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A Li$_2$CO$_3$-Free Li-O$_2$/CO$_2$ Battery with Peroxide Discharge Product

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Owing to its exceptionally high energy potentiality based on Lithium-oxygen chemistry, Lithium-air battery has been boosted as an appealing alternative to current state-of-art Lithium-ion batteries. However, due to the presence of non-O$_2$ components in ambient air, the practical performance of Li-air battery is limited to only few cycles with low energy efficiency. Particularly, once CO$_2$ being incorporated in battery system, Li$_2$CO$_3$ would inevitably formed during discharging, which results serious climbing of charge potential and relevant decomposition of cell components. Herein, with appropriate introduction of electrolyte into aggregated contact-ion-pair (CIP) structure, we demonstrate a Li-O$_2$/CO$_2$ battery cycles via stabilized peroxycarbonate (C$_6$O$_{6}$$_2$) formation in electrolyte rather than Li$_2$CO$_3$, and operates with a very low charge potential (3.5 V). We anticipate that this discovery will provide a rational design strategy for modifying the reaction pathway of Li-O$_2$/CO$_2$ battery, and accelerate the step of evolution from Li-O$_2$ to Li-air batteries.

The remarkably increasing demand for high-energy rechargeable batteries has heightened considerable interests in aprotic Li-air batteries, which can deliver extremely high theoretical gravimetric energy (calculated form reaction of Li with O$_2$) to conventional Li-ion batteries. 1, 2 In fact, most of Li-air batteries have demonstrated cell operations in pure O$_2$ atmosphere, because of the presence of other constituents in ambient air (H$_2$O, CO$_2$, etc.) would inevitably alter reaction pathway and lead to the formation of parasitic products such as LiOH and Li$_2$CO$_3$, resulting poor cyclability and high polarization. 3, 5 However, in order to remove these complications, the introduction of the additional gas purification components leads to substantial increase in the weight and capital cost of battery system, which ineluctably counteract its most sparkling advantage, high energy density. 6

In this case, the development of practical Li-ambient air battery deeply sinks into dilemma.

Recently, the role of water in Li-O$_2$ system has been revealed as a helpful proton-donor. 7, 8 Moreover, as another influential air component, CO$_2$ is of particular interest due to its high solubility in organic electrolyte solvents (~50 times more soluble than O$_2$) and reactivity with superoxide anion (O$_2^-$), the key intermediate and the crime culprit of nucleophilic attack in Li-O$_2$ battery. 3, 9-12 Therefore, involving CO$_2$ within Li-O$_2$ cell would be a center point of penetration for the evolution from Li-O$_2$ to Li-air system. Recently, by suppressing the superoxide-related parasitic reactions, a rechargeable Li-O$_2$/CO$_2$ battery based on Li$_2$CO$_3$ has been introduced with a boosted discharge capacity compared with typical Li-O$_2$ battery. 13, 14 However, the charge voltage was locked above the thermodynamic voltage for the decomposition of Li$_2$CO$_3$ (3.82 V vs. Li/Li$^+$), 3, 15 which lead to low round-trip efficiency (nearly 67 %) and decomposition of other cell components, resulting in rapid cell degradation after several cycles. 14, 16 Besides, the high overpotential appears in Li-O$_2$ cell can also, to some extent, be ascribed to the parasitic production of Li$_2$CO$_3$. 17, 18 In this case, the high decomposition potential of Li$_2$CO$_3$ become the insurmountable barrier limits the practical application of Li-O$_2$/CO$_2$ and Li-air batteries. Although, early works on CO$_2$-incorporated aprotic oxygen reduction process proposed the formation of superoxocarbonate (CO$_3^{2-}$) and/or peroxycarbonate (C$_6$O$_{6}$$_2$$^{2-}$) as probable intermediates, which may deliver lower decomposition potential than carbonate. 3, 9, 10 these metastable intermediates would rapidly suffer from further reduction/dissociation into Li$_2$CO$_4$.

