

# Li-CO<sub>2</sub> Batteries Efficiently Working at Ultra-Low Temperatures

Jiaxin Li, Lie Wang, Yang Zhao, Shangyu Li, Xuemei Fu, Bingjie Wang,\* and Huisheng Peng\*

Lithium-carbon dioxide (Li-CO2) batteries are considered promising energystorage systems in extreme environments with ultra-high CO<sub>2</sub> concentrations, such as Mars with 96% CO<sub>2</sub> in the atmosphere, due to their potentially high specific energy densities. However, besides having ultra-high CO<sub>2</sub> concentration, another vital but seemingly overlooked fact lies in that Mars is an extremely cold planet with an average temperature of approximately -60 °C. The existing Li-CO<sub>2</sub> batteries could work at room temperature or higher, but they will face severe performance degradation or even a complete failure once the ambient temperature falls below 0 °C. Herein, ultra-lowtemperature Li-CO<sub>2</sub> batteries are demonstrated by designing 1,3-dioxolanebased electrolyte and iridium-based cathode, which show both a high deep discharge capacity of 8976 mAh  $g^{-1}$  and a long lifespan of 150 cycles (1500 h) with a fixed 500 mAh  $g^{-1}$  capacity per cycle at -60 °C. The easy-to-decompose discharge products in small size on the cathode and the suppressed parasitic reactions both in the electrolyte and on the Li anode at low temperatures together contribute to the above high electrochemical performances.

## 1. Introduction

Aprotic lithium-carbon dioxide (Li-CO<sub>2</sub>) batteries have attracted increasing interests recently in virtue of their double functions of CO<sub>2</sub> fixation/utilization and energy storage,<sup>[1,2]</sup> which provide promising and economical strategies to simultaneously deal with two vital issues of global warming and energy crisis on the Earth.<sup>[3]</sup> Moreover, utilizing CO<sub>2</sub> as cathode materials makes the energy systems exert unique advantages in aerospace exploration, such as on the Mars with CO<sub>2</sub> concentration of up to 96% in the atmosphere.<sup>[4]</sup> Therefore, a lot of efforts have been made to develop various catalytic cathodes,<sup>[5–8]</sup> electrolyte additives,<sup>[9–11]</sup> and quasi-solid/solid state electrolytes,<sup>[9,12,13]</sup> and design new flexible electrodes<sup>[14–16]</sup> in order to improve their energy/power density, cyclicity, and flexibility toward future practical application.

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It should be noted that the existing studies mainly focus on the working environment at room temperature or even a high temperature of 150 °C.<sup>[17]</sup> However, a significant but hardly mentioned fact lies in that the Li-CO<sub>2</sub> batteries are more likely to be used at low-temperature and even ultra-low-temperature environments. For example, the Mars, a most promising application field for Li-CO<sub>2</sub> batteries, is an extremely cold planet with an average temperature of approximately -60 °C.<sup>[18]</sup> It is conceivable that the operating temperature plays a significant role in the electrochemical behaviors of battery.<sup>[19]</sup> The Li-CO<sub>2</sub> batteries designed for roomtemperature application probably fail to work normally below 0 °C. To be more specific, the decrease of ambient temperature inevitably results in a decreased electrolyte conductivity, slowed electrode reaction kinetics, and poor electrode/

electrolyte interfaces, so that more energy needs to be used to drive the discharge and charge process, thereby leading to an enlarged discharge/charge overpotential and short cyclic life. What is worse, the batteries will thoroughly fail to work at ultralow temperatures (e.g., -60 °C) due to complete solidification of electrolyte. To the best of our knowledge, no study has been available by far for the realization of low-temperature Li-CO<sub>2</sub> battery, not to mention ultra-low-temperature Li-CO<sub>2</sub> battery. We believe that it is necessary to design Li-CO<sub>2</sub> batteries that could work at ultra-low-temperature environments for future realistic application such as Mars exploration.

