

Communication

The Origin of Improved Cycle Stability of Li-O₂ Batteries Using High-Concentration Electrolytes

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Abstract

The intrinsic instability of organic electrolytes seriously impedes practical applications of lithium–oxygen (Li–O₂) batteries. Recent studies have shown that the use of high-concentration electrolytes can suppress the decomposition reaction of electrolytes and help enhance cell reversibility. However, the fundamental nature of concentrated electrolytes' ability to improve the chemical durability and stability of Li–O₂ batteries remains unclear. In this work, we conducted computational studies to elucidate the origin of the enhanced oxidative/reductive stability of three representative solvents—DMSO, DME, and EC—in high-concentration electrolytes. The modeling results identify that Li⁺-solvent complexes, one of the solvate components, are the easiest to decompose in concentrated electrolytes. Thermodynamic and kinetic characterizations reveal that more anions in concentrated electrolytes are responsible for improving the oxidative and reductive stability of electrolytes. In addition, more Li⁺ ions, acting as a scavenging or stabilizing agent for superoxide anion (O₂[−]), also improve the stability of electrolytes against oxidation in Li–O₂ batteries. This work provides a mechanistic understanding of the enhanced cycle stability of a Li–O₂ battery using high-concentration electrolytes.



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1. Introduction

Lithium–oxygen (Li–O₂) batteries are considered to be a potential alternative to Li-ion batteries for transportation applications, owing to their high theoretical specific energy ($\approx 3000 \text{ W h kg}^{-1}$) [1–5]. However, the practical realization of Li–O₂ batteries is still severely hampered by some intrinsic challenges, such as poor cycle life, rapid capacity fading, and low safety, which are closely correlated with the degradation of the electrolytes [6–9].

Based on Li–O₂ battery components (a Li-metal anode, a porous carbon air electrode, and an electrolyte containing a Li salt and an aprotic solvent), electrolyte stability is threatened by the Li metal anode and oxygen radicals generated at the cathode. A Li anode with a highly reducing nature can spontaneously react with most known electrolytes. Esters and ethers can be decomposed by Li to form insoluble byproducts such as lithium oxide (Li₂O), lithium carbonate (Li₂CO₃), and lithium alkyl carbonates, forming a passivation solid electrolyte interphase (SEI) layer. Particularly, dimethyl sulfoxide (DMSO), because of its instability against the Li metal anode, cannot be used directly in practical Li–O₂ batteries.

In addition, as a product of the oxygen reduction process, the superoxide radical (O_2^-) is a strong nucleophile and prone to attack the electron-deficient part of the solvent (i.e., the carbon atoms of carbonyl groups (C=O) and sulfur atoms of sulfoxides (S=O)). This results in the formation of a [solvent– O_2^-] complex, which subsequently undergoes a highly exergonic decomposition reaction. Typically, alkyl carbonates (such as ethylene carbonate (EC), propylene carbonate (PC), and ethers (such as monoglyme (DME) and tetraglyme (G4)) all are susceptible to nucleophilic attack by O_2^- [10,11]. Therefore, the imperative for a practical and safe Li– O_2 battery is to improve the chemical stability of electrolytes.

Recently, reports are coming to demonstrate that highly concentrated electrolytes without free solvents can effectively suppress the dissolution of electrolytes in Li– O_2 batteries [12–14]. Zhang et al. demonstrated that highly concentrated LiTFSI–DME electrolytes (3 M) in Li– O_2 systems can significantly mitigate electrolyte decomposition and enable the reversible operation of both O_2 cathodes and Li anodes [15]. Zhang et al. used the highly concentrated LiTFSI–dimethyl sulfoxide (DMSO) electrolyte strategy to protect the Li metal anode and to improve the cycling stability of Li– O_2 batteries, which breaks the incompatibility of Li metal and DMSO [16]. However, the fundamental reason why concentrated electrolytes improve the life span of Li– O_2 batteries remains the most elusive component. With one after another hypotheses proposed but none satisfactorily rationalizing the disparity of solvent stability in concentrated electrolytes on the molecular scale, this mystery has been confusing the battery and electrochemistry community for last decade.