Thus, effectively interdicting the direct interaction between Li-ion and these metastable intermediate anion would be a feasible solution to stabilize these intermediates and introduce them into the reversible cycle in Li-O$_2$/CO$_2$ system. Recent studies reveals that both the solvation state of Li-ion and the structure of entire electrolyte system can be essentially controlled by adjusting the concentration of salt with specific anion, especially in electrolyte with high dielectric solvent such as dimethyl sulfoxide (DMSO). 19-22 In this work, enlightened by the unique features of super-concentrated electrolytes, 23 we further introduce a aggregated electrolyte system composed of DMSO-sheathed contact-ion-pair (CIP). Different from diluted electrolytes, the polymeric fluid network composed in our specific-introduced electrolyte would efficiently stabilize peroxycarbonate species by effectively restrain its incorporation with Li$^+$. Consequently, we demonstrate a
Li$_2$O$_2$/CO$_2$ battery with an ultralow charge potential (3.5 V vs. Li/Li$^+$) and considerable cycle life. More importantly, free of typical Li$_2$CO$_3$, the newly-proposed battery cycles via pure peroxodicarbonate formation, which not only remedies the inherent defects in CO$_2$-incorporated Li$_2$O$_2$ electrochemistry but also paves the way for more practical Li-air battery system.

Firstly, we want to clarify the influence of CO$_2$ towards aprotic oxygen reduction process. As a remarkably powerful operando characterization method, in-situ Raman spectroscopy with surface enhanced nanoporous gold (NPG, Figure S1) substrate is preferentially employed to investigate the reaction mechanism (Figure S2). Excluding the influence of Li-ion, related discharge products have been initially investigated in gas saturated 0.5 M tetrabutylammonium perchlorate (TBAClO$_4$)-DMSO electrolyte. Without CO$_2$, pure oxygen reduction/oxidation operate upon flat discharge/charge plateaus (2.53/3.01 V, Figure 1a), which ascribe to the conventional O$_2$/O$_2^+$ redox couple. Exemplified by Raman spectra obtained at corresponding discharge state (red trace, Figure 1c), regardless of the strong peaks from DMSO (Figure S3), the newly-produced peaks can be assigned to Au-O (488 cm$^{-1}$) and O-O (1108 cm$^{-1}$) stretches in adsorbed superoxide anion. After trace CO$_2$ being introduced (orange trace, 4/1 volume ratio of O$_2$/CO$_2$, Figure 1c), the discharge potential rapidly climbs up and the corresponding charge curve also distorts into several stages. Segmented analysis (Figure 1d) reveals that peroxodicarbonate (C$_2$O$_6^{2-}$) formed during initial discharging (Figure S4 and S5), which has been further verified by the chemically synthesized species (Figure S6). The related assignment and extended discussion on the reaction pathway and peroxo configuration have been exhibited in Figure S7 and S8. With the consumption of CO$_2$, peroxomonocarbonate (CO$_4^{2-}$) is subsequently validated by the observation of another Au-O adsorption peak appears at lower wavenumber (green peak, point-B, Figure 1d). Continuously, the discharge process returns to the typical oxygen reduction with the production of O$_2^-$ (red peak, point-C, Figure 1d). With the sequential disappearing of corresponding Raman stretches shown in Figure 1d, the subsequent charge process conducts in the order of thermodynamic equilibrium potential of specific reactions:

- **Point C to D (red peak):** $O_2^- \rightarrow O_2 + e^- $ \hspace{1cm} ($E_1 = 2.64$ V vs. Li/Li$^+$)
- **Point D to E (green peak):** $CO_4^{2-} \rightarrow O_2 + CO_2 + 2e^- $ \hspace{1cm} ($E_2 = 2.89$ V)
- **Point E to F (blue peak):** $C_2O_6^{2-} \rightarrow O_2 + 2CO_2 + 2e^- $ \hspace{1cm} ($E_3 = 3.27$ V)

Continuously increasing the ratio of CO$_2$, the discharge processes are fixed within pure C$_2$O$_6^{2-}$ production, and the charging processes are also stabilized at peroxodicarbonate-related 3.49 V plateau. The variation of surface electrochemistry can be ascribed to the relationship between gas diffusion coefficient and related gas consumption rate (current-dependent) within the double electrode layer. The discussion of related dynamic issue has been extended in Figure S8.

However, once Li-ion being introduced, the charge potential plateau quickly rises up to 4.2 V (Figure 1b), and the corresponding Raman results (Figure 1e) demonstrate that
related discharge products are converted from Li$_2$O$_2$ to Li$_2$CO$_3$ in CO$_2$ incorporated condition. More seriously, not only the Li$_2$CO$_3$ cannot be fully decomposed after charging, but the high polarized voltage inevitably leads to the formation of DMSO$_2$, a parasitic product of DMSO oxidation (Figure 1f). Herein, the highly polarization overpotential and the related rigid Li$_2$CO$_3$ decomposition process also present well coincide with our previous results. Consequently, the parasitic reaction and irreversibility directly result in the degradation of cell after merely several cycles (Figure S9). The failure of cell would only become worse on practical carbon-based cathodes due to the decomposition of carbon on high potential. In summary, the high decomposition potential of Li$_2$CO$_3$, the final stable discharge product, directly leads to the instability of the typical Li-O$_2$/CO$_2$ battery system. Although the peroxodicarbonate, a metastable intermediate, can stably exist in Li-free condition, it cannot be effectively utilized due to the diffusion of Li-ion from metal Li anode during a long term running (Figure S10). Enlivened by the redox mediator strategy in Li-O$_2$ battery system, how to essentially restrain the rigid Li$_2$CO$_3$-related reaction pathway, the intrinsic defect for Li-O$_2$/CO$_2$ battery, and efficiently stabilize the soluble peroxodicarbonate product in Li-contained cell become one of the most feasible modification routes.

