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Supporting Information

A Li₂CO₃-Free Li-O₂/CO₂ Battery with Peroxide Discharge Product

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Materials and Methods

1. Chemicals and Electrolyte

Dimethyl sulfoxide (DMSO) (Sigma Aldrich, 99%) was dried over freshly activated 4 Å molecular sieves for several days. Lithium perchlorate (LiClO₄, purity of >98 %, Wako Chemicals) and Lithium Bis(trifluoromethanesulfonyl)imide (LiTFSI, purity of >99 %, Tokyo Chemical Industry Co., LTD, TCI) were dried by heating under vacuum at 80 °C oven 12 hours. Electrolytes with specific salt concentration were prepared and stored in a glove box under Ar atmosphere. The water concentration in the electrolyte measured by Karl Fischer titration was below 75 ppm.

2. Cathode Preparation

The nanoporous gold (NPG) cathode employed in this study was prepared based on the alloy silver/gold leaf (white gold leaf), which purchased from L.A. Gold Leaf Wholesaler U.S. The average thickness of a single piece of 12-K (12-carat, 51%) wt.-% gold, 48% wt.-% silver, 1% wt.-% palladium) white-gold leaf was 120 nm. The white-gold leaf was fully dealloyed by floating on a bath of concentrated nitric acid (purity of 67%, Tokyo Chemical Industry Co., LTD) for 10 minutes, following the published typical procedure.¹⁻² The pore size of NPG is estimated to be 30-50 nm (Fig. S1). The free standing NPG leaves were floated onto distilled water after replacing away the remaining acid solution. In order to guarantee the mechanical stability, 3~10 layers of NPG leaves were overlappingly collected with clean stainless steel mesh substrate (0.11 mm wire diameter, 100 mesh, No. 018100, Nilaco Co. Ltd.). The stainless steel mesh was smoothed and punched in to circular type (7 mm in diameter) as pretreatment. The NPG-based cathode was dried by heating under vacuum at 80 °C oven 12 hours and placed into a separated glass bottle in Ar-filled glove box. On a typically 3-layers overlapped NPG cathode, the specific mass loading is 0.348 mg/cm^2 . In this case, on each piece of cathode (7 mm diameter circle, 0.384 cm²), the absolute mass loading equals to 0.134 mg. Based on specific surface area calculated by Peng et al. (50 m^2/g), the active surface area on each piece of cathode can be extended to 67 cm^2 .

3. Cells Assembly

(a) <u>In-situ Raman cell</u>: the in-situ Raman cell for Li-O₂/CO₂ battery (the photo and schematic of the cell is shown in Fig. S2) has been designed and modified based on the typical in-situ Raman cell for Li-ion battery (Hohsen Corp., Osaka, Japan). In detail, a thin quartz window (thickness, 0.5 mm) has been fixed on the top of the cell as a sight window, through which the laser and Raman singal can fluently get across. The body of the cell is flanked by a pair of gas circuits/channels with Swagelok gas valves, through which the gas-tight glass chamber in the cell can be continuously purged with gas before/during in-situ tests. As a standard two-electrode configuration cell, lithium foil (thickness, 0.4 mm) was assembled at the top and employed as the reference & counter electrode. Under the Li foil, 100~200 μ L of electrolyte was homogeneously dropped onto the glassy fiber filter separator (GF/A, Whatman). Finally, the NPG-based cathode was assembled at the bottom of the cell with the gold-face upward. Note that, a small hole (2~3 mm diameter) was punched upon both Li foil and glass fiber separator, through which the laser can fluently get across. The cell was assembled in an argon-filled glovebox.

(b) <u>Coin cell</u>: The coin cell was assembled in a similar structure as the top-holing 2032 coin cell, which was also employed in our previous work.³ The cell was assembled by successively stacking a lithium foil anode (thickness, 0.4 mm), the glassy fiber filter (GF/A, Whatman) with 50 μ L of electrolyte, the NPG-based cathode with stainless steel mesh substrate. The cell was stored in a gas-tight glass chamber (volume capacity of 650 ml) with Swagelok gas valves for the entrance and exit for purging with a mix gas of O₂/CO₂ (99.99%, Taiyo Nippon Sanso Corp., Japan) before electrochemical tests. The oxygen pressure in the glass chamber was 1 atm. Note that the assembly of the cell was conducted in an Ar-filled glove box that has a dew point of around -90 °C and O₂ content below 5 ppm.

4. Electrochemical Measurements

For the in-situ Raman test, the electrochemical treatments were carried out under control of a potentiostat (Potentiostat/Galvanostat PGSTAT30, Autolab Co. Ltd., Netherlands) at room temperature. The current and potential outputs from the potentiostat were recorded by a multifunction data acquisition module/amplifier (PGSTAT30 Differential Electrometer, Autolab), which was controlled by General Purpose Electrochemical Software (GPES). For the coin pouch cell, the electrochemical measurements were carried out under potential control using the battery tester system HJ1001SD8 (Hokuto Denko) at 25 °C. Typically, before each discharge characterization, the cell was kept on open circuit for 10 h. The open circuit potential (OCP) was approximately 3.1 V in most cases in the study. All of the potentials in this study were referenced to Li/Li⁺.

5. Raman Measurements

The Raman spectra were recorded using a JASCO microscope spectrometer (NRS-1000DT). The excitation light of an air-cooled He–Ne laser at 632.8 nm wavelength was focused on the electrode surface through a 50×long working distance lens (Olympus America Inc.). The confocal slit was adjusted to be 4.0 μ m to minimize the band broadening effect due to the contribution of non-confocal signal. The scattered light was collected in a backscattering geometry along the same optical path as the pumping laser. The power of laser beam delivered to the electrode surface was roughly 10% of the maximum 30 mW laser intensity, unless specified, to avoid degradation to the specific products and/or other cell components. The spectral resolution of the Raman spectra in the study was ca. 1.0 cm⁻¹.

During the in-situ test, the Raman spectrum acquisition time was kept typically 20 s with 1 or 2 accumulations. For the ex-situ Raman test conducted on specific electrolyte, the electrolyte was droped onto a piece of homemade SERS substrate (gold sputtered onto a piece of stainless steel sheet) and sealed into a gas-tight homemade Raman sample holder with a piece of quartz window (thickness 0.5 mm) optimized for the observations. The acquisition time was around 60 s with 3 accumulations.