Herein, we assembled a Swagelok-type Li-CO<sub>2</sub> battery utilizing Li as the anode, lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) in 1,3-dioxolane (DOL) as the electrolyte, and iridium-coated gas diffusion layer (GDL) as the cathode, with the commercially available Parafilm as the cathode-protective layer. Benefited from the ultra-low freezing point, high ionic conductivity, and good electrochemical stability of DOL-based electrolyte at low temperatures and high catalytic activity of iridium cathodes for CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and CO<sub>2</sub> evolution reaction (CO<sub>2</sub>ER), the resulting Li-CO<sub>2</sub> batteries could work efficiently at ultra-low-temperature environments. To be precise, they exhibited a high deep discharge capacity of 8976 mAh g<sup>-1</sup> and a long lifespan of 150 cycles (1500 h) with a limited capacity of 500 mAh g<sup>-1</sup> for each cycle and a current density of 100 mA g<sup>-1</sup> at -60 °C. We found that both the

J. Li, L. Wang, Y. Zhao, S. Li, Dr. X. Fu, Prof. B. Wang, Prof. H. Peng State Key Laboratory of Molecular Engineering of Polymers Department of Macromolecular Science Laboratory of Advanced Materials Fudan University Shanghai 200438, China E-mail: wangbingjie@fudan.edu.cn; penghs@fudan.edu.cn The ORCID identification number(s) for the author(s) of this article







in Li-anode and DOL-based electrolyte

**Figure 1.** Schematic illustration to Li-CO<sub>2</sub> batteries working at the ultra-low-temperature environments. The diagram shows the formation and decomposition of the discharge products during the discharge process (left part) and the charge process (right part). The working mechanism of Li-CO<sub>2</sub> battery is based on electrochemical reaction,  $4Li + 3CO_2 + 4e^- \rightleftharpoons 2Li_2CO_3 + C$  (E = 2.80 V, vs Li<sup>+</sup>/Li).

easy-to-decompose discharge products in small size on cathode and the inhibited parasitic reactions both in electrolyte and on Li anode were responsible for the high electrochemical performances at low temperatures (**Figure 1**).

## 2. Results and Discussion

## 2.1. Design of Ultra-Low-Temperature Li-CO<sub>2</sub> Batteries

The design of ultra-low-temperature batteries generally involves a systematic material selection<sup>[19]</sup> and/or battery structure optimization.<sup>[20]</sup> A highly conductive electrolyte should be first utilized to ensure an efficient ion transport and favorable electrolyte/electrode interfaces at low temperatures.<sup>[21,22]</sup> For the low-temperature electrolyte of Li-CO<sub>2</sub> batteries, DOL, a small cyclic ether molecule, emerged as an ideal candidate due to its good characteristics of a low freezing point of -95 °C (Table S1, Supporting Information), small viscosity and low desolvation energy of solvated Li ion,<sup>[23]</sup> and great capacity to ensure a high cycle efficiency of Li anode.<sup>[24]</sup> While the common tetraglymebased electrolyte was completely frozen at approximately -40 °C, differential scanning calorimetry and Raman spectra showed that the freezing point of DOL-based electrolyte was even below -100 °C, which was obviously a more suitable choice as low-temperature electrolyte than conventional electrolytes (Figures S1 and S2, Supporting Information). DOLbased electrolyte presented a much higher ionic conductivity than tetraglyme-based electrolyte and it even maintained a high conductivity of 2.26 mS cm<sup>-1</sup> at -80 °C (Figure S3, Supporting Information).

Electrochemical impedance spectroscopy was further used to investigate the impact of temperature on the electrochemical behaviors of Li-CO<sub>2</sub> batteries based on DOL and tetraglyme electrolytes. It was found that the former demonstrated a much better low-temperature adaptability than the latter (Figure S4, Supporting Information). However, although DOL as an additive has been introduced to aprotic metal-gas battery to improve battery cycling,<sup>[25]</sup> it was usually not considered as an ideal electrolyte solvent for the room-temperature aprotic metal-gas battery due to inevitable side reactions upon cycling.<sup>[26]</sup> Importantly, those undesirable parasitic reactions related to electrolytes would be obviously inhibited at low temperatures owing to the enhanced electrolyte stability.<sup>[27]</sup> It was noticeable that the electrochemical stability could be improved at the lowered temperature, with a stable voltage window expanding from 3.05 V at 0 °C to 3.53 V at -30 °C and 4.34 V at -60 °C (Figure S5, Supporting Information). Therefore, DOL was here explored as electrolyte solvent for low-temperature Li-CO<sub>2</sub> batteries.