Computational chemistry has significantly advanced this field by elucidating fundamental electronic behaviors and enabling the interpretation of electrolyte activity at the atomic scale. For instance, Zhang et al. demonstrated that cation–solvent interactions reduce solvent reductive stability by analyzing the lowest unoccupied molecular orbital (LUMO) [17]. Bryantsev et al. reported that propylene carbonate (PC) is highly vulnerable to nucleophilic attack by O_2^- and detailed the corresponding reaction mechanism [11]. However, these studies were all conducted in dilute electrolyte solutions, without accounting for the mechanism differences in high-concentration electrolytes.

We decided, herein, to focus on the molecular-level insight into how high-concentration electrolytes suppress the parasitic reactions of the dissolution of electrolytes. As is known, during discharge, metallic Li is oxidized to soluble Li^+ at the anode/electrolyte interface, with electrons transferred to the external circuit ($Li \rightleftharpoons Li^+ + e^-$). At the cathode, oxygen is reduced to O_2^- , which subsequently reacts with Li^+ to form lithium peroxide (Li_2O_2) either via the non-electrochemical pathway [$2Li^+(sol) + 2O_2^-(sol) \rightleftharpoons Li_2O_2$] or the electrochemical pathway [$2Li^+(sol) + O_2^-(sol) + e^- \rightleftharpoons Li_2O_2$], consistent with the solution-mediated mechanism. To elucidate these processes, we perform computational studies to systematically investigate the chemical stability of the solvents DMSO, DME, and EC against O_2^- and Li metal. We find that the O_2^- responsible for triggering solvent oxidation can be stabilized by the high-concentration Li^+ ions. Anions, which combine with Li^+ into contact-ion pairs or aggregate in a concentrated electrolyte, increase the Gibbs energy barrier of the oxidation reaction of the solvent and in turn reduce side reactions. With an increment of the content of anions in Li salt, the reduction decomposition process of the solvent is inhibited, owing to the decreased electron affinities. This work unveils the origin of the enhanced oxidative/reductive stability of solvents in high-concentration electrolytes, and affords fruitful mechanistic insights into developing a practical electrolyte that could realize Li– O_2 batteries with long cycle life.

2. Materials and Methods

Cluster-based density functional theory (DFT) calculations are carried out with the Gaussian 16 package with Becke's three-parameter hybrid method using the Lee–Yang–Parr

correlation functional (B3LYP) and the Grimme's D3 dispersion corrections [18]. The geometrical structures are fully optimized and confirmed as true local minimums by vibrational frequency analyses at a ma-TZVP basis set except for the H element (for which there is no need to consider the dispersion function and thus is at a def2TZVP basis set). Notably, this basis set level has been widely applied in Li-based battery studies [19–21]. Meanwhile, the solvation effect is considered with a solvation model density (SMD) model. The static relative permittivities of DMSO, DME, and EC used for the SMD model are 47.2, 7.2, and 85.1, respectively. The transition state (TS) is searched for each elementary reaction and characterized by an extremum of the potential energy hypersurface having one imaginary frequency that vibrates in the direction of reactants and products respectively. The binding energy (E_b) between the superoxide radical (O_2^-) and solvated Li^+ ions is defined as the following: $E_b = E_{\text{total}} - EO_2^- - E_{Li}$, where E_{total} , EO_2^- , and E_{Li} are the total energy of the O_2^- -solvated Li^+ ion complexes, O_2^- , and solvated Li^+ ions, respectively.

