Rechargeable Batteries

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The Origin of the Reduced Reductive Stability of Ion–Solvent Complexes on Alkali and Alkaline Earth Metal Anodes

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Abstract: The intrinsic instability of organic electrolytes seriously impedes practical applications of high-capacity metal (Li, Na) anodes. Ion-solvent complexes can even promote the decomposition of electrolytes on metal anodes. Herein, first-principles calculations were performed to investigate the origin of the reduced reductive stability of ionsolvent complexes. Both ester and ether electrolyte solvents are selected to interact with Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . The LUMO energy levels of ion-ester complexes exhibit a linear relationship with the binding energy, regulated by the ratio of carbon atomic orbital in the LUMO, while LUMOs of ionether complexes are composed by the metal atomic orbitals. This work shows why ion-solvent complexes can reduce the reductive stability of electrolytes, reveals different mechanisms for ester and ether electrolytes, and provides a theoretical understanding of the electrolyte-anode interfacial reactions and guidance to electrolyte and metal anode design.

Kechargeable batteries have been playing an increasingly important role in our daily life. They have been widely applied to electric vehicles, portable devices, large-scale smart grids, and so on.^[1-3] In response to the rising demand of building better batteries, lithium-ion batteries (LIBs) were firstly commercialized by the Sony Corporation in 1991.^[2,4,5] However, the practical energy density of conventional LIBs has been approaching its theoretical limits. Consequently, new battery systems with high energy density are strongly considered.

A high-capacity electrode is necessary to build a highenergy-density rechargeable battery. In contrast to conventional graphite anodes, various alkali and alkaline earth metal anodes have been strongly considered as promising anode candidates.^[3,6] For instance, the lithium metal anode possesses an ultrahigh theoretical capacity (3860 mAh g^{-1}) and the lowest negative electrochemical potential (-3.040 V vs. the standard hydrogen electrode). Despite a smaller theoretical capacity (1160 mAh g^{-1}), sodium metal anodes can be applied to large-scale energy storage owing to the much lower price of sodium comparing with lithium metal. Besides, one mole of multivalent cations can provide double or even triple amounts of electrons than the Li or Na ions. Therefore, both

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magnesium (Mg) and calcium (Ca) metal anodes are also promising anode candidates. $\ensuremath{^{[7]}}$

Although having great advantages in theoretical energy density, both alkali and alkaline earth metal batteries face many challenging issues. Specifically, the intrinsic instability of conventional organic electrolytes against metal anodes seriously impedes their practical applications.^[8] Most organic electrolyte solvents can be reduced on metal anodes due to the high reactivity of alkali and alkaline earth metals and their low electrode potential, inducing electrolyte depletion, the corrosion of anodes, flammable gasses, and severe safety hazards.^[9–11] More seriously, both lithium and sodium prefer a dendritic growth during plating process.^[4,12] The lithium/ sodium dendrites not only penetrate the separator and cause a short circuit but also aggravate in electrolyte decomposition reactions.

Tremendous strategies have been proposed to address the challenging issues of electrolyte depletion and build a stable electrolyte-anode interface during the past decades.^[4,13] Density functional theory calculations assist screening stable electrolyte solvents with low reduction potentials (below -0.5 V vs. Li/Li⁺).^[14] Various electrolyte additives, such as fluoroethylene carbonate (FEC),^[11,15] lithium nitrate (LiNO₃),^[16] and InF₃,^[17] have been used to induce a stable solid electrolyte interphase (SEI) to stabilize anodes and electrolytes. Highly concentrated electrolytes have been demonstrated to achieve a long lifespan and high Coulombic efficiency in Li and Na metal batteries, indicating the inhibition of side reactions between electrolytes and metal anodes.^[18] Besides, the artificial protective layer is particularly designed to avoid the direct interactions between electrolytes and anodes to impede the electrolyte decomposition.^[19]

Although the electrolyte stability against metal anodes has been improved and a long-lifespan battery has been built recently, the origin of the instability of electrolyte towards metal anodes is far from clear. Recently, the concept of ion– solvent complexes has been proposed to explain the electrolyte decompositions on sodium metal anodes as the ion– solvent complex with a much lower energy level of LUMO (the lowest unoccupied molecular orbital) than that of pure solvents can promote the electrolyte gassing.^[10] However, the applicability of this principle to other alkali metal anodes and even alkaline earth metal anodes should be further explored. More importantly, the origin of the reduced reductive stability of ion–solvent complexes should be carefully probed.