6. Fourier-transform infrared (FTIR) Characterizations

FTIR measurements were carried out on a FT/IR-6200 spectrometer (JASCO Corp.). Typically, 64 interferograms were accumulated for one spectrum with a resolution of 4.0 cm⁻¹. For pretreatment, the cycled cells were transferred into an Ar glove box once the discharge finished, and the cathodes were extracted from the cell and twice rinsed by dimethoxyethane (DME, Sigma Aldrich, 99%) to wash off the electrolyte salt and the residual solvent, and then evaporated in a vacuum chamber,

connected to the glove box, for ~15 min. The dried NPG cathode was scratched off (nearly 1×2 mm²) and then grounded together with potassium bromide (KBr, FTIR grade, purity of >99 %, Sigma Aldrich). The KBr powder was dried in vacuum at 100 °C for 24 hours before using, and the grinding procedure was carried out in an Ar-filled glove box. The mixture powder was pressed into hyaline pellets in vacuum under high pressure (4.0 Mpa) for 5 minutes. For the characterization of electrolyte solution, the cycled electrolyte was uniformly coated onto the KBr pellet in Ar-filled glove box. The KBr-based pellet was sealed in an airtight container and then rapidly transferred into the IR sample loading chamber, in which continuously purged with inert argon gas.

7. Gas Chromatography Mass Spectrometry (GC-MS) Characterizations

The mass spectroscopy performed in this study have been reported in our previous work.⁴ In brief, a custom-built glass vessel (for ex-situ GC-MS) or home-made Li-O₂ cell (for in-situ DEMS) is connected to an 8-port, two-way Gas Chromatograph (GC, Clarus[@] 680, Perkin-Elmer). The inner gas circuits were modified based on B. D. McCloskey et al.⁵ The entire system is hermetically sealed. The Mass Spectrometer (MS, Clarus[@] SQ-8 S, Perkin-Elmer) was calibrated to determine the partial pressure of standard mixture of 200 ppm O₂ and 200 ppm CO₂ in Ar. The estimated accuracy of gas partial pressures is approximately $\pm 10\%$ of the measured values. The volume of the valve in mass spectrometer is 2.0 mL, and the flow velocity of the gas is controlled at 22 mL/min.

(a) Ex-situ GC-MS for carbonate and peroxodicarbonate quantification: For ex-situ GC-MS tests, the cathode (with spearator) is harvested from the discharged cell, and transfered into the glass vessel in Ar-filled golvebox without expose to open air. After the vessel is sealed and attached to the GC-MS apparatus, Ar was allowed to flow through the vessel. After obtaining a stable O_2 and CO_2 baselines by purging (nearly 12 hours), 1 mL of 3 M H₂SO₄ is injected into the vessel through a top valve. Ar gas pulses per 3 min into and outof the vessel are analyzed for O_2 and CO_2 partial pressure until a stable O_2 and CO_2 baselines are obstained, and the total amount of O_2 and CO_2 are integrated by summing each of their contents in all pluses.

(b) <u>In-situ Differential Electrochemical Mass Spectrometry (DEMS) for gas</u> <u>evolution</u>: After discharge process, the residual oxygen in the cell is flushed by Ar. Normally, the flush process would be conducted overnight (nearly 9 hours), until a stable O_2 and CO_2 partial pressures are obtained by monitoring the Ar pulses every 15 min. During charging, Ar gas pulses per 3 min into and outof the vessel are analyzed for O_2 and CO_2 partial pressure. The mass spectrometer absolute sensitivity is calibrated for CO_2 and O_2 , therefore, the evolution rate of them can be obtained.

8. Chemical Titrations

The chemical titration quantification conducted here is modified based on our previous work.⁴ For the titrations of dry cathodes (only titrate for deposited products), the pretreatment processes were similar to those carried out in IR measurements. For the wet cathodes titrations (both deposited and soluble products), the harvested cathodes were directly used without rinsing and evaporating procedures. Besides of this, the glass fiber separator soaked with cycled electrolyte solution was also titrated together with wet cathode in order to collect the full information of soluble products. Note that, in order to promote the accuracy of titration experiments, the entire discharge capacity are extended to 0.4 mAh. Specifically, additional NPG layers are employed in a single cell and the discharge products of several cells are collected together to achieve the 0.4 mAh capacity target. The sample was taken out of the glove box, and put into a conical flask with 5.0 ml of ultrapure DI-water immediately. The flask was vigorously shaken for 20s to promote the complete reaction of both Li₂CO₃ and peroxide (peroxodicarbonate) with H₂O. The involved reaction is as follows:

$$Li_2CO_3 + H_2O = LiHCO_3 + LiOH;$$
$$Li_2C_2O_6 + 2H_2O = H_2O_2 + 2LiOH + 2CO_2;$$

The whole titration process can be divided into two steps: (1) Acid-Base Titration (towards OH^{-}) and (2) Iodometric Titration (towards H_2O_2). For the acid-base titration, the base was titrated using a standardized 5 mM HCl solution, with the end point indicated by 0.1 mL of phenolphthalein in isopropanol. The involved reaction is as follows:

$$LiOH + HCl = LiCl + H_2O;$$

The iodometric titration was straightly followed with the addition of three reagents into the existed solution in sequence: 1 mL of 2 wt% KI aqueous solution, 1 mL of $3.5 \text{ M H}_2\text{SO}_4$ solution and $50 \mu\text{L}$ of Mo-based catalyst solution. The Mo-based

catalyst solution was prepared by dissolving 0.5 g ammonium molybdate $((NH_4)_2MoO_4)$ and 1.5 g of ammonium nitrate (NH_4NO_3) into 5 mL of 30 wt% ammonia aqueous solution, then diluting the solution to 25 mL total using ultrapure DI-water. The resultant solution turned to an orange color due to the formation of I₂. Then, the I₂ was titrated to a faint pale yellow color by employing 5mM Na₂S₂O₃ aqueous solution. 0.5 mL of 1% starch solution was added for precise the end-point detection. The solution rapidly turned to a dark blue color and the titration was resumed till the color was totally disappeared. The involved reaction is as follows:

$$H_2O_2 + 2KI + H_2SO_4 = I_2 + K_2SO_4 + 2H_2O;$$

 $I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI;$

Note that, all of the chemicals employed in titration experiments were purchased from Wako Chemical.

Results and Discussion



Figure S1

Transmission electron microscopy (TEM) images of the nanoporous gold (NPG) employed as cathode material in this study. The TEM images are observed through a JEOL LEM-200CX with an accelerating voltage of 200 kV. The pore size of NPG is estimated to be 30-50 nm, which is very similar with the reported work by Peng et al.²



Photo and schematic of in-situ Raman cell employed in this study.