In dilute electrolyte (Figure 2a), the interaction between [Li(DMSO)$_3$]$^+$ solvation sphere cation and TFSI$^-$ anion is relatively weak, providing the opportunity for the incorporation between Li$^+$ cation and C$_2$O$_6^{2-}$ anion. This directly leads to the further reduction and dissociate breakage of the peroxide O-O bridge, resulting in the formation of Li$_2$CO$_3$. Thus, interdicting the electric interaction between Li$^+$ and C$_2$O$_6^{2-}$ presents as the most essential solution pathway. Neutralizing the charge on Li$^+$ cation by strengthening its interaction with other anion would be a feasible route. Typically, the solvation number of Li$^+$ in DMSO solution has been confirmed as 4.0, which indicates a [Li(DMSO)$_4$]$^+$ monodentate ligand. Herein, we further increase the salt concentration and replace one of the DMSO molecule among the solvation sheath into a larger anion, for example bis(trifluoromethylsulfonyl)amide (TFSI$^-$). Based on the concentration-dependent Raman spectra recorded from various LiTFSI-DMSO electrolytes (Figure 2b and S11), the C-S stretching modes in free DMSO (red peaks, 669/699 cm$^{-1}$) gradually decrease with the increasing salt concentrations, while the corresponding modes in solvated DMSO (green peaks, 680/713 cm$^{-1}$) become dominate. Note that, only the solvated DMSO can be observed in specific super-concentrated electrolyte with 1:3 mole ratio [LiTFSI:DMSO] which indicates that the complex with [Li(DMSO)$_3$]$^+$[TFSI$^-$] aggregated structure has been achieved. More importantly, based on deeper analysis towards S-N stretching mode in TFSI$^-$, the ion association mode in super-concentrated electrolyte (1:3 mole ratio) entirely evolves from "solvent separated ion which indicates that the complex with [Li(DMSO)$_3$]$^+$[TFSI$^-$] aggregated structure has been achieved. More importantly, based on deeper analysis towards S-N stretching mode in TFSI$^-$, the ion association mode in super-concentrated electrolyte (1:3 mole ratio) entirely evolves from "solvent separated ion which indicates that the complex with [Li(DMSO)$_3$]$^+$[TFSI$^-$] aggregated structure has been achieved. More importantly, based on deeper analysis towards S-N stretching mode in TFSI$^-$, the ion association mode in super-concentrated electrolyte (1:3 mole ratio) entirely evolves from "solvent separated ion which indicates that the complex with [Li(DMSO)$_3$]$^+$[TFSI$^-$] aggregated structure has been achieved. More importantly, based on deeper analysis towards S-N stretching mode in TFSI$^-$, the ion association mode in super-concentrated electrolyte (1:3 mole ratio) entirely evolves from "solvent separated ion which indicates that the complex with [Li(DMSO)$_3$]$^+$[TFSI$^-$] aggregated structure has been achieved.

Figure 2. Design of electrolyte structure. (a) Schematic illustrations of electrolyte structure in dilute LiTFSI/DMSO-based Li-O$_2$/CO$_2$ cell, and relevant discharged components. As an intermediate, peroxodicarbonate (C$_2$O$_6^{2-}$) coordinates with solvated Li-ion and dissociates into Li$_2$CO$_3$ as the typical final product. (b) Raman spectra of LiTFSI/DMSO electrolytes with various mole ratios. Spectra are fitted by Gaussian-Lorentzian distribution functions, and the SNS stretch region in TFSI$^-$ (blue outlined) is magnified for clarity. In LiTFSI/DMSO electrolyte with 1:3 mole ratio, neither free DMSO molecule nor Solvent-Separated-Ion-Pair (SSIP) can be observed. Instead, sheathed by DMSO molecules, Li$^+$ and TFSI$^-$ is completely aggregated (AGG) within a Contact-Ion-Pair (CIP) fluid network. (c) Schematic illustration of the newly-introduced super-concentrated fluid network electrolyte composed of [Li(DMSO)$_3$]$^+$[TFSI$^-$]. The electric interaction between Li$^+$ cation and C$_2$O$_6^{2-}$ anion could be effectively interdicted due to the electroneutrality of CIP-composed electrolyte system. As a result, the further reduction from C$_2$O$_6^{2-}$ to CO$_2$ could also be restrained.

