow 2M_2CO_3 + C$ (11), more in situ measurements are needed for the observation of the original generation and decomposition of carbon along with metal carbonates. Additionally, whether alkali metal ions play an important role in the reduction of CO_2 is still unclear, and the influence of supporting electrolyte cations is not considered yet. After all, Reaction 11 is not common in the photochemical and electrochemical conversion of CO_2. Both experimental tests and theoretical computations are needed for further investigations.

Exploring new types of electrolytes with high stability. The electrochemical stability of electrolytes can greatly affect the performances of M–CO_2 batteries, and particular attention should be paid to the electrolyte decomposition during both charge and discharge. Due to the stability of metal carbonates, the charge potentials of M–CO_2 batteries are usually beyond the stability window of most electrolytes. More stable alternatives like ionic liquids and solid-state electrolytes should be developed.

Exploring new cathode materials with high catalytic activity and unique structure. So far, only several pure carbon materials have been used in metal–CO_2 batteries. Clearly, a variety of cathode materials can be utilized to optimize the electrochemical performances referred to metal–O_2 batteries. Seeking highly active catalysts for the decomposition of metal carbonates is the primary future task, since the sluggish kinetic discharging–charging processes dramatically increase the overpotentials, which in turn results in low rate capability, poor cycling stability and energy efficiency. The decomposition of metal carbonates is also important in promoting the electrochemical performances of metal–air batteries. We believe that designing/fabricating special carbon materials including highly active catalysts with a connected 3D space is a promising strategy, since the homogeneous discharged products can be decomposed easily during the charge process without clogging the cathode surface.

Exploring other metal–CO_2 batteries. As reported by Archer et al.,[53] when Mg and Al were tested as anode materials at room temperature, metal–CO_2 batteries only showed low discharge capacity with commensurate discharge potentials. Nevertheless, the authors indicated that those values can be made substantially larger by using a combination of higher operating temperatures and cathode materials with larger surface area. Further studies should be completed on Mg and Al–CO_2 batteries, because these metal anodes are advantageous for their greater earth-abundance and better safety. Even primary batteries are favorable.

In summary, rechargeable room-temperature metal–CO_2 batteries offer an alternative approach towards clean recycling and utilization of CO_2, as advanced electrochemical energy storage devices. We believe that, with continued and extensive efforts to developing effective catalysts and innovative cathode structures, the electrochemical performances of rechargeable metal–CO_2 batteries will be significantly improved. Considering the potential engineering advantage of CO_2 on-board storage, we are confident that rechargeable metal–CO_2 batteries will play an important role in energy storage systems in the future.

Acknowledgements

This work was supported by the NSFC (21473094 and 21421001) and Shanghai Aurisco Industry Co., Ltd. in China.

Received: November 1, 2016
Revised: November 13, 2016

---

[1] P. Friedlingstein, R. A. Houghton, G. Marland, J. Hackler, T. A. Boden, T. J. Conway, J. G. Canadell, M. R. Raupach, P. Ciais, C. Le Quéré, *Nat. Geosci.* **2010**, *3*, 811.
[2] G. P. Peters, G. Marland, C. Le Quéré, T. Boden, J. G. Canadell, M. R. Raupach, *Nat. Clim. Change* **2012**, *2*, 2.
[3] K. Caldeira, A. K. Jain, M. I. Hoffert, *Science* **2003**, *299*, 2052.
[4] J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.* **2014**, *43*, 631.
[5] C. D. Windle, R. N. Perutz, *Coord. Chem. Rev.* **2012**, *256*, 2562.
[6] J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* **2015**, *115*, 12888.
[7] C. Costentin, M. Robert, J.-M. Savéant, *Chem. Soc. Rev.* **2013**, *42*, 2423.
[8] J. Schneider, H. F. Jia, J. T. Muckerman, E. Fujita, *Chem. Soc. Rev.* **2012**, *41*, 2036.
[9] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* **2014**, *114*, 11636.
[10] Y. Zhong, M. Yang, X. Zhou, Y. Luo, J. Wei, Z. Zhou, *Adv. Mater.* **2015**, *27*, 806.
[11] Y. Tang, Y. Zhang, W. Li, B. Ma, X. Chen, *Chem. Soc. Rev.* **2015**, *44*, 5926.
[12] M. K. Debe, *Nature* **2012**, *486*, 43.
[13] C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almansoori, R. O'Hayre, *Science* **2015**, *349*, 1321.
[14] C.-H. Cui, S.-H. Yu, *Acc. Chem. Res.* **2013**, *4*, 1427.
[15] M. Yang, Y. Zhong, J. Ren, X. Zhou, J. Wei, Z. Zhou, *Adv. Energy Mater.* **2015**, *5*, 1500550.
[16] M. Yang, Y. Zhong, X. Zhou, J. Ren, L. Su, J. Wei, Z. Zhou, *J. Mater. Chem. A* **2014**, *2*, 12519.
[17] T. Lin, I.-W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, *Science* **2015**, *350*, 1508.
[18] T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390.
[19] J.-S. Lee, S. T. Kim, R. Cao, N.-S. Choi, M. Liu, K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34.
[20] Q. Sun, Y. Yang, Z.-W. Fu, *Electrochem. Commun.* **2012**, *16*, 22.
[21] Z. Zhang, L. Su, M. Yang, M. Hu, J. Bao, J. Wei, Z. Zhou, *Chem. Commun.* **2014**, *50*, 776.
[22] Z. Zhang, J. Bao, C. He, Y. Chen, J. Wei, Z. Zhou, *Adv. Funct. Mater.* **2014**, *24*, 6826.
[23] Y. Chen, Q. Zhang, Z. Zhang, X. Zhou, Y. Zhong, M. Yan g, Z. Xie, J. Wei, Z. Zhou, *J. Mater. Chem. A* **2015**, *3*, 17874.
[24] H.-G. Jung, J. Hassoun, J.-B. Park, Y.-K. Sun, B. Scrosati, *Nat. Chem.* **2012**, *4*, 579.
[25] M. M. Ottakam Thotiyl, S. A. Freunberger, Z. Peng, Y. Chen, Z. Liu, P. G. Bruce, *Nat. Mater.* **2013**, *12*, 1050.
[26] Z. Zhang, Y. Chen, J. Bao, Z. Xie, J. Wei, Z. Zhou, *Part. Part. Syst. Charact.* **2015**, *32*, 680.
[27] H. Kitaura, H. Zhou, *Energy Environ. Sci.* **2012**, *5*, 9077.