3. Results

Typical sulfone (dimethyl sulfoxide, DMSO), ether (monoglyme, DME), and ester (ethylene carbonate, EC) solvent molecules are selected to interact with the superoxide radical (O_2^-). Figure 1a and Figure S1 show the combining abilities of O_2^- with free solvents (not coordinated to a Li^+ ion), Li^+ -solvents (the solvents which coordinate with a Li^+ ion), and 2(Li^+ -solvents) (the model of a 2:1 mixture of Li^+ : O_2^-). O_2^- exhibits weak binding to free solvents, with binding energies (E_b) ranging from -3.432 to 0.053 eV. In contrast, the Li^+ -solvents prefer to bind with O_2^- and exhibit an E_b of (-4.436) – (-1.036) eV. Based on the electrostatic interaction between Li^+ and O_2^- , O_2^- seems to be stabilized by Li^+ -solvents rather than free solvents. Then we construct a simplified model of a 2:1 mixture of $Li^+ : O_2^-$ (2(Li^+ -solvent)), in order to distinguish it from the 1:1 mixture (Li^+ -solvent), to investigate the effect of Li^+ ion concentration on stabilization for O_2^- . It is found that 2(Li^+ -solvent) has a larger E_b ((-5.187) – (-1.795) eV) when compared with Li^+ -solvent since two Li^+ ions simultaneously combine with O_2^- by electrostatic interaction. This indicates that the stability of O_2^- increases with the concentration of Li^+ ions. Therefore, high-concentration electrolytes will help to stabilize O_2^- and inhibit the subsequent oxidation of solvents by dissolved O_2^- .

In a highly concentrated electrolyte, differently from a dilute solvent where cations and anions are separated by solvents (solvent-separated ion pairs, SSIPs), Li^+ ions are often in the form of contact-ion pairs (CIPs) or aggregates (AGGs) with anions (Figure 1b). To understand the reactivity of free solvents and coordinated solvents to O_2^- and the role of salt concentration, the oxidation process of all three-state solvents is revealed by the transition state search (Figure 1c,d and Figures S2–S4). For the free DMSO (Figure S2), O_2^- captures a proton from the methyl ($-CH_3$) to form a hydroperoxyl radical ($\cdot OOH$). As for the free DME (Figure S3), the C of methylene ($-CH_2-$) is attacked by O_2^- and then DME is decomposed to a methoxy radical ($\cdot OCH_3-$) and $\cdot CH_3O(CH_2)_2O_2$. For the free EC (Figure S4), O_2^- attacks the C of $-CH_2-$, resulting in the O-C bond scission. For clarity, the oxidation mechanisms described above are consistent with the findings on DMSO by Aurbach et al. [22], on DME by Rice et al. [23], and on PC analogues by Li et al. [24].

The coordinated solvents are simplified into a Li^+ -solvent model just for investigating the effect of Li^+ ions on the reactivity of coordinated solvents. Notably, all the Li^+ -solvent species experience the similar nucleophilic substitution (SN_2) reactions with the same active sites (Figures S2–S4). Thus, coordination with Li^+ ions will not change the reaction pathways of solvents with O_2^- .