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Figure 3. Electrochemistry and spectroscopy characterizations. (a) Voltage profiles of Li-O₂/CO₂ (1:1, volume ratio) cells operate in LiTFSI/DMSO electrolyte with different mole ratios (current density: 400 mA/g). b-c, IR spectra collected from the discharged cell components: (b) cathodes and (c) electrolytes. d-f, In-situ Raman spectra recorded during the 1st cycle from cells with various LiTFSI:DMSO mole ratios: (d) 1:20; (e) 1:5; (f) 1:3. g-h, Carbonate and peroxodicarbonate quantifications conducted on discharge cells (fixed 0.4 mAh capacity) with different LiTFSI:DMSO mole ratios: (g) 1:20 and (h) 1:3. CO₂ and O₂ evolution rates are collected after acid treatment, and the integrated amounts of gas (CO₂ and/or O₂) are compared with the corresponding theoretical amounts. The related reaction steps and quantitative comparison are inset for clarity. i-j, DEMS results of gas evolution rates for CO₂ and O₂ during charging in cells with different LiTFSI:DMSO mole ratios: (i) 1:20 and (j) 1:3. The electron number (versus CO₂ and O₂ gas molecule) marked by dash lines are corresponded to the specific reaction pathway listed inset.

Turning back to Li-O₂/CO₂ cell (Figure 3a), by employing highly-concentrated LiTFSI-DMSO electrolyte (1:5 and 1:4 mole ratios), charge plateaus gradually divide into two stages, with a lower peroxodicarbonate-related plateau (3.5 V) appearing during initial (Figure 1a), which coincide with the pair of oxidation peaks observed during corresponding cathodic linear sweeping processes (Figure S16). In particular, the charging plateau keeps at 3.5 V in the electrolyte composed of CIPs (blue trace, 1:3 mole ratio). The relevant transition from carbonate to peroxodicarbonate has been corroborated by IR
results, in which the signal of deposited Li$_2$CO$_3$ (Figure 3b) gradually drops to invisible while the increasing of related adsorption peaks in dissolved peroxodicarbonate become dominated (Figure 3c and S17). Thorough charge plateau assignments are revealed by in-situ Raman investigations (Figure 3d-3f, S18). In dilute electrolyte (1:20, Figure 3d), the incompletely decomposition of Li$_2$CO$_3$ and parasitic oxidation of DMSO (form DMSO$_2$) are clearly revealed. Subsequently, trace signal of peroxodicarbonate appears in concentrated electrolyte during discharge (1:5, Figure 3e), however, production of Li$_2$CO$_3$ still exist and related high decomposition potential ineluctably leads to the formation of DMSO$_2$. Nevertheless, essential change occurs in CIP-composed electrolyte system (1:3, Figure 3f), in which the Li$_2$O$_2$/CO$_2$ cell operates via pure peroxodicarbonate formation/decomposition.

