

Atomic Insights into the Fundamental Interactions in Lithium Battery Electrolytes

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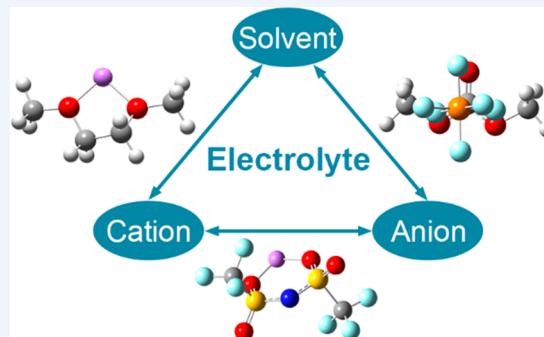
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CONSPECTUS: Building high-energy-density batteries is urgently demanded in contemporary society because of the continuous increase in global energy consumption and the quick upgrade of electronic devices, which promotes the use of high-capacity lithium metal anodes and high-voltage cathodes. Achieving a stable interface between electrolytes and highly reactive electrodes is a prerequisite to constructing a safe and powerful battery, in which electrolyte regulation plays a decisive role and largely determines the long-term and rate performances. The bulk and interfacial properties of electrolytes are directly determined by the fundamental interactions and the as-derived microstructures in electrolytes. Different from experimental trial-and-error approaches, the rational bottom-up design of electrolytes based on a comprehensive and deep understanding of the fundamental interactions between electrolyte compositions and the structure–function relationship is highly expected to accelerate breaking through the bottleneck in current technology and realizing next-generation Li batteries.

In this Account, we afford an overview of our recent attempts toward rational electrolyte design for safe Li batteries based on a comprehensive understanding of the cation–solvent, cation–anion, and anion–solvent interactions in electrolytes. The formation of cation–solvent complexes decreases the reductive stability but increases the oxidative stability of solvent molecules according to frontier molecular orbital theory, whereas the introduction of anions into the Li^+ solvation shell has the opposite function in regulating solvent stability compared with cations. The competitive coordination of anions and solvent molecules with cations directly determines the salt solubility in electrolytes and the formation of ion pairs and aggregates, which widely exist in high-concentration electrolytes and stabilize Li metal anodes. An easy and effective route to dissolve lithium nitrate in ester electrolytes is accordingly proposed. Although anions are hardly solvated in routine solvents, solvents with a high acceptor number or an exposed positive charge site are highly expected to enhance the anion–solvent interaction. The solvation of anions will have a strong influence on electrolytes, including regulating the electrolyte solvation structure and stability, increasing the cation transference number, and promoting salt dissociation. The emerging Li bond theory and big-data approaches, combined with first-principles calculations and experimental characterizations, are also expected to promote rational electrolyte design with much reduced time and expense.

Collectively, with a comprehensive and deep understanding of the fundamental interactions in electrolytes and the structure–function relationship, bottom-up engineering of Li battery electrolytes is expected to be achieved, accelerating the applications of safe high-energy-density Li batteries. The general principles demonstrated in Li batteries are also supposed to be applicable to other battery systems and even universal electrochemistry in solutions, including fuel cells and various electrocatalyses.



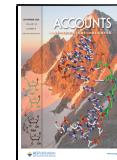
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- Chen, X.; Zhang, X.-Q.; Li, H.-R.; Zhang, Q. Cation–Solvent, Cation–Anion, and Solvent–Solvent Interactions with Electrolyte Solvation in Lithium Batteries. *Batteries Supercaps* **2019**, *2*, 128–131.⁴ *Electrolyte solvation plays an important role in regulating the fundamental cation–solvent, cation–anion, and solvent–solvent interactions in electrolytes. Generally, a larger dielectric constant leads to a weaker interaction.*

1. INTRODUCTION

Batteries play an increasingly important role in contemporary society, powering portable electronics, mobile phones, and long-distance electric vehicles.^{1–6} Building safe high-energy-density batteries is the ultimate goal of battery research, which promotes the use of high-capacity lithium metal anodes and high-voltage cathodes.^{7–9} The high chemical and electrochemical activity of these electrodes puts forward ultrahigh requirements for electrolyte designs. Conventional organic electrolytes are reduced or oxidized to form a solid–electrolyte interphase (SEI) on graphite/Li metal anodes or a cathode–electrolyte interphase (CEI) on cathodes, respectively.¹⁰ The physical and chemical properties of the SEI and CEI are strongly dependent on the electrolyte.^{11–14}

Many strategies have been proposed to achieve high-performance electrolytes and build stable electrolyte–electrode interfaces during the past years, including various solvents, Li salts, and additives.^{11,12,15–21} The electrolyte component interactions largely determine the Li⁺ solvation structure, Li⁺ diffusion properties, electrolyte stability, and electrolyte–electrode interfacial properties. Especially, high-concentration electrolytes (HCEs) and localized high-concentration electrolytes (LHCEs), in which anions are significantly introduced into the Li⁺ solvation shell, were proposed to render a stable interface against Li metal anodes and realize high-performance Li metal batteries.^{22–24} In contrast to routine electrolytes, in which Li⁺ ions are mostly solvated by solvent molecules, anions in the Li⁺ solvation shell can induce a unique SEI that can stabilize Li metal anodes and induce uniform Li deposition. Therefore, understanding the fundamental interactions in electrolytes is very essential to achieve the rational design of high-performance electrolytes for rechargeable Li batteries.

Generally, the fundamental interactions in electrolytes can be classified into cation–solvent, cation–anion, anion–solvent,

and solvent–solvent interactions.⁴ The electrolyte components also influence each other. For instance, the coordination with solvent molecules and anions determines the Li⁺ solvation structure, which further regulates the Li⁺ migration, desolvation, and nucleation. The interaction with Li⁺ ions also changes the redox stability of solvent molecules and anions to further regulate the SEI and CEI formation. Consequently, the fundamental interactions in electrolytes directly determine the bulk and interfacial electrolyte properties and hence the battery performance. Understanding the complicated interactions and their correlations with electrolyte properties is of great significance to probe the working mechanism and achieve the rational design of Li battery electrolytes beyond conventional trial-and-error approaches.