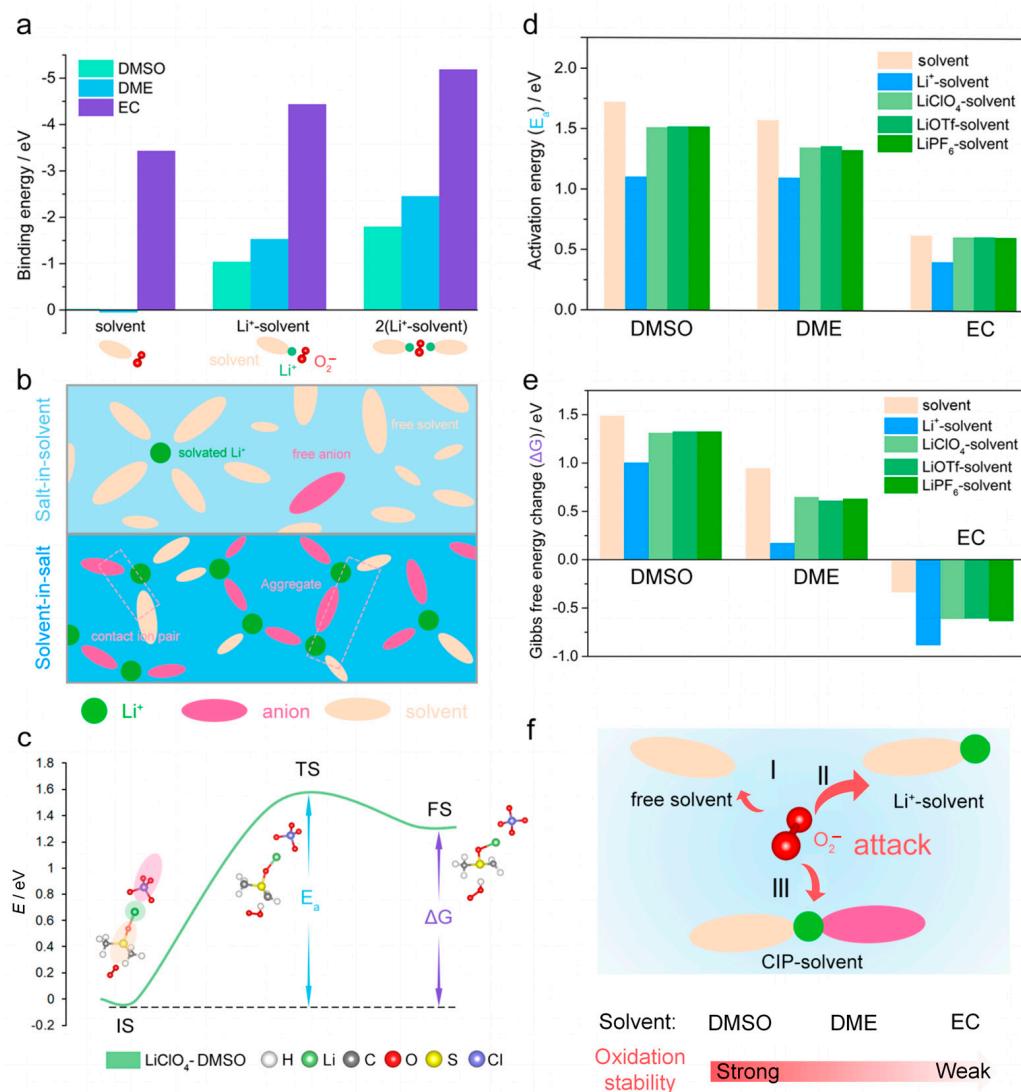


Figure 1. (a) The binding energy (E_b) of O_2^- with free solvents, Li^+ -solvents, and $2(\text{Li}^+ \text{-solvents})$. (b) Schematics of solution structures of a conventional dilute electrolyte and a concentrated electrolyte. (c) The oxidation decomposition process of Li salt-solvents, in which LiClO_4 -DMSO is taken as an example. (d,e) The E_a and ΔG of these solvents, respectively. Solvent can be DMSO, DME, or EC. Li salt can be LiOTf , LiClO_4 , or LiPF_6 . (f) The interaction strength and the corresponding oxidation stability of three local solvent-free solvents, Li^+ -solvents, and Li salt-solvents to O_2^- .

In the oxidation process, DMSO experiences a larger activation energy (E_a) (1.720 eV) than that of DME (1.573 eV) or EC (0.623 eV). In terms of thermodynamics, only the dissociation of EC is endothermic, and yet the dissociations of DMSO and DME are exothermic. DMSO has a larger Gibbs free energy change (ΔG) no matter the condition of the free solvent and Li^+ -solvent. These results show that DMSO is a better candidate as electrolyte in a $\text{Li}-\text{O}_2$ battery and also explain why ether electrolytes such as DME are more stable than ester electrolytes (EC) in a $\text{Li}-\text{O}_2$ battery. We further calculate the highest occupied molecular orbital (HOMO) energy levels of free solvents, Li^+ -solvent complexes, and Li salt-solvent complexes, where the solvents include DME, DMSO, and EC. As is shown in Figure S5, EC consistently exhibits the lowest HOMO energy level among the solvents, regardless of its form. Since molecules with higher HOMO energy levels are more prone to oxidation, these results indicate that EC is the most resistant to oxidation. In addition, compared with the E_a of free solvents, the Li^+ -solvents have lower E_a values, which indicates that the activity of free solvents is lower than Li^+ -solvents in an electrolyte while attaching