More quantitative analysis towards discharge products are conducted based on carbonate/peroxo-species quantification by respectively monitoring CO$_2$/O$_2$ gas evolution rate after acid treatment. Discharged product in conventional dilute system has been confirmed as pure Li$_2$CO$_3$ species without any O$_2$ release (Figure 3g). In stark contrast, O$_2$ evolution further confirms the formation of peroxo-species in super-concentrated electrolyte condition (Figure 3h). Moreover, compared with the theoretical value calculated based on fixed discharge capacity (0.4 mAh), the specific constituent contents of released O$_2$/CO$_2$ mixture present well coincide with the pure production of peroxodicarbonate (C$_2$O$_6^{2-}$), which is also consistent with the related titration results (Figure S19). Finally, differential electrochemical mass spectroscopy (DEMS) is employed to investigate the reaction reversibility by monitoring gas evolution rate. In dilute electrolyte condition (Figure 3i), the rechargeable but irreversible nature of Li$_2$O$_2$/CO$_2$ cell has been revealed due to the incomplete decomposition of Li$_2$CO$_3$ during charging, especially during the last period. As comparison, during the flat 3.5 V charging plateau conducted in super-concentrated electrolyte (Figure 3j), the obtained specific charge-to-mass ratios (2e$^-$/O$_2$ and e$^-$/CO$_2$) well follows the reaction pathway, which defined as: C$_2$O$_6^{2-}$ → O$_2$ + 2CO$_2$ + 2e$. The details of DEMS characterization and corresponding overcharging investigation have been revealed in Figure S20 and S21, in which only trace amount of irreversible gas behavior (around 1.1%) can be observed. Combined with corresponding segmented titration results (Figure S22 and S23), within the margin of error, the peroxodicarbonate-based reversible electrochemical process has been successfully achieved in Li$_2$O$_2$/CO$_2$ cell with CIP-composed electrolyte. Additionally, benefit from the specific solution-based charging process, the low charging potential can be well maintained, which is very similar as the one observed in the redox mediator involved Li$_2$O$_2$ battery system (Figure S24). Moreover, the C$_2$O$_6^{2-}$-related electrochemical behavior can also be observed within the Li$_2$O$_2$/CO$_2$ cell purged with varying gas ratios (Figure S25). More important, the peroxodicarbonate-related pathway can also be realized on a more practical cathode composed by porous carbon material (Figure S26 and S27), indicating the potential for the extension of the newly-proposed mechanism to more practical applications.

![Figure 4](image.png)

For more practical utility, electrochemical performance of the Li$_2$O$_2$/CO$_2$ battery with super-concentrated electrolyte has been revealed in Figure 4. With the current density raising from 200 to 600 mA/g (Figure 4a), the polarization degree do not drastically increase, and the charge plateau still keeps below 3.6 V at 600 mA/g (blue trace), which is far more below the voltage observed in typical Li$_2$O$_2$/CO$_2$ battery operates with dilute electrolyte (black dash trace). Besides, the full discharge capacity has been extended to 753 mAh/g (2.6 V cutoff voltage), and most of the initial capacity (92%) is retained after 20 full cycles in super-concentrated electrolyte (Figure 4b and S28). More importantly, compared with the typical energy efficiency of Li$_2$O$_2$/CO$_2$ cell performed in dilute electrolyte, the corresponding value has been significant promoted in our specific-designed battery system. Furthermore, cycling with a cut-off capacity of 200 mA/h (Figure S29), the corresponding cell exhibits a stable discharge/charge windows at 2.8/3.5 V over 100 cycles. Different from typical Li$_2$O$_2$/CO$_2$ cells, which suffer from rapid degradation after several cycles due to inevitable accumulation of inactive Li$_2$CO$_3$ (Figure S29), the cell assembled with CIP-composed electrolyte keeps cycling base on peroxodicarbonate species, with its formation/decomposition corroborated by in-situ Raman spectroscopy (Figure 4c). After extended cycling (above 143 cycles), polarization upon charging can be gradually observed,
which would be attributed to the diffusion and shuttling of soluble discharge product (Figure S30 and S31). We believe that the related irreversible shuttling and diffusion can be effectively restrained via morphology modification on both porous cathode materials and separators in the future.

Conclusions

In conclusion, in order to remedy the inherent defect of conventional Li-O$_2$/CO$_2$ battery and revolutionarily change the energy storage carrier from typical carbonate to peroxodicarbonate, a super-concentrated electrolyte composed of DMSO-solvated contacted ion-pair (CIP) has been introduced. During cycling, the polymeric fluid network within our rationally-introduced electrolyte system effectively stabilizes the peroxodicarbonate by interdicting its further reduction into Li$_2$CO$_3$, which successively lead to obviously decreasing of charge potential (from 4.2 to 3.5 V) and remarkable boost the energy efficiency. For the first time, the Li$_2$O$_2$/CO$_2$ battery cycles via pure peroxodicarbonate formation has been realized, and rigorously corroborated by sufficient in/ex-situ characterizations. In addition, based on the formation/decomposition of peroxodicarbonate species, rate-capability and cyclability has been well achieved in specific Li-O$_2$/CO$_2$ battery system, which delivers a relatively good stability upon cycling. In general, not being limited into Li-O$_2$/CO$_2$ battery, the unique features of super-concentrated electrolyte strategy would provide an enlightening insight to the construction of various advanced electrochemical energy storage application. Moreover, we anticipate that the stabilization of peroxodicarbonate species would accelerate the step of evolution from Li-O$_2$ to practical Li-ambient air battery, as well as to other possible utilization into field of CO$_2$ battery and revolutionarily change the energy storage carrier from typical carbonate to peroxodicarbonate.

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Notes and references