In this Account, we afford an overview of the fundamental interactions in electrolytes and correlate the interactions with electrolyte properties. These interactions are divided into three classes: (1) cation–solvent interactions to regulate the redox stability of solvent molecules; (2) cation–anion interactions to control the salt solubility and the formation of ion pairs and aggregates; and (3) anion–solvent interactions to regulate the solvation behaviors of anions and radicals. After that, Li bond theory and emerging high-throughput screening/machine-learning methods are introduced into electrolyte research based on a comprehensive understanding of the atomic interactions in electrolytes.

2. OVERALL REVIEW OF FUNDAMENTAL INTERACTIONS IN ELECTROLYTES

The experimental and theoretical examination of solvents or solutions is among the most difficult tasks in physical chemistry, as the interaction between species in solvents or solutions are much stronger than that in gases, which can be treated well by the kinetic theory, yet much weaker than that in solids, which can be described well by the laws of solid-state physics.²⁵ Solutions can hardly be described well by a simple formula quantitatively because of the short-range-ordered but long-range-disordered structure, which is even complicated case by case.

In Li battery electrolytes, the cations, Li⁺, are coordinated by solvent molecules or anions, whereas anions are hardly solvated because protic solvents are less used and both the large radius and the delocalized charge of anions also greatly weaken their interaction with the solvent. The local ordered solvation structure is mainly regulated by the strong cation–solvent and cation–anion interactions, while isolated solvation species remain disordered at long range because of the weak interactions between coordinated/free solvent molecules/anions. These interactions belong to intermolecular forces, including ion–ion, ion–dipole, and dipole–dipole forces. In classical physical models, the potential energies of these three forces are given by

$$U_{\text{ion-ion}} = -\frac{1}{4\pi\epsilon} \frac{z_1 z_2 e^2}{r} \quad (1)$$

$$U_{\text{ion-dipole}} = -\frac{1}{4\pi\epsilon} \frac{ze\mu \cos\theta}{r^2} \quad (2)$$

$$U_{\text{dipole-dipole}} = -\frac{1}{(4\pi\epsilon)^2} \frac{2\mu_1^2 \mu_2^2}{3k_B Tr^6} \quad (3)$$

where ϵ is the dielectric constant, ze is the charge of the ion, μ is the dipole moment of the dipole, r is the distance between ions or the centers of dipoles, θ is the dipole angle relative to the line joining the ion and the center of the dipole, k_B is the Boltzmann constant, and T is the absolute temperature.^{4,25}

Typically and ideally, the ion–dipole, ion–ion, and dipole–dipole forces play a major role in regulating the cation–solvent, cation–anion, anion–solvent, solvent–solvent interactions, but the practical condition is much more complicated than the physical models. First, ions or molecules with a permanent dipole moment can induce a dipole moment in a neighboring ion or molecule, which further induces a dipole–induced dipole force. Second, even for a molecule without a permanent dipole moment, the continuous electronic movement can result in a small dipole moment, which can polarize the electron system of the neighboring atoms and induce an instantaneous dipole–induced dipole force. Third, and more importantly, except for physical electrostatic interactions, additional bonding interactions between electron-pair donors (EPDs) and electron-pair acceptors (EPAs) are often formed in electrolytes, which can be explained by the Lewis acid–base interactions. For example, Li^+ acts as an EPA to accept an electron pair from a solvent molecule or anion, which acts as an EPD. The electron transfer and even the overlap of orbitals of the EPA and EPD make the Lewis acid–base interaction very complicated and hard to describe by a simple formula.

Although the fundamental interactions in electrolytes can hardly be described by the eqs 1–3 exactly, the role of the dielectric constant of the solution is highlighted. The interactions between species in solution can be greatly weakened as a result of the solvation effect, which is directly regulated by the dielectric constant. For a specific component interaction in different solvents, a larger dielectric constant of the solvent leads to a weaker binding energy of the interaction. As a result, it is possible to change the binding energy trend and hence regulate the solvation structures, as different fundamental forces have different sensitivities to the dielectric constant.

First-principles calculations, including the Hartree–Fock method and density functional theory (DFT), are powerful for determining the interaction strength between two species and have achieved great success in battery research.^{8,26–28} Both the van der Waals forces and solvation effects can also be described well. Therefore, the recent development of theoretical simulations enables a quantitative description of fundamental interactions in Li battery electrolytes to understand the solvation structures and correlate them with the electrolyte properties and battery performance (Figure 1). Although solvent–solvent interactions play an important role in determining the bulk properties of the solvent, such as the melting and boiling points, dielectric constant, and viscosity, they are often much weaker than the other interactions and mainly contributed by van der Waals forces. Therefore, only the cation–solvent, cation–anion, and anion–solvent interactions are discussed in detail in the following.

3. CATION–SOLVENT INTERACTIONS

Cations are always solvated by solvent molecules in electrolytes. The cation–solvent interactions play a major role in regulating solvent stability and cation (de)solvation and transport behaviors. Frontier molecular theory is applied to explain the redox stability of solvents in the following. The difference between the lowest unoccupied molecular orbital

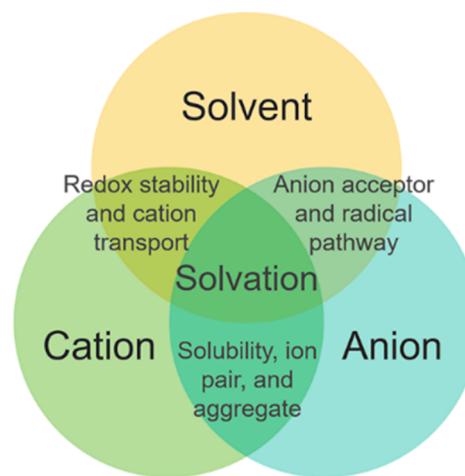


Figure 1. Schematic of fundamental interactions in electrolytes and related structure–function relationship.

(LUMO) and highest occupied molecular orbital (HOMO) energy levels and the redox potential should be clarified. The former are derived from approximate electronic structure theory when investigating electronic properties of isolated molecules, and they do not indicate species participating in redox reactions. The latter is directly related to the Gibbs free energy difference between the reactants and products in redox reactions. The HOMO and LUMO energy levels and the redox potential reveal the electrolyte stability from two different viewpoints and have no direct relationship.