Assignment of the corresponding stretching modes in Raman spectra of pure DMSO solvent and 0.5 M LiClO₄-DMSO electrolyte, which recorded on the sputtered gold surface with surface enhance effect. The peak positions and name of the modes have been noted near the corresponding peaks.⁶ Besides, the configuration of a single DMSO molecule ((CH₃)₂SO) are also shown for clarity.



Extended in-situ Raman spectra (corresponded to Fig. 1d) recorded from the cell with Li-free TBACIO₄-DMSO electrolyte with O₂/CO₂ (4/1 mole ratio) mix gas condition. The assignment of Au-O and O-O stretches in adsorbed reduced oxygen species (peroxo-dicarbonate, peroxo-monocarbonate and superoxide, respectively) are noted for clarity.⁷⁻⁸ Besides, based on the corresponding reaction energy (kcal/mol),⁹ the thermodynamic equilibrium potential calculation of related products are listed in the following tables.

During the initial stage of discharging, the relative high concentration of CO_2 species dissolved in electrolyte drives the reduction process follow the peroxodicarbonate pathway ($2CO_2/O_2$). Due to the decreasing of CO_2 concentration, the reaction pathway gradually converts to peroxomonocarbonate pathway (CO_2/O_2). Finally, with the exhausting of CO_2 , the discharge process restores to the typical oxygen reduction pathway with the formation of superoxide. In a precisely opposite way towards discharging, charge process follows the order of each thermodynamic equilibrium potentials in the co-existence environment with 3 formed discharge products.



Figure S5.

Capacity dependence of the related Raman peak areas collected from the Li-free (TBA) DMSO electrolyte (O_2/CO_2 ratio is 4/1, same with the orange trace shown in Figure 1a) during in-situ SERS measurement upon (a) discharging and (b) charging, respectively.

Both the peak areas of Au-O and O-O stretches in adsorbed peroxo-dicarbonate $(C_2O_6^{2-})$; peroxo-monocarbonate (CO_4^{2-}) and superoxide (O_2^{-}) have been normalized and plotted. The corresponding groups of Au-O and O-O stretches share the same capacity dependent variation trends. Besides, the capacity dependence of related species further reveal the reaction sequence, which is quite coincide with the proposed reaction mechanism present in Figure 1d and Figure S4.



Schematics of peroxodicarboate synthesize procedures and Raman spectra recorded from the corresponding intermediates and products.

The synthesis procedures present above are modified on the basis of previous reports,¹⁰⁻¹² and the production of specific products are further proved by Raman spectroscopy. In detail, lithium hydroxide monohydrate is saturated in water and added into the excess hydrogen peroxide (30%) solution during ice-bath. In corresponding Raman spectra, the peak assigned to LiOH gradually decreased with the aging/stirring time, and a new peak (833 cm⁻¹) gradually grow up in a relative lower frequency region than the O-O stretch in H₂O₂ (877 cm⁻¹). The newly-produced peak can be attributed to the O-O stretch in lithium hydro-peroxide (LiOOH).⁴ During subsequently purging with CO₂, the LiOOH-related peak gradually reduces (blue peak), and another new peak (red peak, 872 cm⁻¹) in peroxides region (O-O stretch region) grows up with the simultaneously increasing of Li₂CO₃. Based on the reaction pathway noted above, the newly-observed peak can be further assigned to peroxo-dicarbonate (LiPC₂O₆).¹¹⁻¹²



The proposed configurations of $C_2O_6^{2-}$.

Based on Sawyer et al.,⁸ two reaction pathways are listed above. In pathway-A, in order to obtain $C_2O_6^{2-}$, CO_2 gas was bubbled into the TBAO₂-contained (superoxide anion) electrolyte solution without any electrochemical treatment. As a result, the obtained white solid product can be assigned to C₂O₆²⁻ with an anhydride linkage configuration, which present an O-O stretch around 1000 cm⁻¹ in corresponding Raman spectrum. For the reaction in bulk solution, pathway-A might be favored due to the strong electrostatic repulsion between CO_4^- and O_2^- (in pathway-B). However, in the O₂/CO₂ cell (as shown in Figure 1a), the electrochemical O₂/CO₂ reduction processes (O₂⁻ and CO₄⁻ production) are continuously proceeded upon discharging. Since the diffusion coefficient of O_2 (9.75*10⁻⁶ cm²/s) is much higher than CO_2 $(1.5*10^{-6} \text{ cm}^2/\text{s})$ in DMSO solution, the production of O₂⁻ becomes dominate. In this case, once produced, the CO_4^- would rapidly react with O_2^- within the double electrode layer, resulting in the formation of CO42- (not C2O6-, the superoxo-related intermediate in pathway-A). As a result, the reaction pathway-B becomes dominate during electrochemical O_2/CO_2 reduction, resulting in the formation of $C_2O_6^{2-}$ with peroxide linkage configuration, which shares the same configuration with peroxo-dicarbonate (K₂C₂O₆, etc.). Therefore, the related Raman peak near 888 cm⁻¹ (879 cm⁻¹ in Figure 1d) can be rationally assigned to the O-O stretch in $C_2O_6^{2-}$ with a peroxide linkage configuration.



Figure S8.

Capacity dependence of the related Raman peak areas collected from the Li-free (TBA) DMSO electrolyte during in-situ SERS measurement upon discharging. The O_2/CO_2 ratio and discharge current density are different: (a) $O_2/CO_2=4/1$, 200 mA/g; (b) $O_2/CO_2=4/1$, 400 mA/g (same with the orange trace condition shown in Figure 1a); (c) $O_2/CO_2=3/1$, 400 mA/g (same with the dark yellow trace condition shown in Figure 1a); (d) $O_2/CO_2=3/1$, 800 mA/g.

Based on the capacity dependent variation trend of related Raman peaks, the information of corresponding reaction pathway (electrochemical reduction pathway and adsorbed species) and related reaction sequences can be effectively collected. The related reaction pathway can be summarized as follows:

$$O_2 + e^- \rightarrow O_2^-; O_2^- + CO_2 \rightarrow CO_4^-$$

 $CO_4^- + O_2^- \rightarrow CO_4^{2-}; [CO_2 + O_2 + 2e^- \rightarrow CO_4^{2-}(CO_2/O_2 = 1/1)]$
 $CO_4^{2-} + CO_2 \rightarrow C_2O_6^{2-}; [2CO_2 + O_2 + 2e^- \rightarrow C_2O_6^{2-}(CO_2/O_2 = 2/1)]$

Note that, although the solubility of CO₂ is much higher than O₂ (in DMSO solvent), the diffusion coefficient of CO₂ $(1.5*10^{-6} \text{ cm}^2/\text{s})^{13}$ is also much lower than O₂ $(9.75*10^{-6} \text{ cm}^2/\text{s})^{14}$, the dominate influence issue would be focus on the CO₂

consumption speed (depends on current density) and CO_2 supply rate (depends on diffusion coefficient of CO_2 in electrolyte).