Iridium was found to be favorable for  $CO_2RR$  and  $CO_2ER$  in electrocatalysis studies, and has been used to improve the electrochemical performances of Li-CO<sub>2</sub> batteries.<sup>[28,29]</sup> But it was never explored in the low-temperature energy-storage devices. In this work, iridium-coated GDLs were utilized as the cathodes of Li-CO<sub>2</sub> battery (Figures S6 and S7, Supporting Information). In addition, considering that Li-CO<sub>2</sub> battery is a semi-open system of which electrolyte experiences an unavoidable continuous evaporation through its porous cathode, especially exposed to a relatively high-temperature environment,<sup>[30]</sup> the Parafilm (CO<sub>2</sub> permeable<sup>[31]</sup>) was skillfully utilized as a cathode protective layer to suppress the volatilization of electrolyte (Figure S8, Supporting Information) and further extend the operating life of Li-CO<sub>2</sub> battery (Figure S9, Supporting Information).

# 2.2. Electrochemical Performances of Li-CO<sub>2</sub> Batteries at Low Temperatures

The influence of temperature on the electrochemical performances of Li-CO<sub>2</sub> batteries was then carefully investigated. When they were used as the primary batteries, the deep discharge capacity could reach 14 720 mAh g<sup>-1</sup> at 0 °C and 8976 mAh g<sup>-1</sup> at -60 °C, with a cut-off voltage of 2.0 V and a current density of 100 mA g<sup>-1</sup> (**Figure 2a**). In comparison, the capacitances of Li-CO<sub>2</sub> batteries based on the iridium cathodes were much higher than those using GDL cathodes, proving iridium was favorable for the discharge reaction (Figures S10 and S11, Supporting Information). Besides, no noticeable voltage drop appeared on the discharge plateaus even if the current density increased from 50 to 500 mA g<sup>-1</sup> at -60 °C





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**Figure 2.** Electrochemical performances of Li-CO<sub>2</sub> batteries at low temperatures. a) Deep discharge curves at a current density of 100 mA  $g^{-1}$ . b–d) Selected discharge and charge profiles with a limited capacity of 500 mAh  $g^{-1}$  and a current density of 100 mA  $g^{-1}$  at 0, –30, and –60 °C, respectively. e) Comparison of long-term cycling performance of Li-CO<sub>2</sub> batteries at 0, –30, and –60 °C.

(Figure S12, Supporting Information), further showing a high low-temperature adaptability and good rate performance of the Li-CO<sub>2</sub> system. The discharge and charge capacitance of Li-CO<sub>2</sub> batteries in argon were much lower than those in CO<sub>2</sub> at corresponding temperatures (Figure S13, Supporting Information), indicating a negligible capacity contribution from Li ion adsorption effect in cathode to the total capacity. The results also reflected that the oxidation stability of electrolyte was improved with the decreasing temperatures, which was consistent with the linear sweep voltammetry results in Figure S5 (Supporting Information). In particular, the charge curve in argon was featureless until about 4.8 V at -60 °C. The enhanced oxidation stability would enable DOL-based electrolyte to withstand the increased charge polarization at -60 °C.

When used as secondary batteries, the long-term cyclic stability of Li-CO<sub>2</sub> batteries at low temperatures was carefully investigated with a cut-off capacity of 500 mAh g<sup>-1</sup> and a current density of 100 mA g<sup>-1</sup> at 0, -30, and -60 °C (Figure 2b–d). At 0 °C, the mid-capacity potential gap for the first cycle of the Li-CO<sub>2</sub> system was 0.85 V, increasing to 1.35 V at the 30th cycle, followed by a final failure after 40 cycles. Unexpectedly, although there was an inevitable expanded polarization gap at the first cycle, the Li-CO<sub>2</sub> batteries showed an enhanced cyclic stability at decreased ambient temperatures. As operating

temperature decreased to -30 °C, the batteries could be discharged and charged stably for 69 cycles, and their lifespan even further extended to 150 cycles (1500 h) at -60 °C. In addition, the cyclicity of Li-CO<sub>2</sub> batteries based on iridium and GDL cathodes at different temperatures was also carefully compared in Figures S14 and S15 (Supporting Information). It was found that a significant decrease in the polarization gap and a substantial increase in the cycle number achieved when iridium was introduced as catalyst, and up to 150 cycles could be achieved for the Li-CO<sub>2</sub> batteries with iridium-coated cathodes at -60 °C. In contrast, the Li-CO<sub>2</sub> batteries failed after 23 cycles without the iridium. Overall, the above results indicated that the Li-CO<sub>2</sub> batteries based on iridium cathodes could work stably both as primary or secondary batteries at ultra-low temperatures. Besides, the Li-CO<sub>2</sub> batteries also proved to be able to work stably at room temperature of 25 °C (Figures S16 and S17, Supporting Information). To the best of our knowledge, the Li-CO<sub>2</sub> batteries here were the first aprotic metal-gas batteries both with high capacitance and good cyclicity at such a low temperature reported to date (Table S2, Supporting Information).