3.1. Reductive Stability

The coordinated cations attract electrons from solvent molecules and reduce the LUMO energy level of the solvent molecules.¹ Consequently, the solvent molecules in the cation solvation shell much more easily obtain electrons from the anode to be reduced and cause electrolyte gassing, compared with free solvent molecules in the electrolyte. This principle is applicable to many cation–solvent systems, including Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} cations and ester and ether solvents (Figure 2a).² Generally, multivalent cations (Mg^{2+} and Ca^{2+}) induce a larger binding energy and a more obvious decrease in the LUMO energy level compared with monovalent cations (Li^+ , Na^+ , and K^+). Besides, the LUMO energy level decrease has only a linear relationship with the binding energy in ester solvents. Specifically, the LUMO is composed of the carbon and oxygen 2p orbitals in the carbonyl functional group in cation–ester complexes, which is same as that of ester solvents. The coordinated cations can regulate the ratio of the carbon 2p orbital in LUMOs, and this ratio is strongly related to the binding energy, resulting in a linear relationship between the binding energy and LUMO energy level decrease. However, cations completely change the LUMO composition in cation–ether complexes. There is no clear relationship between the binding energy and the LUMO energy level decrease in the ether system.

Beyond thermodynamic analyses, the kinetic behavior of cation–solvent complexes has been investigated through nudged elastic band (NEB) and ab initio molecular dynamics (AIMD) calculations.³ Taking 1,3-dioxolane (DOL) as an example, coordination with Li^+ can decrease the barrier for the DOL ring-opening reaction from 3.00 to 0.56 eV, which is also verified by AIMD simulations (Figure 2b). The breaking of a C–O bond in a DOL molecule is always accompanied by the

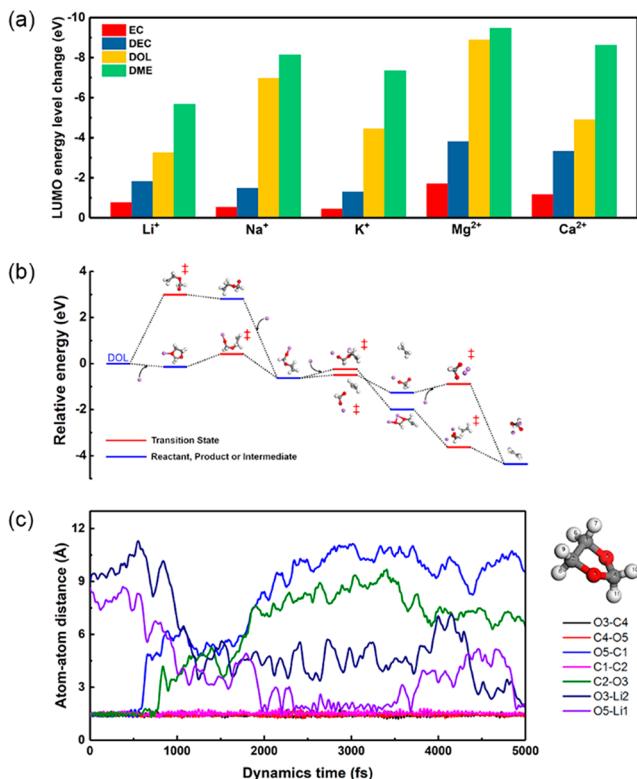


Figure 2. Regulation of solvent reductive stability by coordinated cations. (a) Summary of LUMO energy level changes after the formation of cation–solvent complexes. (b) Decomposition mechanism of DOL on Li metal anodes. (c) Time evolution of the bond lengths from MD simulations of DOL and Li metal. The H, Li, C, and O atoms are shown in white, purple, gray, and red, respectively. Reproduced with permission from (a) ref 2 and (b, c) ref 3. Copyright 2018 Wiley-VCH and 2017 Elsevier, respectively.

formation of a Li–O bond, and therefore, Li⁺–DOL complexes promote DOL decomposition (Figure 2c).

The theoretical results are also validated by experimental investigations. During *in situ* optical microscopy observations, electrolytes with Li/Na salts, in which cation–solvent complexes are formed, react with Li/Na metal anodes much more violently and more gases are produced from the decomposition of electrolytes compared with pure solvents.¹ Besides, the reduction potential of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) DOL electrolyte (0.21 V) is higher than that of 0.1 M LiTFSI DOL electrolyte (0.12 V), as more cation–solvent complexes are formed in the former than in the latter.²

3.2. Oxidative Stability

Similar to the lowering of the LUMO energy level, the coordination with cations also decreases the HOMO energy level of solvent molecules (Figure 3).²⁹ Therefore, it is harder for solvent molecules in Li⁺ solvation shells to lose electrons and be oxidized compared with free solvent molecules. For instance, in the glyme electrolytes with LiTFSI salts, Li⁺ can coordinate with the oxygen of glyme solvent molecules or TFSI⁻ anions (Figure 3a,b). The Li⁺ decreases the HOMO energy level from -11.45 to -15.51 eV and from -11.46 to -14.90 eV for triglyme (G3) and tetraglyme (G4) solvents, respectively. Although further coordination with a TFSI⁻ anion can increase the HOMO energy levels, they are lower than those of isolated G3 and G4 molecules (Figure 3c). As

expected, the formation of Li⁺–glyme complexes can improve the oxidative stability of electrolytes, which is further validated by linear sweep voltammetry tests (Figure 3d,e). With increasing Li salt concentration, more Li⁺–glyme complexes and less free glyme molecules existed in the electrolyte, resulting in an increased oxidation potential.

The principle discussed above is also applicable to other glyme solvents (monoglyme and diglyme) and cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺).³⁰ The mutual attraction between the cation and glyme is mainly contributed by electrostatic and induction interactions. The latter are especially important in the multivalent cation–glyme complexes. Besides, multivalent cations generally induce a stronger interaction and have a more obvious influence on the HOMO energy level of solvent molecules than monovalent cations.