At a relative higher O_2/CO_2 ratio (4/1) and higher current (400 mA/g), with the rapid consumption of the CO₂ within the double electrode layer, the supply of CO₂ (determined by the diffusion coefficient) cannot fully meet its consumption rate. In this case, the surface electrochemical reaction pathway gradually convert from the $C_2O_6^{2-}$ -related pathway (CO₂/O₂=2/1) to CO₄²⁻-related pathway (CO₂/O₂=1/1), even O₂⁻-related pathway. However, at a relative lower current density (200 mA/g), the supply of CO₂ can meet its consumption rate (CO₂/O₂=2/1), resulting a pure $C_2O_6^{2-}$ -related pathway as shown in (a). In a similar way, the pure $C_2O_6^{2-}$ -related pathway can be kept at 400 mA/g under a lower O₂/CO₂ ratio (3/1) as shown in (c). While the transformation from $C_2O_6^{2-}$ -related to CO₄²⁻-related pathway can also be observed at higher current density (800 mA/g) as shown in (d).



Cycling performance of conventional Li-O₂/CO₂ (1:1 mole ratio) with Li-contained DMSO-based electrolyte. Corresponding in-situ Raman spectra collected at the end of discharge/charge states on typical cycles are shown below.

Regardless of the production of Li_2CO_3 during discharging, two severely problems are successively revealed: (1) the obtained Li_2CO_3 species cannot be fully decomposed during charging, and the residual Li_2CO_3 gradually accumulates, resulting the blocking of surface active sites on cathode and final degradation of cell. This is also the most essential problem limiting the cyclability of typical Li-O₂/CO₂ battery. (2) Besides, due to the incompletely decomposition of Li₂CO₃, the un-employed charge capacity are negatively consumed in the related oxidation of DMSO-based electrolyte on the relative high potential, resulting the formation of dimethyl sulfone (DMSO₂) species.¹⁵⁻¹⁶ In summary, the high polarization potential (~4.2 V vs. Li/Li⁺) exhibits in typical Li-O₂/CO₂ battery seriously threaten the stability of the related cell components (more severe in carbon-based practical cell), and becomes the inherent defect limiting the practicality of the typical Li-O₂/CO₂ battery.



Galvanostatic discharge/charge profiles of several cycles observed in cell with Li-free TBAClO₄-DMSO-based electrolyte in Li-O₂/CO₂ (1:1 mole ratio) condition. Corresponding in-situ Raman spectra collected at the end of discharge/charge states on typical cycles are shown below.

Compared with the cycling performance observed in typical Li-contained cell (Fig. S6), the initial charging plateau hold at 3.5 V, which assigned to the peroxodicarbonate-related reaction pathway. However, during cycling, the charge plateau gradually separate and stabilize at 4.2 V over 20 cycles. In related in-situ Raman spectra, instead of peroxodicarbonate, the Li₂CO₃ can be gradually observed during cycling. The appearance of Li-ion can be attributed to the inevitable diffusion of Li-ion from counter side (Li foil counter electrode). Thus, even though the peroxodicarbonate can stably exist in Li-free condition, this stability cannot maintain in practical Li battery system due to the unescapable introduction of Li-ion.



Raman and IR spectra of LiTFSI/DMSO electrolyte solutions with different mole ratios. The assignment of stretching modes in Bis(trifluoromethanesulfonyl)imide (TFSI) structure are noted. Besides, the molecular structure of TFSI are listed above for clarity. Specifically, among Raman spectra, the blue-shift (move to higher wavenumber) of both S-N symmetric stretch and SO₂ in-plane symmetric stretch delivers the relevant structural variation of TFSI.



Figure S12

(a) Schematics of typical ion association modes. (b) Corresponding sketches of the solvation structures in conventional diluted electrolyte and super-concentrated electrolyte with 1:3 (LiTFSI:DMSO) mole ratio. Peak positions of the (c) CSC symmetric stretch (in DMSO), and (d) SNS symmetric stretch (in TFSI) in various LiTFSI/DMSO electrolytes.

Typically, there are two different types of ion pair species between the solid state (RX) and the free ions state (R⁺ + X⁻): contact ion pair (CIP, R⁺ | X⁻) and solvent separated ion pair (SSIP, R⁺ || X⁻).¹⁷⁻¹⁸ Among specific LiTFSI/DMSO based electrolyte solutions, the diluted one is composed by $[Li(DMSO)_4]^+$ + TFSI⁻ (SSIP) and free DMSO molecules, while the one with specific 1:3 mole ratio is composed by $[Li(DMSO)_3]^+$ + TFSI⁻ (CIP). The evolution from SSIP to CIP can be further proved by the relevant structural changes.¹⁹ With the increasing salt concentration, the blue-shift of CSC symmetric stretch in DMSO indicates the reduction of free DMSO, and the corresponding blue-shift of SNS symmetric stretch in TFSI also proves the direct contact between TFSI⁻ anion and Li⁺ cation within CIPs.¹⁹⁻²⁰ As a result, the polymeric fluid network has been built by aggregated CIPs in super-concentrated electrolyte with 1:3 (LiTFSI:DMSO) mole ratio.



Raman spectra of LiTFSI-DMSO and LiClO₄-DMSO solution. Both of their mole ratios (salt:DMSO) are kept at 1:3. The proposed sketches of the corresponding solvation structures are respectively noted for clarity.

Herein, although both of the solutions share the same salt:DMSO mole ratio, specific CIPs ([Li(DMSO)₃]⁺ + TFSI⁻) can stable exist in LiTFSI-based solution, while the CIPs exhibit unstable in LiClO₄-based solution, with some of free DMSO and SSIPs remain in the corresponding solution. Based on Pearson's hard soft acid base (HSAB) theory,²¹ hard acids (Li⁺) prefer hard bases (F⁻, Cl⁻, etc.) and soft bases (TBA⁺, solvated Li⁺, etc.) prefer soft acids (TFSI⁻, etc.). In this case, as a suitable soft base, TFSI⁻ anion can fit well with the specific soft cation solvation sphere ([Li(DMSO)₃]⁺), and the related structure can keeps stable. However, as a relative hard base (higher anion dissociation energy and smaller ionic radius, higher charge density), ClO₄⁻ anion could not fit well the corresponding solvation sphere, resulting the co-existence of free DMSO, SSIPs and CIP.²²⁻²³ Therefore, the anastomotic feature between specific cation solvation sphere and incorporated anion is also essentially important for the formation of CIP.