# 2.3. Discharge Product Analysis of Li-CO<sub>2</sub> Batteries at Low Temperatures

It is generally believed that the cycling life of aprotic metalgas battery is closely related to the morphology and composition of discharge products.<sup>[32,33]</sup> Therefore, to understand why an enhanced cyclicity was achieved in the Li-CO<sub>2</sub> batteries at -60 °C, we compared the cathode before assembled into a Li-CO<sub>2</sub> battery and after taken out of the Li-CO<sub>2</sub> battery that had worked at different temperatures using several techniques. Both ex situ X-ray diffraction spectroscopy and Fourier transform infrared spectroscopy confirmed the formation of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) after discharge and subsequent complete decomposition after charge (Figures S18 and S19, Supporting Information). More attention was paid to the battery reversibility at -60 °C in view of the slowed CO2RR and CO2ER kinetics at such a low temperature. Comparing the ex situ C 1s X-ray photoelectron spectra (Figure 3a,b and Figure S20, Supporting Information) and Raman spectra (Figure S21, Supporting Information) of the cathodes before being assembled into and re-collected from the discharged/charged batteries at -60 °C, we found that the discharge products were completely decomposed after recharge on cathodes. To be more specific, the appearance and disappearance of characteristic peaks of 290.3 eV in C 1s X-ray photoelectron spectra and 1089 cm<sup>-1</sup> in Raman spectra related to Li<sub>2</sub>CO<sub>3</sub> demonstrated a good reversibility of Li-CO<sub>2</sub> batteries at ultra-low-temperature environments, which was consistent with the previous results of the X-ray diffraction spectra (Figure S18, Supporting Information) and Fourier transform infrared spectra (Figure S19, Supporting Information).

Besides, ex situ Raman spectroscopy was performed on carbon-free iridium-coated nickel foam cathodes to study the discharge products at -60 °C. The emergence of characteristic G-band at around 1600 cm<sup>-1</sup> complementally demonstrated the presence of carbon in discharge products (Figure S22, Supporting Information). Besides, the decomposition details of discharge products were revealed by in situ differential electrochemical mass spectrometry analysis during charging at an ultra-low-temperature environment (Figure S23, Supporting Information). The significantly enhanced CO<sub>2</sub> signal and unnoticeable O<sub>2</sub> signal demonstrated a dominant co-oxidation reaction of Li<sub>2</sub>CO<sub>3</sub>/carbon and a slight self-decomposition reaction of Li<sub>2</sub>CO<sub>3</sub> co-existed in the charge stage. The above processes followed the following reactions,  $2\text{Li}_2\text{CO}_3$ +C→4Li<sup>+</sup>+3CO<sub>2</sub>+4e<sup>-</sup> and  $2\text{Li}_2\text{CO}_3$ →4Li<sup>+</sup>+2CO<sub>2</sub>+O<sub>2</sub><sup>-</sup>+3e<sup>-</sup>, in accordance with some ever-reported room-temperature Li-CO<sub>2</sub> batteries.<sup>[16]</sup>

Even with the same chemical nature, the morphology of discharge products varied significantly with temperature. After the initial discharge at 0 °C, the primary smooth cathode was covered by flakes in sizes of 100-300 nm (Figure 3c and Figure S24a,d, Supporting Information). With further decreasing temperature to -30 and -60 °C, the products evolved to spherical particles in diameters of 50-70 nm (Figure 3d and Figure S24b,e, Supporting Information) and 30-50 nm (Figure 3e and Figure S24a,d, Supporting Information), respectively (Figure 3e and Figure S24c,f, Supporting Information). As a distinct comparison, the morphology and size distribution of discharge products at different temperatures were counted and compared in Figure 3i and Table S3 of the Supporting Information. On the one hand, the production of flake/particle-shaped products rather than conformal film-like products indicated the formation of discharge products probably followed a solutiongrowth mechanism instead of a surface-mediated pathway.[34] The products formed through the solution-growth pathway were generally believed to be easier to decompose, thus contributing to high capacity and avoiding early battery death.<sup>[35,36]</sup> On the other hand, the morphology and structure of discharge products were found to greatly affect the reversibility and lifespan of metal-gas batteries.<sup>[28,32,37]</sup> Scanning electron microscopy images further showed that the product particles were completely removed from the cathode after the first recharge at different temperatures (Figure 3f-h). However, some undecomposed products remained on the cathode at 0 °C after ten cycles. In contrast, there was no visible product residue after the tenth recharge at -30 and -60 °C (Figure S25, Supporting Information). In particular, the reversibility of Li-CO<sub>2</sub> battery at the tenth cycle at -60 °C was also confirmed by C 1s X-ray photoelectron spectroscopy (Figure S26, Supporting Information).