3.3. Solvent Regulation

Solvents have different (electro)chemical stabilities and affinities toward Li⁺ ions in electrolytes, rendering solvent regulation strategies for electrolyte design. For instance, fluoroethylene carbonate (FEC) has a lower LUMO energy level and more easily obtains electrons from the anode than ethylene carbonate (EC) and diethyl carbonate (DEC) because of the strong electron-withdrawing effect of the F functional group (Figure 4a–f).³¹ As a result, FEC preferentially reacts with Li metal anodes and induces a LiF-rich SEI (Figure 4g–j), which is widely reported to stabilize the electrolyte–anode interface effectively and induce uniform Li deposition. Besides, FEC preferentially coordinates with Li⁺ ions compared with other ester and ether solvents, such as dimethyl carbonate (DMC) and 1,2-dimethoxyethane (DME). Specifically, 39% of FEC but only 27% of DMC and 20% of DME molecules are coordinated with a Li⁺ ion during MD simulations at 298 K.³² FEC is more reactive with Li metal anodes because of the formation of Li⁺–FEC complexes and the reduced LUMO energy level.

Beyond solvent stability, solvent regulation is supposed to change the electrolyte energetics, dynamics, and ion transport properties. For instance, both the structural heterogeneity and solvent fluctuation in Li⁺ solvation decrease with increasing EC concentration ([EC]) in a ternary mixture of EC, DMC, and ethyl methyl carbonate (EMC). On the contrary, the electrolyte viscosity increases with increasing [EC]. The changes in solvation structure and electrolyte viscosity caused by [EC] contribute to the ionic conductivity oppositely, inducing a nonmonotonic behavior of the ionic conductivity according to [EC].³³

Aqueous electrolytes are another important branch for Li metal battery electrolytes. However, aqueous electrolytes have a very limited electrochemical stability window (1.23 V) because of the hydrogen evolution reaction (HER) at the anode and the oxygen evolution reaction (OER) at the cathode. Regulating the acidity/alkalinity makes a compromise between the cathodic and anodic stability but cannot extend the intrinsic electrochemical stability window. Coordination with Li⁺ can adjust the water reactivity. As expected, a high oxidation potential is observed in highly concentrated aqueous electrolytes (HCAEs) based on LiTFSI salts because of the deprived population of free water molecules.³⁴ The TFSI⁻ anions appear in the Li⁺ solvation shell because of the lack of water solvent molecules in HCAEs, which induces a LiF-rich interphase on the anode and lowers the reduction potential of water. As a result, a much expanded electrochemical stability

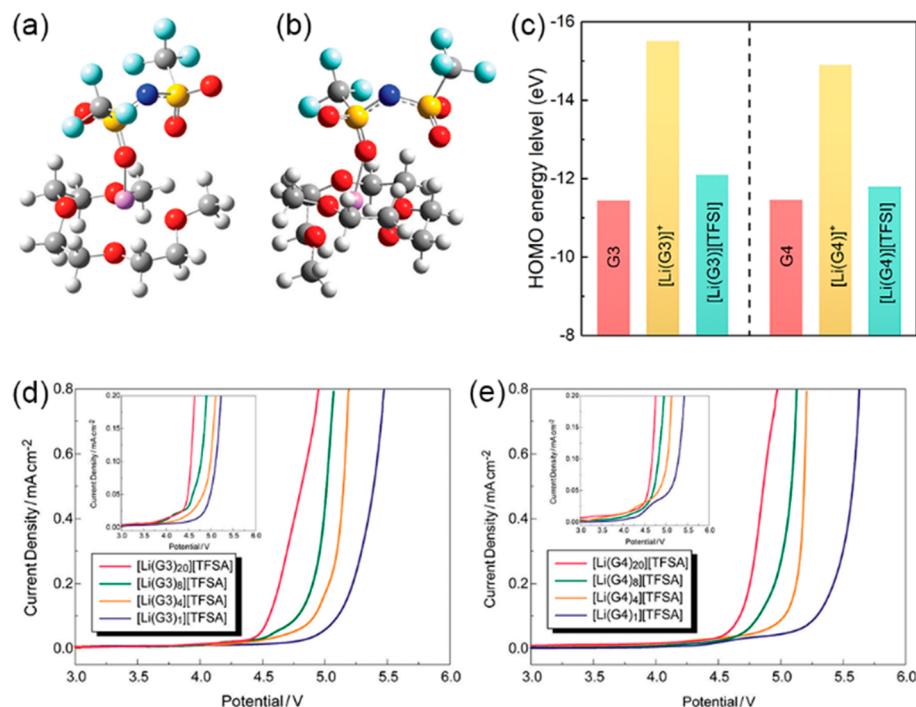


Figure 3. Regulation of solvent oxidative stability by coordinated cations. (a, b) Optimized geometrical structures of (a) $[\text{Li}(\text{G3})_1]\text{[TFSI]}$ and (b) $[\text{Li}(\text{G4})_1]\text{[TFSI]}$ complexes. The H, Li, C, N, O, F, and S atoms are shown in white, purple, gray, blue, red, light blue, and yellow, respectively. (c) summary of HOMO energy level. (d, e) Linear sweep voltammograms of (d) $[\text{Li}(\text{G3})_x]\text{[TFSI]}$ and (e) $[\text{Li}(\text{G4})_x]\text{[TFSI]}$ ($x = 1, 4, 8$, and 20). Reproduced from ref 29. Copyright 2011 American Chemical Society.

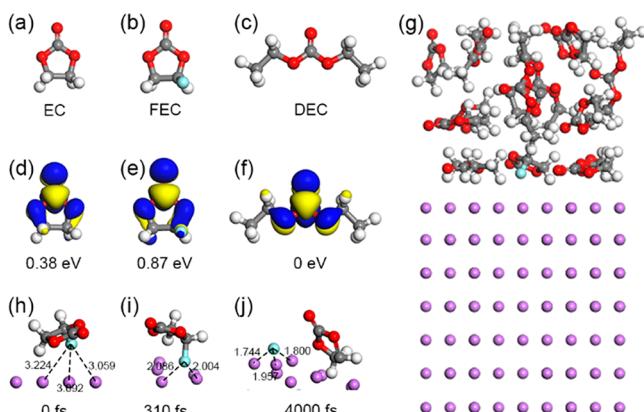


Figure 4. Solvent regulation to build a stable electrolyte–electrode interface. (a–c) Geometrical structures of (a) EC, (b) FEC, and (c) DEC molecules. (d–f) LUMOs and corresponding relative HOMO energy levels of (d) EC, (e) FEC, and (f) DEC molecules. (g) The AIMD model. (h–j) Time evolution of FEC decomposition on Li metal anodes at (h) 0, (i) 310, and (j) 4000 fs. Reproduced with permission from ref 31. Copyright 2017 Wiley-VCH.

window of around 3.0 V is achieved in 21 M LiTFSI aqueous electrolytes.³⁴

4. CATION–ANION INTERACTIONS

Most Li salts are considered to be strong electrolytes in water, with the Li^+ ions and anions completely separated from each other by solvent molecules. Compared with water, the dielectric constants of organic electrolytes are often much lower, and the Li^+ –anion interactions are not weakened effectively. As a result, Li salts are not completely dissociated, and the Li^+ –anion interaction greatly influences the formation

of contact ion pairs and aggregates, further regulating the Li salt solubility, ionic conductivity, and Li^+ transference number.