Stability assessment of O₂-saturated LiTFSI/DMSO electrolyte solutions with different mole ratios: (a) stability towards Li foil; (b) electrochemical stability at high oxidation potential; (c) Proposed mechanism for the discussion on the stability of DMSO-based electrolyte.

For the stability towards Li metal (reduction stability), dilute electrolyte (1:20 mole ratio) gradually turns yellow during aging, which indicates the existence of relevant parasitic reactions.^{19-20, 24-25} In contrast, the yellowish color gradually fades with the increasing concentration of electrolytes, and the one with 1:3 mole ratio keeps clear colorless after 3 months. For the electrochemical oxidization stability, the related oxidization decomposition potential increase with LiTFSI concentration, which means the decomposition become harder in concentrated electrolyte.

The relevant promotion of stability can be further ascribed to the reduction of free DMSO molecules in concentrated electrolyte. In Li-O₂ battery system (also Na-O₂

battery system),^{19, 25} the typical electrolyte employing DMSO solvent is not stable against Li metal (high reducibility). The original cause of the incompatibility of Li metal and DMSO is ascribed to the lack of formation of a stable passivation layer (SEI film) on the Li metal surface from reduction products of DMSO (and related lithium salt). The instability issue of Li metal anode becomes an intrinsic defect of the Li–O₂ battery using the typical diluted DMSO-based electrolyte.¹⁹ Actually, the inner/original reason can be assigned to the excess free DMSO solvent molecules cannot well coordinate with Li⁺ cation, resulting the related reaction between DMSO free molecule and exposed Li metal surface. However, in the super-concentrated LiTFSI-DMSO electrolyte solution, there exists no free DMSO molecule in the solvated polymeric-fluid-network, Li[(DMSO)₃]-TFSI.²⁵ This specific structure has been proved by the spectroscopic evidence (Figure SX and other related works) and theoretical calculation (the super-concentrated electrolytes possess higher activation energy barriers than the free DMSO solvent)¹⁹. In this case, due to the lack of free DMSO molecules, the stability (oxidization and reduction) of super-concentrated LiTFSI-DMSO electrolyte solution has been efficiently enhanced. Besides, the stability against the nucleophilic attack from superoxide anion radical would also been improved in pure Li-O₂ battery system.¹⁹⁻²⁰



(a) Galvanostatic discharge/charge profiles (at 250 mA/g current density) of Li-O₂ cells fabricated by SWCNT-based porous carbon cathode and LiTFSI-DMSO electrolyte with different mole ratios: 1:3 (super-concentrated) and 1:20 (diluted), respectively. (b) XRD patterns of the discharged cathodes collected from the Li-O₂ cell assembled with different electrolyte concentrations.

Based on the electrochemical behaviors observed in different electrolyte concentrations, the higher polarized overpotential (both ORR and OER) can be rationally attributed to the slower ORR/OER kinetics in the super-concentrated electrolyte system. However, turn to the related XRD results of the discharge product, besides of the typical Li₂O₂ products, LiOH can be clearly observed in the diluted electrolyte system (black trace), which cannot be observed in super-concentrated Li-O₂ cell system (blue trace). The formation of LiOH in diluted electrolyte system indicates the introduction of additional proton source, which can be ascribed to the decomposition of DMSO (superoxide-related nucleophilic attack). In typical diluted system, superoxide anion radical would attack the free DMSO solvent molecule, resulting the formation of dimethyl sulfone (DMSO₂) and hydroxide (OH⁻).^{16, 26-27} The decomposition of DMSO-based electrolyte would inevitably lead to the degradation of Li-O₂ cell. While in the super-concentrated electrolyte system composed by solvated contact-ion-pair, not any free DMSO solvent molecule exist in the electrolyte. In this case, the related nucleophilic attack would, in some extent, be efficiently restrained, resulting the formation of typical Li₂O₂ discharge product. This

phenomenon also present well coincide with recent reports on the related DMSO-based super-concentrated electrolyte system in Li-O₂ cell.²⁰



Anodic linear potential scan at 10 mV/s between 3.0 V and 4.5 V after a typical galvanostatic discharge process in various electrolyte systems with different LiTFSI:DMSO mole ratios.

Regardless of the polarized climbing caused by electrolyte oxidization decomposition, two separated peaks can be observed. The anodic peak at higher potential dominates in relatively dilute electrolyte (red and orange traces) systems, which can be assigned to the decomposition of carbonate. With a lower thermodynamic equilibrium potential, the peroxodicarbonate-related peak gradually become dominate with the increasing salt concentrations. This variation trend of related peaks exhibits well coincide with the transition of related voltage plateaus observed during galvanostatic charging process (shown in Fig. 3a).



(a) Schematics of peroxodicarbonate observation based on various vibrational spectroscopies (Raman and IR). (b) Raman and (c) IR spectra recorded from related cathode (red trace, Raman) and electrolyte (red trace, IR), which harvested from the discharged Li-O₂/CO₂ cell with 1:3 (LiTFSI:DMSO) mole ratio. The in-situ Raman spectra of OCP cathode and IR spectra of pristine/fresh electrolyte are shown for comparison (black traces). Each of their differential/subtracted spectrum are also offset for clarifying the corresponding peaks assigned to discharge products. Besides, the molecular structure of peroxodicarbonate (C₂O₆²⁻) and the assignment of related stretching modes are noted for clarity.

The most essential difference between the pair of characterizations focus on the observation nature of different stretching modes. In Raman spectra, due to the enhanced Raman signal near the SERS gold substrate, Au-O (surface interaction bond) and O-O stretches (press close to the gold surface) of the adsorbed peroxodicarbonate present very strong signals and tend to be clearly detected/observed. While the blindness of other stretching modes on Raman spectra can be mainly attributed to the restriction of Raman spectroscopy (very limited surface enhance signal). In this case, we provide related IR spectra to remedy the defect and further prove the existence of peroxdicarboante (C₂O₆²⁻). As a result, other stretching modes in C₂O₆²⁻ can be clearly

observed in IR spectra collected from discharged electrolyte, and all of them are well consistent with the related assignment of standard peroxo-dicarbonate species.⁷



(a) In-situ Raman spectra recorded during the initial cycle in $Li-O_2/CO_2$ cells with various LiTFSI:DMSO mole ratios. Peak intensities of (b) O-O stretch in peroxodicarbonate and (c) CO₃ symmetric stretch in Li_2CO_3 are normalized according to each of their maximum value. The related intensity color mapping are shown as a function of discharge/charge capacity (x-axis) and LiTFSI:DMSO mole ratios (y-axis), respectively.