Herein, the stability of typical ether (1,3-dioxolane [DOL] and 1,2-dimethoxyethane [DME]) and ester (ethylene carbonate [EC], diethyl carbonate [DEC], propylene carbonate [PC], and fluoroethylene carbonate [FEC]) electrolyte solvents towards Li, Na, K, Mg, and Ca metal anodes was

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comprehensively investigated through first-principles calculations. All ion-solvent complexes exhibit a lower energy level of the LUMO compared with pure solvents. The ionester complexes present a good linear relationship between its LUMO energy level change and the binding energy as well as the ratio of carbon atomic orbital contribution in the LUMO. The ion-ether complexes exhibit significant LUMO energy level changes as the LUMOs are mainly composed of metal atomic orbitals. This work demonstrates the wide applicability of ion-solvent complex chemistry, uncovers the differences between ether and ester electrolyte systems, unveils the origin of the reduced reductive stability of the complexes, and affords fruitful mechanistic insights into the rational design of stable electrolytes and safe alkali and alkaline earth metal batteries.

Typical ester (EC, DEC, PC, and FEC) and ether (DOL and DME) electrolyte solvents (Figure 1) are selected to interact with Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , respectively. The metal cations prefer to bind with the carbonyl oxygen (O1 in Figure 1 a–d) rather than cyclic oxygen (O2 and O3 in



Figure 1. The optimized geometrical structures of a) EC, b) PC, c) DEC, d) FEC, e) DOL, and f) DME molecules. H white, C gray, O red, F light blue. Atomic numbering is provided.

Figure 1 a–d) for ester solvents. The optimized geometrical structures of ion–ester complexes and corresponding visual LUMOs are presented in Figure 2 and the Supporting Information, Figure S1. The metal cations bind with one cyclic oxygen atom in DOL or two cyclic oxygen atoms in DME simultaneously. The optimized geometrical structures of ion–ether complexes and corresponding visual LUMOs are shown in Figure 3.

The binding energy between ions and solvents and the LUMO energy level changes (Δ LUMO) before and after binding are summarized in Figure 4a and the Supporting Information, Table S1. Generally, all complexes exhibit much lower LUMO energy levels comparing with pure solvents, indicating solvents decompose more easily on metal anodes once they are complexed with metal cations in electrolytes, which agrees with bond length analyses that the C–O bond length of carbonyl group in ester and -C-O-C- group in ether increases after binding with a cation (Supporting Information, Table S2). This phenomenon is more significant in the ion–ether complexes that a larger Δ LUMO ranging from -3.25 to -9.46 eV was observed, comparing with that of



Figure 2. The visual LUMOs and corresponding optimized geometrical structures of ion-solvent complexes. a) Li⁺-EC. b) Na⁺-EC. c) K⁺-EC. d) Mg²⁺-EC. e) Ca²⁺-EC. f) Li⁺-DEC. g) Na⁺-DEC. h) K⁺-DEC. i) Mg²⁺-DEC. j) Ca²⁺-DEC. H white, Li purple, C gray, O red, Na green, Mg blue, K yellow, Ca orange. The red and green regions of LUMOs represent the positive and negative parts of orbitals, respectively.



Figure 3. The visual LUMOs and corresponding optimized geometrical structures of ion-solvent complexes. a) Li⁺-DOL. b) Na⁺-DOL. c) K⁺-DOL. d) Mg²⁺-DOL. e) Ca²⁺-DOL. f) Li⁺-DME. g) Na⁺-DME. h) K⁺-DME. i) Mg²⁺-DME. j) Ca²⁺-DME. H white, Li purple, C gray, O red, Na green, Mg blue, K yellow, Ca orange. The red and green regions of LUMOs represent the positive and negative parts of orbitals, respectively.

ion–ester complexes (-0.31 to -3.80 eV). Besides, the Δ LUMO of multivalent-cation–ester complex is larger than that of monovalent-cation–ester complex. However, this regular is not detectable in the ion–ether complexes, as Na⁺–ether complexes exhibit a large Δ LUMO while Ca²⁺– DOL complex exhibits a small Δ LUMO, which is induced by the complicated LUMO components of ion–ether complexes discussed in the following section.