4.1. Salt Solubility

The competitive coordination of Li ions to anions and solvent molecules directly determines the solubility of Li salts in electrolytes (Figure 5).⁴ The PF_6^- anion has a smaller binding energy with a Li^+ ion than the other anions, such as tetrafluoroborate (BF_4^-), bis(fluorosulfonyl)imide (FSI^-), TFSI⁻, and nitrate (NO_3^-), explaining its great solubility in a variety of Li battery electrolytes (Figure 5a). Among the two early-developed Li salts, BF_4^- has a higher ion pairing tendency and lower solubility due to its larger binding energy compared with PF_6^- . Although FSI^- and TFSI⁻ also have fairly large binding energies, the entropy effect induced by their large size promotes salt dissociation and results in a good solubility. On the contrary, NO_3^- has the strongest interaction toward Li ions among the five anions, agreeing with wide experimental reports that LiNO_3 cannot be dissolved in most electrolyte solvents. Besides, the two electronegative oxygen atoms in a DME molecule can coordinate with a Li^+ ion simultaneously, inducing a large binding energy between Li^+ and DME. DME is consequently regarded as a good solvent to dissolve Li salts, including LiNO_3 (Figure 5b). Simultaneously, the Li^+ –anion interaction is not weakened significantly because of the small dielectric constant of DME, which is beneficial to form contact ion pairs in DME electrolytes.

LiNO_3 has been widely reported as an excellent electrolyte additive to induce a stable SEI and uniform Li deposition.^{35–37} Especially, the introduction of LiNO_3 can significantly improve the Coulombic efficiency in Li–sulfur (Li–S) batteries. However, the poor solubility of LiNO_3 in ester electrolytes, which possess better oxidative stability than ether solvents, blocks its wide applications. Consequently, dissolving LiNO_3

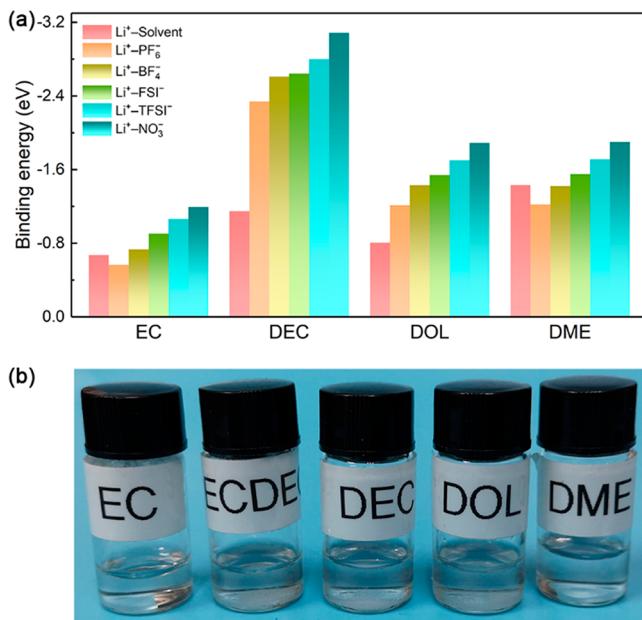


Figure 5. Cation–anion interactions in electrolytes. (a) Summary of binding energies between Li^+ ions and solvent molecules/anions in different solvents. The binding energy between Li^+ and BF_4^- was recalculated using the same method as for the other anions. (b) Experimental dissolution behavior of LiNO_3 in a series of solvents. Reproduced with permission from ref 4. Copyright 2019 Wiley-VCH.

in ester electrolytes is an important topic in this field. EC has a very large dielectric constant of 89.8, which is even larger than that of water (80.2 at 20 °C), and is supposed to dissolve LiNO_3 . However, EC is a solid at room temperature, and DMC is often used as cosolvent to keep the liquid state of EC/DEC electrolytes, in which LiNO_3 cannot be dissolved because of the much smaller dielectric constant of the mixture. Dissolving LiNO_3 in liquid EC at a high temperature (e.g., 40 °C) and then introducing DEC as a cosolvent to maintain the liquid state of the solution is a feasible way to dissolve LiNO_3 in EC/DEC electrolytes (Figure 5b).

4.2. (Localized) High-Concentration Electrolytes

Beyond the solubility of Li salts, the Li^+ –anion interaction also regulates the solvation structures and bulk/interfacial properties of electrolytes. Li^+ is mostly solvated by solvent molecules in dilute electrolytes. As the salt concentration increases, there are fewer and fewer free solvent molecules, and the ratio of anions to solvent molecules in the Li^+ solvation shell increases. The participation of anions in the Li^+ solvation shell changes the Li^+ desolvation behavior and induces an inorganic-rich SEI, which is supposed to stabilize Li metal anodes.^{38,39} However, an ultrahigh Li salt concentration sacrifices electrolyte ionic conductivity and increases the battery cost. In order to keep the solvation structure in HCEs, nonsolvating fluorinated ether, which has a weak interaction with Li ions, is introduced into the electrolyte. Although the apparent salt concentration is decreased, the solvation structure remains the same as that in the HCE. As a result, the LHCE has a similar function as the HCE but improved ionic conductivity, reduced viscosity, and lower expense (Figure 6).²³

Regulating the Li^+ –anion interaction is the key to designing high-performance HCEs and LHCEs and understanding the working mechanism. As discussed in section 3.2, the presence of anions in the solvation shell can increase the HOMO energy