[28] F. Li, T. Zhang, Y. Yamada, A. Yamada, H. Zhou, *Adv. Energy Mater.* **2013**, *3*, 532.
[29] F. Li, Y. Chen, D.-M. Tang, L. Z. Jian, C. Liu, D. Golberg, A. Yamada, H. Zhou, *Energy Environ. Sci.* **2014**, *7*, 1648.
[30] Z. Ma, X. Yuan, L. Li, Z.-F. Ma, D. P. Wilkinson, L. Zhang, J. Zhang, *Energy Environ. Sci.* **2015**, *8*, 2144.
[31] A. C. Luntz, B. D. McCloskey, *Chem. Rev.* **2014**, *114*, 11721.
[32] L. Grande, E. Paillard, J. Hassoun, J.-B. Park, Y.-J. Lee, Y.-K. Sun, S. Passerini, B. Scrosati, *Adv. Mater.* **2015**, *27*, 784.
[33] Z. Chang, J. Xu, Q. Liu, L. Li, X. Zhang, *Adv. Energy Mater.* **2015**, *5*, 1500633.
[34] S. Xu, S. Lau, L. A. Archer, *Inorg. Chem. Front.* **2015**, *2*, 1070.
[35] Trends in Atmospheric Carbon Dioxide, http://www.esrl.noaa.gov/gmd/ccgg/trends/ (accessed: November, 2016).
[36] J. D. Wadhawan, P. J. Welford, E. Maisonhaute, V. Climent, N. S. Lawrence, R. G. Compton, H. B. McPeak, C. E. W. Hahn, *J. Phys. Chem. B* **2001**, *105*, 10659.
[37] J. L. Roberts, T. S. Calderwood, D. T. Sawyer, *J. Am. Chem. Soc.* **1984**, *106*, 4667.
[38] K. Takechi, T. Shiga, T. Asaoka, *Chem. Commun.* **2011**, *47*, 3463.
[39] S. R. Gowda, A. Brunet, G. M. Wallraff, B. D. McCloskey, *J. Phys. Chem. Lett.* **2013**, *4*, 276.
[40] S. K. Das, S. Xu, L. A. Archer, *Electrochem. Commun.* **2013**, *27*, 59.
[41] Y. S. Mekonnen, K. B. Knudsen, J. S. G. Mýrdal, R. Younesi, J. Højberg, J. Hjelm, P. Norby, T. Vegge, *J. Chem. Phys.* **2014**, *140*, 121101.
[42] H. Lim, H. Lim, K. Park, D. Seo, H. Gwon, J. Hong, W. Goddard, H. Kim, K. Kang, *J. Am. Chem. Soc.* **2013**, *135*, 9733.
[43] Y. Liu, R. Wang, Y. Lyu, H. Li, L. Chen, *Energy Environ. Sci.* **2014**, *7*, 677.
[44] Z. Zhang, Q. Zhang, Y. Chen, J. Bao, X. Zhou, Z. Xie, J. Wei, Z. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 6550.
[45] X. Zhang, Q. Zhang, Z. Zhang, Y. Chen, Z. Xie, J. Wei, Z. Zhou, *Chem. Commun.* **2015**, *51*, 14636.
[46] X. Hu, J. Sun, Z. Li, Q. C. Chen, J. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 6482.
[47] F. Montmessin, J.-L. Bertaux, E. Quémerais, O. Korablevb, P. Rannoua, F. Forgetc, S. Perriera, D. Fussend, S. Lebonnoisc, A. Rébéraca, E. Dimarellisa, *Icarus* **2006**, *183*, 403.
[48] D. G. Kwabi, T. P. Batcho, C. V. Amanchukwu, N. Ortiz-Vitoriano, P. Hammond, C. V. Thompson, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2014**, *5*, 2850.