The obtained information can be systematically summarized as follows:

1) In dilute electrolyte (1:20 and 1:10 mole ratio), Li₂CO₃ acts as the only observable discharge product, which suffers from incomplete decomposition during charging. Besides, parasitic production of DMSO₂ can be observed at high polarized potential.

2) In concentrated electrolyte (1:5 and 1:4 mole ratio), as the newly-observed products, peroxodicarbonate share the similar increasing trend with Li₂CO₃ during discharging. Prior to the decomposition of Li₂CO₃, peroxodicarbonate has been oxidized during initial stage of charging. Unfortunately, DMSO₂ and residual Li₂CO₃ still can be observed after charging.

3) Most importantly, in super-concentrated electrolyte (1:3 mole ratio), formation of Li_2CO_3 cannot be observed anymore, and the discharge product is totally replaced into peroxodicarbonate, which also completely be decomposed during charging. Besides, no any parasitic DMSO₂ can be detected during a reversible cycling.



Titration analysis on discharged Li-O₂/CO₂ cells with various LiTFSI/DMSO based electrolytes: (a) Carbonate quantification; (b) Peroxide quantification. Note that, the information of soluble discharge products can be obtained from the difference between wet (cathode+electrolyte) and dry (cathode). Details of quantification have been introduced in experimental section.

Based on the obtained LiOH (x mol, acid/base titration), and H_2O_2 (y mol, iodometric titration), the amount of Li_2CO_3 (x-2y mol) and $Li_2C_2O_6$ (y mol) can be quantified, respectively:

$$Li_2CO_3 + H_2O = LiHCO_3 + LiOH;$$
$$Li_2C_2O_4 + 2H_2O = H_2O_2 + 2LiOH + 2CO_2$$

In the related cell with dilute electrolyte, the discharge products are dominated with Li_2CO_3 , which deposited on cathode surface (no difference between wet and dry during carbonate quantification). Besides, the amount of titration results are well consistent with the theoretical value calculated from the discharge capacity (0.4 mAh equals to 3.75 µmol Li₂CO₃; $4Li^+ + O_2 + 2CO_2 + 4e^- \rightarrow 2Li_2CO_3$). While, with the increasing of salt concentration, the production of Li₂CO₃ gradually being replaced by the soluble peroxodicarbonate (only can be detected in electrolyte). In particular, in the Li-O₂/CO₂ cell with 1:3 (LiTFSI:DMSO) mole ratio (super-concentrated CIPs), peroxodicarbonate becomes the only observable discharge product, and the titrimetric amount of it fit well with proposed peroxide-pathway: $O_2 + 2CO_2 + 2e^- \rightarrow C_2O_6^{2-}$.



(a-b) DEMS results collected during charging (and another 300 mAh/g overcharging)process in super-concentrated electrolyte system (1:3, LiTFSI:DMSO). (c)Galvanostatic charging curve for electrolyte (without discharging).





Mass spectra (in-situ DEMS) collected during charging (overcharging) process in super-concentrated electrolyte (1:3 mole ratio, LiTFSI : DMSO).

The details of GC-MS experiments and data processing has been present below. After discharging process, helium (He) background gas (m/z=4) is continuously purged till the fragments of CO₂ (m/z=44) and O₂ (m/z=32) become relatively stable. Within all of the MS spectra, the intensity of He background (m/z=4) has been normalized to 100% for comparison. At the OCP state (point-A), except for the He (m/z=4), other fragments (m/z=15, 45, 63, 78, etc.) can be ascribed to the vaporized dimethyl sulfoxide (DMSO) electrolyte solvent. In order to eliminate the signal of DMSO, we subtract the signals of DMSO-related fragments and protrude the CO₂ (m/z=44) and O₂ (m/z=32) fragments. In the end of charge process (Point-D), the evolution rates of CO₂ and O₂ suffer from a rapid decrease and drop to zero. During the subsequent overcharging process (Point-E), there present no obvious evolution of CO₂ nor O₂. However, another pair of new peak can be observed (m/z=79 and 94), which can be attribute to the related fragment from parasitically produced dimethyl sulfone (DMSO₂) by-product (produced from electrochemical decomposition of DMSO solvent). The standard mass spectra of O₂, CO₂, DMSO and DMSO₂ can be found in related MS databases (ChemSpider, Spectral Database for Organic Compounds, SDBS, and restek, etc.).



Titration analysis towards specific products during initial discharge/charge cycle in related Li-O₂/CO₂ cells with different LiTFSI:DMSO mole ratios: (a) Carbonate quantification; (b) Peroxide quantification.

The quantitative information of related discharge products during cycling exhibit well coincide with the variation trends recorded from in-situ Raman observations. Regardless of the pure formation/decomposition of Li₂CO₃ or peroxodicarbonate in each of their specific electrolyte systems, the variation trends present more interesting in the concentrated electrolyte system (green bars, 1:4 mole ratio), in which both of them co-exist as products. Both of them keep increasing during discharging, while peroxodicarbonate firstly be decomposed during initial stage of subsequent charging process, remains the amount of Li₂CO₃ starts to be decomposed at the relative later charging stage (corresponding to the higher charge potential plateau shown in Fig. 3a)



Titration analysis towards specific products after charging in related Li-O₂/CO₂ cells with different LiTFSI:DMSO mole ratios.

Compared with the totally decomposed peroxodicarbonate species, Li₂CO₃ cannot be completely decomposed after entirely charging process, which seriously influence the reversibility and cyclability of related Li-O₂/CO₂ batteries. This related incompletely decomposition phenomenon revealed here is well consistent with the results obtained on corresponding in-situ Raman spectra (Fig. 3d, 3e and S15).



> Similar Point: Soluble electron carrier leads to low overpotential upon charging

> Different Point: $C_2O_6^{2-}$ is discharge product, while redox mediator is just a agent/additive

Figure S24

Representation of the solution-pathways present in the redox mediator involved Li-O₂ battery system and peroxodicarbonate-based Li-O₂/CO₂ battery system, respectively.