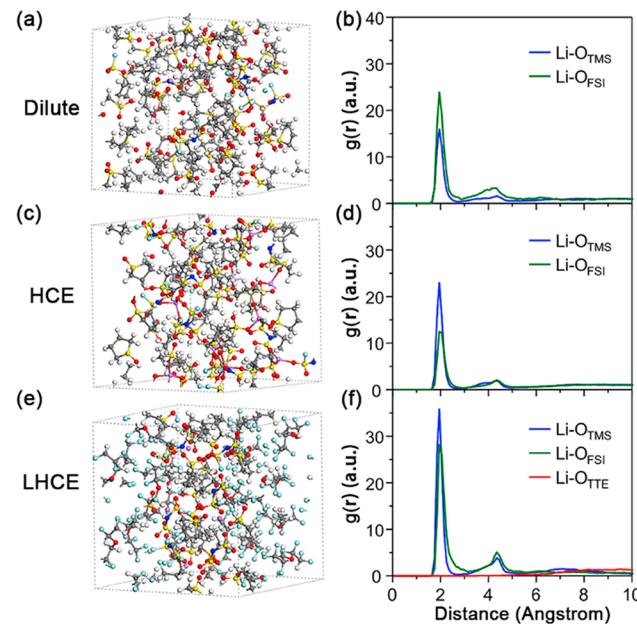


Figure 6. (a, c, e) Geometrical structures and (b, d, f) radial distribution functions, $g(r)$, from MD simulations for (a, b) a dilute electrolyte, (c, d) an HCE, and (e, f) an LHCE. Reproduced with permission from ref 23. Copyright 2018 Elsevier.

level of solvent molecules. Similarly, the LUMO energy level should also be increased. The anions can improve the reductive stability of solvent molecules, which explains the good compatibility between Li metal anodes and HCEs/LHCEs. Besides, large aggregates are formed in HCEs, which have slow kinetics and can resist the violent side reactions between liquid electrolytes and Li metal anodes.

4.3. Anion Regulation

Similar to solvent regulation, regulation of anions in the solvation shell can also change the desolvation behavior of Li^+ ions and the bulk/interfacial properties of electrolytes (Figure 7). The NO_3^- anion possesses a larger binding energy toward a Li^+ ion than FSI^- . The NO_3^- anion is also able to coordinate with two Li^+ ions simultaneously, resulting in the formation of large aggregates (Figure 7a,b). More importantly, the introduction of NO_3^- can change the type of bonding of FSI^- to Li^+ . In electrolytes with only FSI^- , FSI^- coordinates with Li^+ through $\text{Li}-\text{O}$ and $\text{Li}-\text{N}$ bonds (Figure 7c,d). The $\text{Li}-\text{F}$ interaction between FSI^- and Li^+ appears when NO_3^- is added to the electrolyte (Figure 7e), which promotes the complete decomposition of FSI^- on Li metal anodes and induces a LiF -rich SEI.⁴⁰

Compared with Li^+ –solvent interactions, Li^+ –anion interactions are more complicated and diverse. First, anions often possess more than one coordination site toward a Li^+ ion, and the bonding type can vary. Second, anions can coordinate with two Li^+ ions simultaneously and produce aggregates, greatly differing the electrolyte structure from that in dilute electrolytes. Third, Li^+ –anion interactions are generally stronger but more sensitive to the electrolyte environment than Li^+ –solvent interactions. As a result, the Li^+ (de)solvation structure, bulk transport, and interfacial reactions can be greatly changed by regulating the anions in the solvation shell.