to O_2^- in a Li-O₂ battery. The decomposed solvent is the solvent with Li⁺ ions instead of free solvents. Except for the impact of the coordination with Li⁺ ion on the oxidation of solvents, salt concentration also plays an unignorable role. Therefore, the contact-ion pair between a Li⁺ ion and an anion is used to represent the highly concentrated state of the electrolyte, while the Li⁺ ion-coordinated solvents (CIP-solvents) are taken as the target of the oxidation reaction in a high-concentration electrolyte. The common anions such as CF₃SO₃⁻ (OTf⁻), ClO₄⁻, and PF₆⁻ are selected to participate in the oxidation process of solvents. As shown in Figures S2–S4, the oxidation pathways of CIP-solvents are similar to those of free solvents and Li⁺-solvents. However, the coordinated anions increase the Gibbs energy barriers for all the solvents compared with those of Li⁺-solvents. These raised barriers indicate that with the increased salt concentration, the anions in salts also play a role and significantly mitigate electrolyte decomposition and stabilize the electrolyte against O₂⁻, resulting in considerably enhanced cycling stability. This is explained by the fact that anions redistribute the charge of Li⁺ ions and weaken the effect of Li⁺ ions on reaction bonds compared with the reaction bonds in a Li⁺-solvent. Additionally, Figure 1e exhibits the ΔG of the oxidation of all the solvents in different forms by O₂⁻ and shows that just like the ΔG of free solvents and Li⁺-solvents, the oxidation reactions of CIP-DMSO and CIP-DME are exothermic while the oxidation process of CIP-EC is endothermic. In addition to slow kinetics, the introduction of anions also raises the ΔG level of Li⁺-solvents' oxidation, which makes the thermodynamics of the decomposition of the solvents harder. Figure 1f summarizes the interaction strength and corresponding oxidation stability of three local environments—free solvents, Li⁺-solvent complexes, and Li salt-solvent complexes—with O₂⁻. Among them, free solvents exhibit the weakest reactivity toward O₂⁻, followed by Li salt-solvent complexes, while Li⁺-solvent complexes show the strongest reactivity. In comparison with DME and EC, DMSO in all forms demonstrates the highest oxidation resistance, whereas EC-containing species display the lowest oxidation stability.

In the charging process, except for Li⁺ deposition ($Li^+ + e^- \rightarrow Li$), the electrolyte is easily reduced. In order to determine the cause of the high reduction stability of high-concentration electrolytes, the reduction process of all aforementioned three-state solvents is revealed by the calculations of electron affinity (EA) (Figure 2a). As shown in Figure 2b, Li⁺-solvents, due to the introduction of a positively charged Li⁺, exhibit a higher EA than that of free solvents and Li salt-solvents. This result shows that Li⁺ may preferentially compete for electrons, reducing the solvent's ability to acquire electrons. We then calculate their LUMO values (Figures S6 and S7), which further support this conclusion. However, the EA and LUMO energy levels only reflect the overall electron-accepting ability of the complex and do not specifically indicate which part of the complex acquires the electrons. Then we specially carry out the calculation of the transition state in the reduction process of solvent molecules. As shown in Figure 2c and Figures S8–S10, compared with the E_a of free solvents and Li salt-solvents, the Li⁺-solvents have positive E_a values, which indicates that the activity of free solvents or Li salt-solvents is higher than Li⁺-solvents in an electrolyte while attaching to e⁻ in Li-O₂ batteries. In addition, during the charging process, the E_a of most electron-accepting reactions of free solvents and Li salt-solvent complexes is 0 eV, indicating their occurrence spontaneously without requiring E_a. Furthermore, compared with the other two solvents, DME molecules seem to have greater reduction stability in whatever coordination structure they are in. Moreover, DMSO exhibits the lowest reductive stability compared with DME and EC, which is consistent with its instability against the Li metal anode. However, under high electrolyte concentrations, a substantial fraction of Li⁺-DMSO complexes is formed, and these complexes display a more positive E_a than free DMSO, indicating enhanced reductive stability. This result is also consistent with the findings of Zhang et al. [16]. The above results also indicate that the origin of high

electrolyte concentrations promoting the stability of solvent reduction is due to the presence of large amounts of Li^+ , which slows down the solvent reduction kinetics.