To further probe the differences between ester and ether solvents, the Δ LUMO are plotted against the binding energy (Figure 4b). The Δ LUMO of ester solvents exhibits a good linear relationship with the binding energy. The stronger



Figure 4. a) Summary of LUMO energy level changes of the ion– solvent complexes comparing with pure solvents. b) The correlation between the LUMO energy level change and binding energy. c) The correlation between the LUMO energy level change and the ratio of C atomic orbital contribution in LUMOs.

interaction between a solvent molecule and a cation, the worse instability of as-obtained complexes. This finding affords a new guidance to electrolyte screening. However, this trend is not applicable to ether solvents. Consequently, although cations can reduce the LUMO level of complexes, the mechanisms in ester and ether solvents are different. Intuitively, cations interact with the carbonyl oxygen of the ester but the cyclic oxygen of the ether. The electronic structures of these two oxygen groups are totally different, resulting in different LUMOs of ester- or ether-based complexes. Specifically, the LUMOs of ion-ester complexes are mainly contributed by the atomic orbitals of carbon and oxygen in the carbonyl group (Figure 2; Supporting Information, Figure S1). While the metal atomic orbitals almost compose the LUMOs of ion-ether complexes (Figure 3). This can explain why only a linear relationship between Δ LUMO and binding energy is observed in the ion-ester complexes. Besides, the binding energy has a positive correlation with the changes of a specific C-O bond length rather than the metal-O bond length (Supporting Information, Figure S2, Tables S2 and S3). The C-O bond length increases after binding with a cation, indicating the weakening of C-O bonds and reduced stability of the ion-solvent complexes (Supporting Information, Figure S2). This agrees well with the LUMOs analyses that ion-solvent complexes reduce reduction stability of electrolytes. Therefore, the excellent coherence among the Δ LUMO, binding energy, and changes of C–O bond length in ion-ester complexes is closely related to the carbonyl group.

As LUMO energy level is determined by its component atomic orbitals, a quantitative relationship between LUMO energy level and the ratio of a specific atomic orbital in LUMO is thus expected. The LUMOs of ion–ester complexes consist of the 2p orbitals of carbon and oxygen atoms in the carbonyl group. Herein, the ratio of carbon 2p orbital in LUMOs (C% in LUMOs) is selected as the descriptor. An excellent linear relationship between the Δ LUMO and C% in LUMO was found (Figure 4c). The C% in LUMO of pure EC, DEC, PC, and FEC are 71.93%, 72.77%, 72.71%, and 71.59%, respectively (Supporting Information, Figure S3 and Table S4). Once complexed with a cation, the electrons in carbonyl group are drawn to the metal atom due to the strong electron-withdrawing effects of cations. The contribution of carbon 2p orbital in LUMOs consequently increases, which further reduces the LUMO energy level. Consequently, the stronger electron-withdrawing effect (Mg²⁺ > Ca²⁺ > Li⁺ > Na⁺ > K⁺), the higher ration of carbon atomic orbital in LUMOs, the larger binding energy, and the huger change of LUMO energy level.

Comparing FEC and PC with EC, the electron-withdrawing F-functional group in FEC reasonably reduces the LUMO energy level while the electron-releasing methyl group in PC increases the LUMO energy level (Figure 4c; Supporting Information, Figure S4). The Δ LUMO is also strongly associated with the strength of electron-withdrawing/ releasing effects. Owing to different interaction directions with carbonyl groups, the electron-withdrawing F-functional groups and metal cations result in the decrease and increase of C% in LUMOs, respectively.