The employment of redox mediator in Li-O₂ battery system would efficiently reduce the charge overpotential. Actually, the overpotential in Li-O₂ cell can be mainly attributed to the polarization upon electrochemically Li₂O₂ decomposition. The solid (cathode)-solid (insulated Li₂O₂ toroid particle) contact mode would inevitably lead to the high overpotential. Acting as a flowing electron carrier/agent, the introduction of soluble charge redox mediator species (TTF, TEMPO, LiI, LiBr, etc.) would essentially change the rigid solid-solid electrochemical contact to the solid-liquid chemical contact mode, resulting the reduction of charge potential.²⁸⁻³¹ Herein, with the employment of super-concentrated electrolyte, the discharge product itself has been essentially changed, from solid Li_2CO_3 to soluble $C_2O_6^{2-}$. The evolution design form "solid-pathway" to "solution-pathway" herein present very similar as the one introduced in the redox mediator involved Li-O₂ battery system. In this case, the low charging potential in both systems can be rationally attribute to the solution pathway. To some extent, the specific design strategy (turning the insoluble product to soluble product) has been enlightened from the related reports on redox mediator concept in Li-O₂ battery system. However, there exist essential difference between them. The nature of redox mediator (in Li-O₂ cell) is the introduction of additional soluble electron carrier between solid Li_2O_2 (discharge product) and cathode, but not turning the Li_2O_2 to another soluble peroxo-related product. While, in the current $Li-O_2/CO_2$ system, the peroxo-dicarbonate itself is the soluble discharge product.



Galvanostatic discharge/charge profiles (at 400 mA/g current density) of cells purged with various volume/mole ratio of O_2/CO_2 mixed gas in CIP-composed super-concentrated LiTFSI-DMSO (1:3) electrolyte. The $C_2O_6^{2-}$ -related reaction pathway/plateau do not suffer from an obvious change with the variation of supplied gas ratio (in the bulk space).



Galvanostatic discharge profiles (2.3 V vs. Li/Li^+ cutoff potential) observed on SWCNT-based porous carbon cathodes in newly-introduced $Li-O_2/CO_2$ cell (red trace) and typical $Li-O_2$ cell (blue trace).

Compared with the typical Li-O₂ cell, the discharge capacity of Li-O₂/CO₂ cell (peroxodicarbonate related electrochemical process) reveals its superiority. However, for a more practical battery system, there still remains a long way to improve this newly-introduced system. Herein, we provide several related optimization design strategies for further modification:

<u>a) Cathode Design Strategy:</u> Similar as the typical Li-O₂ battery system, the high capacity rely on the high specific surface area and high active sites on the cathode surface. In this case, enlarge the specific surface area (rational design of porous structure/size/distribution, etc.) and enrich the active catalytic sites (introduce suitable surface catalyst) reveal to be effective strategies for cathode modification. Besides, the rational design of pore structure can also restrain the related shuttling of soluble peroxodicarbonate species during long term cycling, which is very similar as the strategies conducted in Li-S battery to prevent the shuttle of polysulfide.

b) Separator Design Strategy: The shuttling of soluble discharge product would also limit the practical application of this system. In this case, corresponding modification on separator design would helpful. For example, employing MOF-based or Nafion-based separator to restrain the shuttling of soluble peroxodicarbonate to the Li anode side, building an artificial anode protection layer to restrain the degradation of Li metal, etc.

c) Electrolyte Design Strategy: The solubility of peroxodicarbonate essential limit the capacity stored in this system. In this case, without destroying the structure of soluble peroxodicarbonate, enlarging its solubility by the introduction of suitable electrolyte additives would improve the capacity of this newly-introduced battery system.

<u>d) Cell Structure Design Strategy:</u> The reaction pathway presents very sensitive towards gas ratio (O_2/CO_2) and current density. In this case, optimization the gas ratio and current density (gas consumption rate) is also a very important factor for practical application. Herein, we provide another two strategies on cell structure: 1) A closed battery system. Firstly, we can purged a certain amount/ratio of O_2/CO_2 gas into a closed battery system, then the cell can be cycled in a relative stable gas environment. Also, we can prefill the cathode with certain amount of Li_2CO_3 and Li_2O_2 , then the cell can be activated by a pre-charging process, resulting the releasement of certain ratio of O_2/CO_2 . After the pre-charging activating process, the cell can be cycled in a closed battery system. 2) Flow redox battery system. The capacity of the cell has been limited by the solubility of peroxodicarbonte in the electrolyte trapped within the porous cathode. In this case, driving the flowing of the electrolyte (stored with soluble discharge product) in a flow redox battery system can largely improve the capacity.



a) Voltage profiles of Li-O₂/CO₂ cells operate in LiTFSI/DMSO electrolyte with different mole ratios (current density: 200 mA/g), the cathodes are fabricated by SWCNT porous carbon. (b) Voltage profiles of typical cycles at 200 mA/g with fixed capacity of 200 mAh/g during 20 cycles. The mass loading of SWCNT is 0.3~0.5 mg/cm². (c) Ex-situ Raman spectra collected from cathodes; (d) FTIR spectra harvested from electrolytes after related discharging/charging processes in different electrolyte systems (typically-diluted vs. super-concentrated). (e) Quantitative titration results for the carbonate and peroxide species in corresponding cell assembled with different electrolytes.

electrochemical behaviors observed The on porous carbon cathode (SWCNT-based) present similar as the ones collected on nano-porous gold (NPG) cathode. Fabricated by typical diluted electrolyte (mole ratio of LiTFSI : DMSO=1:20), the Li- O_2/CO_2 cell present very high charge potential (black trace, Figure S25), and the corresponding discharge product has been proved as deposited Li₂CO₃ by Raman spectroscopy (not any obvious signal from soluble product collected by IR). While the Li-O₂/CO₂ cell assembled with super-concentrated electrolyte (mole ratio of LiTFSI : DMSO=1:3) present a lower charge potential plateau (around 3.6 V vs. Li/Li⁺), which can keep around 20 cycles. Similar with the discharge product observed on NPG cathode, herein, peroxodicarbonate-related IR peaks can be clearly observed from the discharged electrolyte, while no obvious deposited product can be observed on the cathode. Besides, the titration results further confirm the different reaction products produced in the two electrolyte systems. In this case, the 3.6 V charge plateau can be rationally assign to the electrochemical decomposition of peroxo-dicarbonate, which is produced in Li-O₂/CO₂ cell assembled with super-concentrated LiTFSI/DMSO electrolyte. The peroxodicarbonate-related (electro)chemical process can be preliminarily realized on practical porous carbon cathode. Compared with the gold-based cathode, the catalytic activity of carbon would be weaker on the carbon-based cathode. The lower charge potential plateau observed on NPG-based cathode (0.1 V lower than SWCNT-based cathode) may be ascribed to the related difference towards catalytic activity of cathodes. However, as the related characterizations shown above, the C₂O₆²-related discharge/charge reaction pathways did not present any obvious/essential change between gold and carbon cathodes.