[49] D. Sharon, M. Afri, M. Noked, A. Garsuch, A. A. Frimer, D. Aurbach, *J. Phys. Chem. Lett.* **2013**, *4*, 3115.
[50] S. Xu, Y. Lu, H. Wang, H. D. Abruña, L. A. Archer, *J. Mater. Chem. A* **2014**, *2*, 17723.
[51] S. Xu, S. Wei, H. Wang, H. D. Abruña, L. A. Archer, *ChemSusChem* **2016**, *9*, 1600.
[52] W. I. Al Sadat, L. A. Archer, *Sci. Adv.* **2016**, *2*, e1600968.
[53] S. Xu, S. K. Das, L. A. Archer, *RSC Adv.* **2013**, *3*, 6656.
[54] S. K. Das, S. Xu, A. Emwas, Y. Lu, S. Srivastava, L. A. Archer, *Energy Environ. Sci.* **2012**, *5*, 8927.
[55] L. Su, Z. Zhou, X. Qin, Q. Tang, D. Wu, P. Shen, *Nano Energy* **2013**, *2*, 276.
[56] C. J. Barile, A. A. Gewirth, *J. Electrochem. Soc.* **2013**, *160*, A549.
[57] U. Sahapatsombut, H. Cheng, K. Scott, *J. Power Sources* **2013**, *243*, 409.
[58] G. M. Veith, N. J. Dudney, J. Howe, J. Nanda, *J. Phys. Chem. C* **2011**, *115*, 14325.
[59] R. Wang, X. Yu, J. Bai, H. Li, X. Huang, L. Chen, X. Yang, *J. Power Sources* **2012**, *218*, 113.
[60] S. Meini, N. Tsiouvaras, K. U. Schwenke, M. Piana, H. Beyer, L. Lange, H. A. Gasteiger, *Phys. Chem. Chem. Phys.* **2013**, *15*, 11478.
[61] C. Ling, R. Zhang, K. Takechi, F. Mizuno, *J. Phys. Chem. C* **2014**, *118*, 26591.
[62] S. Yang, P. He, H. Zhou, *Energy Environ. Sci.* **2016**, *9*, 1650.
[63] J. Q. Zhao, Y. Wang, *J. Mater. Chem. A* **2014**, *2*, 14947.
[64] B. Yao, Z. Ding, X. Feng, L. Yin, Q. Shen, Y. Shi, J. Zhang, *Electrochim. Acta* **2014**, *148*, 283.
[65] Y. Zhong, L. Su, M. Yang, J. Wei, Z. Zhou, *ACS Appl. Mat. Interface* **2015**, *182*, 559.
[66] N. Tian, C. X. Hua, Z. X. Wang, L. Q. Chen, *J. Mater. Chem. A* **2015**, *3*, 14173.
[67] T. Zhang, H. Zhou, *Nat. Commun.* **2013**, *4*, 1817.
[68] M. Hong, H. C. Choi, H. R. Byon, *Chem. Mater.* **2015**, *27*, 2234.
[69] S. Tong, M. Zheng, Y. Lu, Z. Lin, J. Li, X. Zhang, Y. Shi, P. He, H. Zhou, *J. Mater. Chem. A* **2015**, *3*, 16177.
[70] P. Tan, Z. H. Wei, W. Shyy, T. S. Zhao, X. B. Zhu, *Energy Environ. Sci.* **2016**, *9*, 1783.
[71] K. Németh, G. Srajer, *RSC Adv.* **2014**, *4*, 1879.
[72] D. Kodama, M. Kanakubob, M. Kokuboa, S. Hashimotoa, H. Nanjob, M. Katoa, *Fluid Phase Equilib.* **2011**, *302*, 103.
[73] H. Kawanami, A. Sasaki, K. Matsuia, Y. Ikushima, *Chem. Commun.* **2003**, 896.
[74] R. Angamuthu, P. Byers, M. Lutz, A. L. Spek, E. Bouwman, *Science* **2010**, *327*, 313.