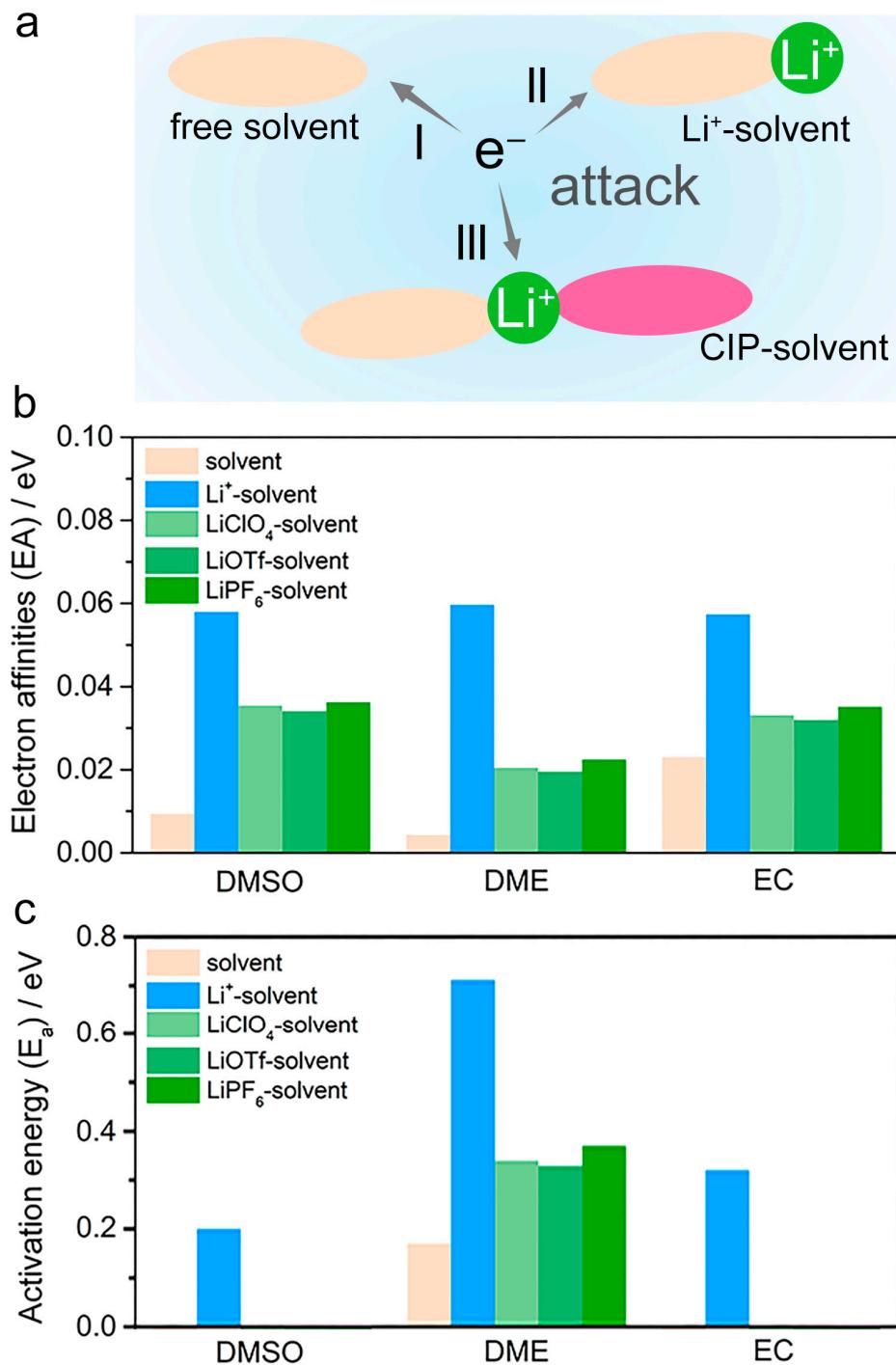


Figure 2. (a) Schematic illustration of three local solvents (free solvent, Li^+ -solvent, and Li^+ -salt-solvent) attacked by e^- . (b,c) are the EA and E_a of these solvents, respectively. Solvent can be DMSO, DME, or EC. Li salt can be LiOTf , LiClO_4 , or LiPF_6 .