Here, the improved cyclicity of Li-CO<sub>2</sub> batteries at low temperatures was explained in terms of the morphology differences of discharge products under different temperatures (Figure 3j). The nucleation of products was easier to occur at low-temperature of -60 °C than at 0 °C, while the growth process of products was slowed at -60 °C.<sup>[38,39]</sup> As a consequence, more small granular products accumulated loosely on the cathode after discharge at -60 °C, whereas larger product particles were deposited on the electrode surface at the end of discharge at 0 °C. In addition, the oxidation of insulating products usually proceeds from the solution-solid interphase region toward the inside of insulators due to the limitation of electron-tunneling distance.<sup>[40]</sup> So that the product particles in small size are more favorable for decomposition during charging because of the increased interfaces and oxidation sites.<sup>[40]</sup> It is generally thought that the "death" of metal-gas battery is related to the accumulation of undecomposed insulating products on

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**Figure 3.** Morphology of discharge products and cyclic reversibility of Li-CO<sub>2</sub> batteries at low temperatures. a,b) C 1s X-ray photoelectron spectra of the iridium-based cathodes after the initial discharge and recharge at -60 °C. Scanning electron microscopy images of c-e) the discharged and f-h) recharged cathodes at 0, -30, and -60 °C (inset, schematic illustration to the morphology of discharge products). i) Histograms of size distribution of discharge products at 0, -30, and -60 °C (inset, the enlarged graphs of histograms at -30 and -60 °C). The superimposed curve line represents a fitted Gaussian distribution. j) A schematic illustrating the impact of temperature on the formation and decomposition of discharge products. Scale bars of (c)-(h), 500 nm.

cathode upon cycling, which will cause the blockage and passivation of porous cathodes. Therefore, low-temperature products in reduced sizes were easier to decompose and less likely to remain on cathode after charging, which probably contributed to a better cyclicity. In addition, scanning electron microscopy images showed that the iridium was able to influence the morphology of discharge products. Without iridium, the products tended to form a film-liked structure around the electrode surface, especially at -60 °C, instead of the production of loosely stacked particles on the iridium cathode (Figure S27,





Supporting Information). Different from iridium-based cathodes, no significant correlation between temperature and product size was observed on GDL electrodes. After further charging, there were still some undecomposed product residues on the electrode surface, which should be a reason related to the short battery lifespan.

## 2.4. Stability Analysis of Li-CO<sub>2</sub> Batteries at Low Temperatures

In addition to the accumulation of undecomposed products on cathodes, severe parasitic reactions upon cycling were also considered as an important reason for the early failure of metal-gas battery. To illustrate, the failed Li-CO<sub>2</sub> battery could be reactivated by replacing the corrosive anode with a fresh Li sheet.<sup>[41]</sup> It was also exemplified by the Li-air battery with longer life by using the protected anode and/or highly stable electrolyte.<sup>[26,42]</sup> Herein, we performed ex situ <sup>1</sup>H-nuclear magnetic resonance analysis for the fresh and used electrolytes and X-ray diffraction characterization on the pristine and removed Li anodes from the cycled Li-CO<sub>2</sub> batteries. As shown in the <sup>1</sup>H-nuclear magnetic resonance spectra (**Figure 4**a–c), there was no obvious evidence for the parasitic reactions of recollected electrolytes at -30 and -60 °C, while the electrolyte underwent serious side reactions including the decomposition and ring-opening polymerization of DOL molecules after ten cycles at 0 °C. The results indicated that some adverse reactions associated with electrolyte were effectively restrained at lowered temperatures even in an expanded operation voltage window.