However, the situations in ion-ether complexes are very different and more complicated than that in ion-ester complexes. The changes of C-O bond length of DOL after binding with a cation are more significant than that of EC and DEC and the binding energies between a cation and DME are larger than that between a cation and EC/DEC (Supporting Information, Figure S2a). These huge differences result in a huge change of LUMO of ion-ether complexes. The LUMOs of DOL and DME are composed of the carbon and oxygen atomic orbitals (Supporting Information, Figure S3e,f, Table S5). However, the LUMOs of ion-ether complexes are contributed by the metal atomic orbitals (Figure 3; Supporting Information, Table S6). In other words, the binding with a cation completely changes the LUMOs of solvents. The atomic orbitals of Li, Na, K, Mg, and Ca are very different from each other, resulting in very different LUMOs of various ion-DOL/DME complexes. Therefore, there is no general principle when correlating the Δ LUMO with binding energy. Although the LUMOs of ion-ether complexes are composed of metal atomic orbitals, the reductive stability of the solvents is reduced. Firstly, the C-O bond is weakened as its length increases, indicating the decomposition reactions of such complexes on metal anodes become easier. Secondly, the LUMOs of ion-ether complexes partially consist of d orbitals of metal atoms, which can accept lone pair electrons from oxygen and forms coordinate bonds and assist the breaking of C-O bond in DOL and DME. Last but not the least, experimental in situ optical observations have validated that ion-ether complexes can promote the gas evolution from electrolyte on lithium and sodium metal anodes.^[10]

Inspired by the interesting and significant results from LUMO, we tried to find a similar principle for the HOMO (the highest-occupied molecular orbital), as the oxidative stability enhancement of Li⁺–glyme complexes were already validated.^[20] All ion–solvent complexes exhibit a lower HOMO comparing with corresponding pure solvent, demon-

strating the enhanced stability of solvents once they are complexed with ions (Supporting Information, Figure S5). In contrast to the LUMO, the change of HOMO energy level exhibit a positive correlation with binding energy in both ester and ether electrolytes (Supporting Information, Figure S6). Although HOMOs are all composed by the atomic orbital of an oxygen in solvents and no more descriptor describing the change of HOMO level were discovered currently, the change of HOMO energy level is also related to the electronwithdrawing strength of different cations (Supporting Information, Table S1).

Although different mechanisms in ion-ester and ionether complexes, the formation of such complexes can both reduce the reduction stability of electrolyte on metal anodes. The cations induce a strong electron-withdrawing effect and thus regulate the ratio of carbon atomic orbitals in LUMOs of ion-ester complexes to reduce the LUMO level, thus promoting the decomposition of ester electrolytes. The Δ LUMO reasonably presents a good linear relationship with the binding energy and the change of C-O bond length. Simultaneously, the cations can completely change the LUMO of ion-ether complexes, resulting in a low-energylevel LUMO composed by metal atomic orbitals. To validate the theoretical predictions to some degree, linear-scan voltammetry (LSV) tests were conducted to determine the electrochemical window and DOL is taken as an example. Two kinds of concentration DOL electrolytes, 1.0 and 0.1M LiTFSI [lithium bis(trifluoromethanesulfonyl)imide], are prepared. The 0.1M electrolytes with less ion-solvent complexes formed exhibit lower redox potential than that of 1.0 м electrolytes with more ion-solvent complexes formed (Supporting Information, Figure S7), indicating the better stability of 0.1M electrolytes against metal anodes. Both LSV and LUMO results also agree with previous studies that solvent with Li/Na salts produce gas more violently than pure solvent on Li/Na metal anodes.[10]

In conclusion, the origin of the reduced reductive stability of ion-solvent complexes on alkali and alkaline earth metal anodes are comprehensively investigated through first-principles calculations. The mechanisms on reduced reductive stability are proposed for both ester and ether electrolytes. The complexed cations can regulate the contribution ratio of carbon 2p orbitals in LUMOs of ion-ester complexes to reduce the LUMOs level. The Δ LUMOs consequently exhibit a good positive correlation with the changes of C–O bond length and binding energy. The ion-ether complexes exhibit a larger binding energy or a more significant change of C-O bond length comparing with ion-ester complexes, resulting in completely different LUMOs that are composed of metal atomic orbitals. This work uncovers the reason why ion-solvent complexes can promote electrolyte decomposition on metal anodes and explains well the differences between ester and ether electrolytes, providing fruitful mechanistic insights into electrolyte-anode interfacial reactions and mechanistic strategies for exploring stable electrolytes and metal anodes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anodes · electrolyte additives · electrolyte stability · ion-solvent complexes · rechargeable batteries

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