Figure 3 shows the function principle of non-aqueous $\text{Li}-\text{O}_2$ batteries and the summary of how concentrated Li salts inhibit side reactions in electrolytes using DMSO, DME, and EC as solvents. During discharge, metal Li is oxidized to a soluble Li^+ cation at the anode/electrolyte interface and the electron is transferred to the outer circuit ($\text{Li} \leftrightarrow \text{Li}^+ + e^-$). At the cathode side, oxygen is reduced to an O_2^- species (superoxide radical). It further

reacts with Li^+ to form lithium peroxide (Li_2O_2) either by $2\text{Li}^+(\text{sol}) + 2\text{O}_2^-(\text{sol}) \rightleftharpoons \text{Li}_2\text{O}_2$ (non-electrochemical) or $2\text{Li}^+(\text{sol}) + \text{O}_2^-(\text{sol}) + \text{e}^- \rightleftharpoons \text{Li}_2\text{O}_2$ (electrochemical), based on the solution-mediated mechanism. In concentrated electrolytes, Li^+ -solvent complexes decompose most readily, while the presence of additional anions enhances electrolyte stability against oxidation and reduction. In this work, we focused exclusively on how high Li-salt concentrations suppress side reactions in the electrolytes. However, high-concentration electrolytes also have potential drawbacks for $\text{Li}-\text{O}_2$ batteries. They are typically associated with increased viscosity, which can lower ionic conductivity and thereby impair rate performance. To address these intrinsic limitations of concentrated electrolytes, some studies have diluted high-concentration electrolytes with an inert solvent (a diluent) that dissolves water but not the inorganic salt, producing local high-concentration electrolytes [25,26]. Such electrolytes, while reducing the salt concentration, can lower viscosity and improve wettability, which warrants careful consideration.