**Figure 4.** Stability analysis of the electrolytes and Li anodes cycled at different temperatures. a) Chemical structures of DOL and possible side products. b,c) <sup>1</sup>H-nuclear magnetic resonance spectra of the fresh and used electrolytes after one and ten cycles at 0, -30, and -60 °C. d,e) X-ray diffraction patterns of the pristine and used Li anodes after one and ten cycles at 0, -30, and -60 °C.

Similarly, X-ray diffraction patterns showed that the an undesirable side product of lithium hydrate (LiOH) appeared on the Li anode surface after ten cycles at 0 °C, which could result from the reactions of Li anode with moisture or electrolyte.<sup>[27]</sup> As a comparison, there was not any detectable LiOH signal on Li anodes cycled at -30 and -60 °C (Figure 4d,e), proving that some unwanted side reactions on Li anodes were inhibited at lower temperatures. In addition to the improved electrolyte stability, the reduced water content in batteries at low temperatures probably also contributed to the better cyclicity of Li-CO<sub>2</sub> batteries. In reality, even if the thoroughly dried materials were used at the initial battery assembly, it was still difficult to completely remove the moisture from battery during long-term operation due to the entrance of environmental water and the degradation of electrolyte, which inevitably induced unwanted side reactions and thus shortened the battery life. However, these parasitic reactions related to moisture could be inhibited at ultra-low temperatures due to the reduced and even nonexistent moisture and the enhanced stability of electrolyte.<sup>[27]</sup> Furthermore, Fourier transform infrared spectra demonstrated that there were less undesired side reactions on cathodes during recharging at -60 °C (Figure S19, Supporting Information). Overall, the reduced working temperature was found to be effective to inhibit the unwanted side reactions in Li-CO<sub>2</sub> batteries and it was considered as another important reason for the improved low-temperature cycle performance.

# 2.5. Application Demonstration of Li-CO<sub>2</sub> Batteries at Low Temperatures

Considering that Li-CO<sub>2</sub> batteries were most likely to find important applications on the Mars, we made a proof-of-concept demonstration for the ultra-low-temperature Li-CO<sub>2</sub> batteries. As shown in **Figure 5**a, Li-CO<sub>2</sub> battery utilized CO<sub>2</sub> in the environment and outputted a stable voltage to power a light-emitting diode as representative consumer electronic product on an astronaut model in an ultra-low-temperature environment of -70 °C (achieved by dry ice). Figure 5b,c complementally illustrates that the Li-CO<sub>2</sub> batteries could be used to power electronic devices in low-temperature environment. Besides, the batteries could also work stably at low temperatures varied according to realistic temperature fluctuations over a period of time on the Mars (Figure 5d).<sup>[43]</sup>

## 3. Conclusion

To summarize, we have, for the first time, realized efficient ultra-low-temperature Li-CO<sub>2</sub> batteries that exhibited a high capacity up to 8976 mAh g<sup>-1</sup> and a superb lifespan of 150 cycles (1500 h) with a fixed capacity of 500 mAh g<sup>-1</sup> at -60 °C. The formation of easy-to-decompose discharge products in small size on cathode and the suppressed side reactions in electrolyte and on anode were discovered to contribute together to the enhanced cyclic stability at descending temperatures (e.g., -60 °C). This work provides a general and effective paradigm in the development of high-performance metal-gas batteries operating at low temperatures.

## 4. Experimental Section

*Materials*: Lithium metal (Li, 99%, China Energy Lithium Co., Ltd.), LiTFSI (trace metals basis, 99.95%, Sigma-Aldrich), DOL (anhydrous, 99.9%, Sigma-Aldrich), tetraglyme (tetra ethylene glycol dimethyl ether, 99.0%, Aladdin Reagent), *N*-methyl-2-pyrrolidinone (NMP, 99.0%, Aladdin Reagent), and iridium (20% iridium/C, RG, Adamas) were used in this work. Polyvinylidene fluoride (PVDF, average Mn of ~130 000, Kynar HSV 900), nickel foam (Ni foam, with a thickness of about 1 mm), GDL (YLS-26), and glass fiber separators (Whatman grade GF/A: 1.6  $\mu$ m) were purchased from Soochow Hengshenglong Energy Technology Co., Ltd. Parafilm M (Parafilm) was provided by Bemis Co., Ltd. The Ni foam, glass fiber separators, and GDL were dried in a vacuum oven at 80 °C for at least 12 h before use. The other reagents and materials were used as received without further treatment.