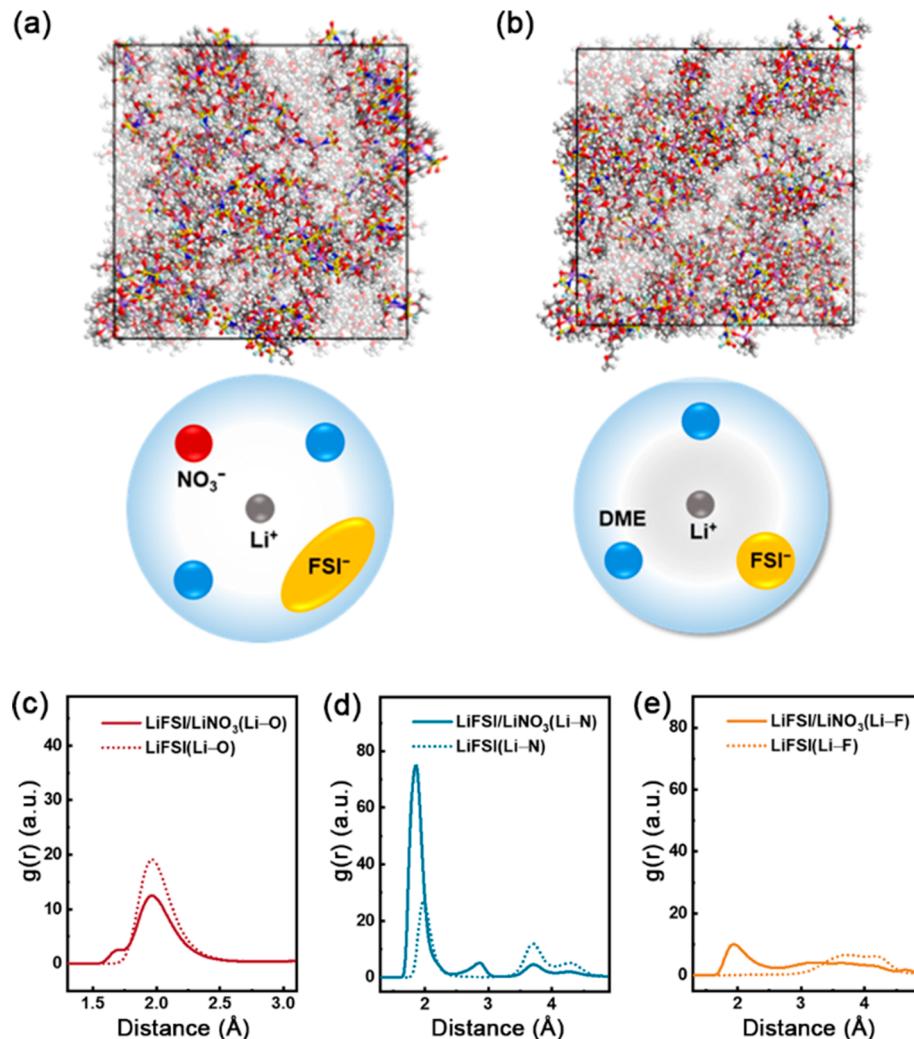


Figure 7. Regulation of anions in the Li⁺ solvation shell. (a, b) Geometrical structures from MD simulations and corresponding schematics of (a) LiFSI/LiNO₃ and (b) LiFSI electrolytes. The H, Li, C, N, O, F, and S atoms are shown in white, purple, gray, blue, red, green, and yellow, respectively. (c–e) $g(r)$ plots for (c) Li–O, (d) Li–N, and (e) Li–F distances in MD simulations. Reproduced from ref 40. Copyright 2019 American Chemical Society.

5. ANION–SOLVENT INTERACTIONS

In contrast to water, which is both electrophilic and nucleophilic, solvents used in Li batteries are only nucleophilic to avoid active protonation reactions. Li salts with large-radius anions are used to ensure desirable solubility in organic electrolytes, which often have a small dielectric constant. Both the large radius and delocalized charge of the anions weaken their interaction with solvent molecules, to which van der Waals forces make a major contribution. Therefore, anions in Li battery electrolytes are considered unsolvated in most cases, and anion solvation is rarely studied. However, the solvation of anions is supposed to change the stabilities of solvent molecules and anions, the cation solvation structures, the diffusivity of anions, and thus the cation transference number. More importantly, electrolyte solvation can stabilize radicals in solution and thus regulate interfacial side reactions and working mechanisms in batteries.

5.1. Solvation of Anions

Solvents with a large acceptor number or an exposed positively charged site are supposed to form a strong interaction with anions. For example, tris(pentafluorophenyl)borane (TPFPB),

in which the electron-deficient B atom acts as the electron acceptor, can form a strong interaction toward BF₄⁻ and PF₆⁻, with free energy changes of -24.4 and -12.7 kcal/mol, respectively (Figure 8a,b). The free energy changes are larger than those between anions and conventional ester solvents, which are mostly connected by F–H interactions. For instance, EC delivers free energy changes of -7.5 and -8.9 kcal/mol toward BF₄⁻ and PF₆⁻, respectively. Besides, anions prefer cyclic over linear carbonates, as the former are more polar because of the ring constraint (Figure 8c,d). The F–H interaction between anions and carbonate solvent molecules is also confirmed by MD simulations and electrospray ionization mass spectrometry (Figure 8e).⁴¹ However, it is still difficult to define the “anion solvation shell” in conventional solvents because of the loose attraction between anions and solvent molecules.

Although the formation of an anion solvation shell is difficult in routine electrolytes, its potential functions can be expected. First, anions should have an opposite influence on the stability of solvent molecules compared with cations, reducing the oxidative stability and improving the reductive stability. Second, the formation of anion–solvent complexes should

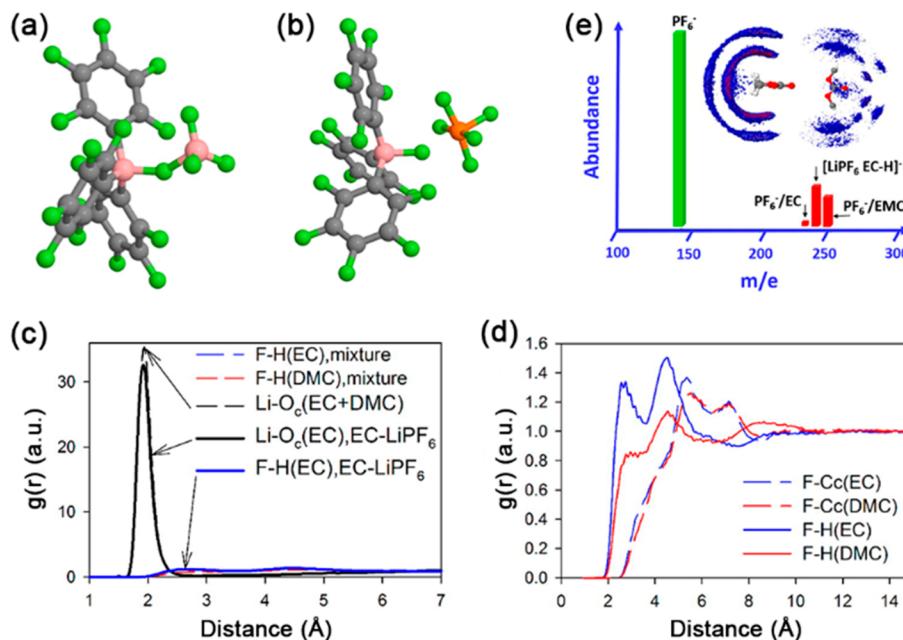


Figure 8. Anion solvation in electrolytes. (a, b) Optimized geometrical structures of (a) TPFPB– BF_4^- and (b) TPFPB– PF_6^- complexes. The B, C, F, and P atoms are shown in pink, gray, green, and orange, respectively. (c, d) $g(r)$ plots for LiPF_6 in EC and EC/EMC electrolytes. (e) Typical mass spectra via electrospray ionization and (inset) 3D isosurface rendering of F in PF_6^- around DMC and EC molecules. Reproduced from ref 41. Copyright 2015 American Chemical Society.

reduce the anion mobility in electrolytes and hence increase the cation transference number, which is beneficial to good rate performance. Third, anion solvation is supposed to promote salt dissociation, increasing the salt solubility in electrolytes. Fourth, the cation solvation structure also changes with the enhancement of anion–solvent interactions, indirectly regulating the cation desolvation and interfacial reaction behaviors. With a delicate design of electrolyte solvents with a high acceptor number or anion acceptors, like TPFPB, it is possible to achieve anion solvation in electrolytes, delivering a different solvation structure and solution chemistry in Li batteries.