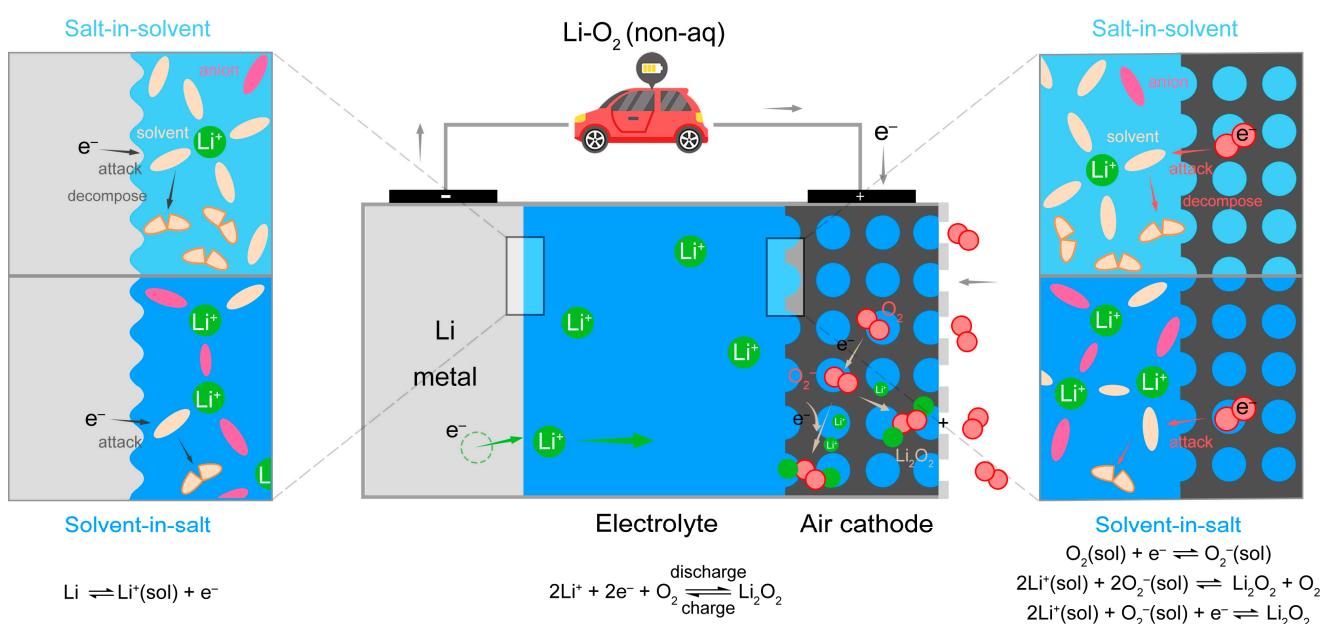


Figure 3. Schematic illustration of the operating principle of non-aqueous $\text{Li}-\text{O}_2$ batteries and a summary of how concentrated Li salts suppress side reactions in the electrolyte.

Although our work did not examine the solvation structure of (local) high-concentration electrolytes, prior studies [27–29] indicate that the key distinction between (local) high-concentration and dilute electrolytes is the formation of more CIP and AGG. Our study therefore provides only general insights into atomic-level interactions in high-concentration electrolytes, without addressing the full range of solvation structures. This limitation underscores the need for further investigation.

4. Conclusions

We addressed the origin of how concentrated electrolytes using DMSO, DME, EC as solvents improve the chemical durability and stability of $\text{Li}-\text{O}_2$ batteries. Li salts, especially anions, are responsible for the improvement of the oxidative/reductive stability of electrolytes at the cathode/anode, playing the role of scavenging or stabilizing agents in electrolytes. In concentrated electrolytes, Li^+ -solvent complexes are the easiest to decompose and the introduction of anions can enhance the stability of electrolytes against oxidation/reduction. We believe that our findings offer insights into the role of electrolyte properties in the chemistry of $\text{Li}-\text{O}_2$ batteries.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries11100349/s1>: Figure S1: The optimized geometrical structures of O_2^- with free solvents, Li^+ -solvents, and 2(Li^+ -solvents); Figure S2: The decomposition process of free DMSO, Li^+ -DMSO, and DMSO-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by O_2^- ; Figure S3: The decomposition process of free DME, Li^+ -DME, and DME-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by O_2^- ; Figure S4: The decomposition process of free EC, Li^+ -EC, and EC-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by O_2^- ; Figure S5: HOMO energy levels of free solvents, Li^+ -solvents, and Li salt-solvents, where the solvents include DME, DMSO, and EC; Figure S6: LUMO energy levels of free solvents, Li^+ -solvents, and Li salt-solvents, where the solvents include DME, DMSO, and EC; Figure S7: The visual LUMOs of free solvents, Li^+ -solvents, and Li salt-solvents, where the solvents include DME, DMSO, and EC; Figure S8: The decomposition process of free DMSO, Li^+ -DMSO, and DMSO-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by e^- ; Figure S9: The decomposition process of free DME, Li^+ -DME, and DME-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by e^- ; Figure S10: The decomposition process of free EC, Li^+ -EC, and EC-Li salt (including $LiClO_4$, $LiOTf$, and $LiPF_6$) by e^- .

Author Contributions: W.F. and X.L. contributed equally to this work. W.F. and X.L. carried out the calculations and wrote the manuscript. The other authors (G.L., K.Y., P.W., M.L., C.Z., L.M. (Lei Miao), J.W., C.L., J.H., H.J. and L.M. (Licheng Miao)) discussed the data and commented on the manuscript. The project was supervised by H.J. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original raw data presented in this study and used to support its conclusions can be made available by the authors upon reasonable request to the corresponding authors.

Conflicts of Interest: Authors Wei Fan, Xu Liu, Guangqian Li, Ke Yu, Peng Wang, Min Lei, Ce Zhen, Lei Miao, Jialiang Wang, Chun Li, Junliang Hou, Hongtao Ji are employees of SinoRail Data Technology Co., Ltd. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The authors declare that this study received funding from the SinoRail Data Technology Co., Ltd. The funder was not involved in the study design, collection, analysis, interpretation of data, the writing of this article or the decision to submit it for publication.

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