Preparation of Materials and Assembly of Li-CO<sub>2</sub> Batteries: Both the preparation of materials and the assembly of Li-CO<sub>2</sub> batteries were carried out in an argon gas-filled glove box, where both  $O_2$  and H<sub>2</sub>O contents were maintained below 0.1 ppm. The electrolyte was prepared by dissolving 2.87 g LiTFSI in 10 mL DOL to obtain 1.0 м solution. Before the battery assembly, several pieces of sacrificial Li chips were added to the electrolyte in order to chemically dry the electrolyte through the reaction of Li metal with trace moisture, and the above treatments continued for at least 3 d.[44] The cathodes were prepared by a spray casting method. First, iridium powder and PVDF binder were mixed at a weight ratio of 9:1 and grinded well in an agate mortar. Next, the ground powder was dispersed in NMP solvent and sonicated for 2 h in an ultrasonic cleaner to obtain a homogeneous dispersion. Third, the dispersion was sprayed on the conductive surface of GDL with a catalyst load of 0.10-0.15 mg cm<sup>-2</sup>. The above spraying process was conducted at 180 °C to facilitate the volatilization of NMP solvent and the sprayed cathodes were further dried thoroughly in a vacuum oven at 150 °C for 12 h before being transferred to the glove box. The Li-CO2 battery was finally fabricated by stacking a Li sheet, two pieces of glass fiber separators, 200 µL DOL-based electrolyte, an iridium cathode, a layer of Ni foam, and Parafilm protective layer in sequence in a Swagelok-type battery with an open hole on the cathode side.<sup>[45]</sup>

Electrochemical Measurements: The fabricated Li-CO<sub>2</sub> batteries were transformed to home-made sealed glass test bottles. Before the measurements, the test bottles were flushed with high-pure  $\rm CO_2$  (99.99%, Shanghai Tomoe Gases Co., Ltd) for 1  $h^{[16]}$  and then transferred to an ultra-low-temperature refrigerator (DW-86L286, Haier Co., Ltd) or a constant temperature humidity chamber (LRHS-101-LH, Shanghai Linpin Instrument Stock Co., Ltd). All measurements were started after a 12 h open circuit voltage step to ensure the equilibrium of batteries  $^{\left[22\right]}$  Both applied current (mA  $g^{-1}$ ) and fixed cycle capacity  $(mAh g^{-1})$  were normalized to the weight of catalyst loaded on cathodes. The electrochemical measurements were carried out on the LAND cycler (CT2001A, Wuhan LAND Ltd.) and electrochemical workstation (CHI 660E, Shanghai Chenhua Ltd.). The ionic conductivity measurement was carried out in a home-made test device with two parallel stainlesssteel electrodes (1 cm  $\times$  1 cm) as blocking electrodes submersed in DOL-based electrolyte. The ionic conductivity values of electrolytes and the impedance plots of batteries were obtained by measuring the electrochemical impedance spectroscopy of the home-made device or a battery under different temperatures with a bias voltage of 5 mV and a scan frequency from  $10^5$  to 0.1 Hz and fitting these plots with an equivalent circuit model by the Z-View software. The stable voltage window of electrolyte was investigated by linear scan voltammetry measurement with a three-electrode testing system consisting of a glass carbon electrode as working electrode and two Li sheets as counter and reference electrodes. The open-circuit voltage of the three-electrode device was first tested and the voltage was set to scan negatively from the open-circuit voltage to 0 V with a sweep rate of 1 mV  $s^{-1}$ . After that, the device stood for some time and was set to scan positively from a new open circuit voltage to 5.2 V.<sup>[46]</sup> Part of scan curve was truncated to show a clear stable voltage window.







**Figure 5.** Application demonstration of ultra-low Li-CO<sub>2</sub> batteries. a) A possible application situation of ultra-low-temperature Li-CO<sub>2</sub> batteries in the future Mars expedition. The battery powers a light-emitting diode as consumer electronic device on an astronaut model in an ultra-low-temperature environment of -70 °C achieved by a dry ice bath (inset, the enlarged photograph of illuminated light-emitting diode). The battery immersed in a dry ice bath b) lighting up a blue light-emitting diode and c) powering an electronic watch. d) Voltage–time curve of a Li-CO<sub>2</sub> battery that is discharged under ambient temperatures varied based on realistic temperature fluctuations over a certain time on the Mars.