Discussion of proposed determining factors for the capacity in Li-O₂/CO₂ battery operates with peroxodicarbonate-based pathway. Galvanostatic discharge curves of Li-O₂/CO₂ battery assembled with CIP-composed electrolyte system at a fixed current of 50 μ A on NPG cathodes: (a) fabricated with different amount of electrolyte; (b) assembled with different layers of NPG leaf cathode, (c) Proposed schematic of the related discussion.

As a soluble discharge product, the solubility of peroxo-dicarbonate in specific CIP-composed LiTFSI-DMSO electrolyte can be regarded as one of the most essential determining factor for the capacity of the cell. However, as shown in (a), the amount of electrolyte volume injected into the cell seems do not obviously influence the discharge capacity. While, on the contrary, as shown in (b), the capacity perform proportional to the mass loading of NPG cathode, which is very similar as the behavior of deposited/insoluble Li₂O₂ product observed in Li-O₂ battery. In fact, the amount of injected electrolyte in the bulk (out of NPG pore) have no relationship of the "available" amount of electrolyte. Only the electrolyte trapped inside the NPG pore can act as a container of soluble peroxodicarbonate discharge species. In another word, the limitation of capacity only rely on the amount of redundant electrolyte trapped inside the pore in the cathode. In this case, the amount of redundant electrolyte do not

influence the stored amount of peroxodicarbonate product (as shown in a). The nature of this phenomenon is totally different form the deposited Li2O2 observed in Li-O₂ cell.

In this case, the solubility of peroxo-dicarbonate cannot be obtained by the volume of bulk electrolyte solution. As shown in (b), with the increasing of the NPG layer, the amount of electrolyte trapped within the porous cathode become higher, resulting in the boosting of related discharge capacity. In this case, we can roughly calculate the solubility of peroxo-dicarbonate based on the volume of electrolyte trapped inside the porous cathode: 2.7 mol/L (0.1 mAh electric quantity, equals to 1.87μ mol Li₂C₂O₆, dissolved into 0.69 μ L trapped electrolyte).

Note that, the practical solubility value should be lower, because peroxo-dicarbonate would inevitably diffuse into the bulk solution in the cell. Actually, this diffusion of the discharge product to the bulk would lead to the low coulombic efficiency (as shown in Figure 4b) and the related shuttling of soluble discharge product would also become an threaten for the stability of Li metal anode (will be discuss in Figure S29 below). Beside of the solubility issue, there are also several determining factors for the discharge capacity, for example: the diffusion coefficients of gas, the discharge current (gas consumption rate), and the porous structure of cathode (storage volume of electrolyte), etc. Therefore, if we can find a balance among these various influence factors, the practical discharge capacity in the corresponding cell would be further extended by cathode morphology modification (material design route).



Figure S29

(a) Voltage profiles of typical cycles at 400 mA/g with fixed capacity of 200 mAh/g during 100 cycles. (b) Discharge-charge voltage hysteresis against cycle number recorded from a. Corresponding profiles obtained from cells cycled with varying LiTFSI:DMSO mole ratios are shown for comparison. The corresponding in-situ Raman spectra collected at the end of each discharge (red) and charge (blue) states among typical cycles are present in Figure 4c.



(a) Galvanostatic discharging/charging profiles of subsequent cycles (after the 100 cycles shown in Figure 4). (b) FTIR spectra collected from the cycled electrolyte after specific cycles. Note that, the $C_2O_6^{2-}$ -related adsorption peaks observed remains after the 143th cycle (blue trace) can be assigned to the undecomposed discharge product diffused within the bulk electrolyte solution, which accumulated during prolonged cycling. (c) Proposed schematic of the diffusion-related discussion and corresponding further modification strategies.

Besides of the stable cycling performance present in Figure 4, several factors/defects would also lead to the cell degradation during prolonged cycling. After the charging process of the 143th cycle, some residue peroxo-dicarbonate can be observed in the bulk electrolyte, and the charging potential suffer from gradual polarization. The polarization can be attributed to the diffusion of soluble discharge product to the bulk electrolyte solution, which cannot be fully decomposed due to the dynamic issue. Besides, similar with the polysulfide (in Li-S battery) and the redox mediators (in Li-O₂ battery), the soluble discharge product (electron carrier) would diffuse to the Li anode side, and the related shuttling would lead to the degradation of

Li anode during long time cycling. Although the soluble discharge product trapped within porous cathode cannot diffuse out, the ones produced on the surface can easily diffuse to the bulk solution. In this case, being the most essential advantage for this CIP-composed Li-O₂/CO₂ battery system, the solubility of peroxo-dicarbonate also threatens the lifetime of specific cell, which acts as a kind of "double-edged sword". In this case, enlightened by the various modification strategies towards polysulfide and redox mediators, the related diffusion and shuttling of soluble peroxo-dicarbonate product would be efficiently restrained via several specific strategies, for example: rational porous design to restrain the evolution/diffusion of discharge product to the bulk, design a suitable separator to prevent shuttling (solid separator, MOF-based separator, Nafion-based separator, etc.), design a anode protecting layer, etc. In summary, taking full advantage of this soluble discharge product (low overpotential, less parasitic decomposition, etc.) and avoiding its shortcoming/defect by rational modification strategies would be the next step for the development of this system.



Galvanostatic discharge profiles observed on flat gold cathodes in typical Li-O₂ system and newly-introduced Li-O₂/CO₂ system. After initial discharge process (2.3 V vs. Li/Li⁺ cut-off potential), the cells are set free at OCV state for 2 hours aging. Then (without charging), another discharge process are conducted. The schematic of cell is shown inset.

Based on this specific electrochemical design, the difference between soluble peroxodicabonate and insoluble Li₂O₂ product can be revealed.

For typical Li-O₂ system, once the cathode surface has been blocked/covered by insoluble Li_2O_2 product at the end of 1st discharging, without decomposition of deposited Li_2O_2 (charging), the next discharging process cannot be conducted (negligible 2nd discharge capacity). For the newly-introduced Li-O₂/CO₂ system, the obtained soluble peroxodicarbonate product can diffuse away to the bulk during 2 hours aging. In this case, even without charging process, there still present certain amount of discharge capacity during 2nd discharging.

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