Analytical Sample Preparation: To prepare the analytical samples, the batteries were discharged and recharged after one or ten cycles with a cut-off capacity of 500 mAh  $g^{-1}$  at 100 mA  $g^{-1}$  (i.e., the conditions used for long-term cycling). The electrolyte samples were prepared by the following steps for <sup>1</sup>H nuclear magnetic resonance characterization. The pristine electrolyte samples were prepared by adding 100  $\mu$ L fresh electrolyte to 1 mL dimethyl sulfoxide-d6.<sup>[10]</sup> The electrolyte-containing separators and cathodes were taken out of the cycled batteries and transferred to 1 mL dimethyl sulfoxide-d6 and stood for 24 h to obtain the cycled electrolyte samples. The residual solvent peak of dimethyl sulfoxide was taken as an internal reference. The following steps were taken to prepare the electrode samples for X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and scanning electron microscopy analysis. The discharged/cycled batteries were first disassembled in a glove box, and the removed cathodes were washed thoroughly with DOL solvent. Then, the wet cathodes were transferred to the transition compartment of glove box. They were repeatedly evacuated three times and kept in vacuum state for 1 h at least to accelerate solvent to evaporate. After that, the dried cathodes were taken back to the glove box and stored in open glass bottles overnight for 12 h prior to testing. The fresh and the used Li anodes taken out of the cycled batteries were sealed by polyimide film to avoid direct exposure to air. All the above samples were stored in argon before the materials characterizations.

*Materials Characterization*: All the following measurements were carried out on the side of electrodes facing separators. The structure of cathodes were characterized by X-ray diffraction spectroscopy (Bruker AXS D8 powder X-ray diffractometer, Cu K $\alpha$  radiation, 40 kV, 40 mA), Fourier transform infrared spectroscopy (Nicolet 6700, equipped with a diamond attenuated total reflectance accessory, GladiATR, PIKE Technologies), field-emission scanning electron microscopy (Zeiss ultra 55, operated at 5 kV, all samples sputter-coated with a 1 nm thick gold nanoparticles), Raman spectroscopy (Horiba LabRAM HR Evolution Spectrometer, 532 nm laser excitation wavelength, equipped with a cryogenic liquid nitrogen fitting), and X-ray photoelectron spectroscopy (PHI 5000C & PHI 5300, Mg, 250 W, 14 kV) at room



temperature. X-ray photoelectron spectra were calibrated with a carbon peak at 284.8 eV as a reference. <sup>1</sup>H nuclear magnetic resonance characterization for electrolyte was recorded at Bruker AVANCE III HD (400 MHz) at room temperature. The freezing point of electrolyte was measured using TA Q2000 differential scanning calorimeter, with 10 mg electrolyte sample sealed in a preweighed aluminum sample pan with a TA sealing lid and another same sealed aluminum pan as the reference pan. The sealed pans were first cooled down from 25 to -80 °C at a rate of 10 °C min<sup>-1</sup> and then equilibrated at -80 °C for 10 min, followed by a heating-up step from -80 to 30 °C with a rate of 5 °C min<sup>-1</sup>. Raman spectroscopy was also used to characterize the electrolyte at different temperatures.

In Situ Differential Electrochemical Mass Spectrometry Analysis: The gas evolution during charging was investigated in a Swagelok-type Li-CO<sub>2</sub> battery by in situ differential electrochemical mass spectrometry (i-DEMS 100, ion source: EI, 70 eV, detector: SEM, 1100v, Shanghai Linglu Instruments Co., Ltd). Dry ice bath was utilized here to provide an ultralow-temperature environment for the experiments. To avoid the impact of dry ice sublimation on the test, the tested battery was submersed in excess dry ice in a foam incubator covered with a foam lid, and new dry ice was supplemented regularly to ensure a stable temperature of approximately -70 °C during the standing and testing process. In the measurements, the battery was first discharged at a current density of 0.05 mA  $\rm cm^{-2}$  for 90 min and then the residual gas in the battery was constantly flushed by argon with a flow rate of 0.8 mL min<sup>-1</sup> until stable partial pressure signals of argon,  $CO_2$ , and  $O_2$  were obtained. Finally, the battery was recharged at 0.05 mA  $cm^{-2}$  for 90 min with the gas pulse signals recorded per 3 s during charging.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## Keywords

high electrochemical performance, Li-CO<sub>2</sub> battery, ultra-low temperature

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