5.2. Solvation of Radicals

As an important branch of high-energy-density Li batteries, Li–S batteries have attracted wide interest recently.^{8,19} Sulfur molecules are reduced to various lithium polysulfides and finally Li_2S during discharge in Li–S batteries. The soluble sulfur-containing species afford Li–S battery special solvation chemistry compared with the other Li batteries. In the most used DOL/DME electrolytes, polysulfide radicals can hardly exist because of their high reactivity. Solvents with a large dielectric constants, such as dimethyl sulfoxide, are reported to effectively increase the solubility of short-chain polysulfides and stabilize polysulfide radicals, especially $\text{S}_3^{\bullet-}$ radical.^{42–44} The existence of $\text{S}_3^{\bullet-}$ radical in electrolytes regulates the conversion mechanism among sulfur-containing species and delivers a solvation-mediated radical pathway (Figure 9).⁴²

6. NEW THEORY AND METHODS IN ELECTROLYTES

6.1. Li Bond Theory

Similar to H bonds, Li bonds can be formed between Li donors and Li acceptors (Figure 10). The recent introduction of Li-bond theory into Li batteries affords a new viewpoint for the understanding of intermolecular interactions between Li-containing species.⁴⁵ For instance, lithium polysulfides are

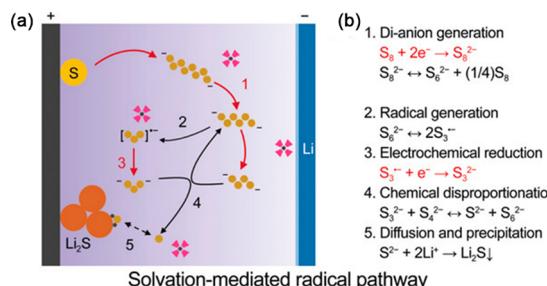


Figure 9. Solvation-mediated radical pathway in Li–S batteries. (a) Schematic of sulfur reduction progress and (b) corresponding mechanisms. Reproduced with permission from ref 42. Copyright 2018 Wiley-VCH.

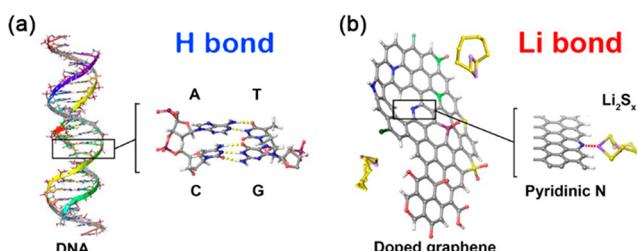


Figure 10. Schematics of (a) H bonding in DNA molecules and (b) Li bonding in Li–S batteries. Reproduced with permission from ref 46. Copyright 2017 Wiley-VCH.

anchored on heteroatom-doped carbon frameworks through Li bonds, which are confirmed to be dipole–dipole interactions.⁴⁶ The strong anchoring effect induced by the Li bonds is supposed to resist the dissolution of polysulfides in electrolytes and prevent shuttling of polysulfides in a working battery. Besides, Li bonds are widely formed in electrolytes to regulate the fundamental interactions. For example, cation–anion pairs act as Li donors and further coordinate with solvent molecules

to form ion–solvent complexes. The electrolyte stability is consequently regulated by the as-formed Li bonds according to the ion–solvent chemistry discussed above. More importantly, the Li bond evolution dynamics influences the Li^+ transport, desolvation, nucleation, and deposition behaviors.

In spite of many similarities, the differences between Li bonds and H bonds are obvious.⁴⁵ Different from the covalent bond character of H bonds, Li bonds are more electrostatic and have no saturation or directionality limitations because of the metallic nature of Li atoms. As a result, Li bonds are typically stronger than H bonds. Besides, the Li atom is more shared between the coordinated atoms, making Li transfer in Li bonds easier than H transfer in H bonds. Besides, Li transfer is less sensitive to the properties of coordinated ligands than H transfer. The difference between H bonds and Li bonds can explain different solution chemistries in aqueous and non-aqueous electrolytes in Li batteries.

6.2. High-Throughput Screening and Machine-Learning Methods

Combined with first-principles calculations, high-throughput screening and machine-learning methods play an increasingly important role in electrolyte studies. Starting from a huge molecule database, high-throughput quantum-chemical calculations can effectively downselect candidates on the basis of successive property evaluation (Figure 11).⁴⁷ Several descrip-

the prediction of a specific property of a new material without too much time expense. Combined with high-throughput screening methods, it is able to achieve quick electrolyte design, in which understanding the fundamental interactions in electrolytes plays a decisive role. On the basis of this idea, the Electrolyte Genome Project, which is a part of Materials Project, is proposed for battery electrolyte material discovery.⁴⁸ The well-established big-data approach can help to accelerate battery material discovery, including the electrolyte, anode, and cathode materials, and simultaneously aid in understanding the fundamental science in Li batteries.

7. SUMMARY AND OUTLOOK

Designing highly stable electrolytes has been strongly considered as a key technology for building safe high-energy-density Li batteries through the construction of high-capacity Li metal anodes and high-voltage cathodes. In this Account, we have reviewed our recent progress to understand the fundamental interactions in Li battery electrolytes at the atomic level, including cation–solvent, cation–anion, and anion–solvent interactions. The recently developed Li bond theory and high-throughput screening and machine learning methods have also been introduced into electrolyte studies. Looking forward, some challenging but promising directions still remain, including the following.

(1) *Interfacial Structures and Reactions.* Most previous studies are based on bulk electrolyte models, while the electrolyte–electrode model is less considered. Electrolyte solvation structures on electrode surfaces can be very different from bulk structures because of the specifically adsorbed ions on electrode surfaces and the formation of electrical double layers, which directly determine the interfacial electrochemical and chemical reactions. The electrode potential also greatly influences the interfacial adsorption and reaction. Besides, organic electrolytes decompose on the electrode surface to form a SEI or CEI layer, which makes the interfacial structure and reaction more complicated. As a result, a comprehensive and deep understanding of Li^+ desolvation and transport from the bulk electrolyte to the electrode is still lacking.

(2) *Electrochemistry in Nonaqueous Solutions.* Most classical electrochemical models are built in water solutions, which differ from organic electrolytes in Li batteries. On one hand, the organic solvation environment greatly influences the fundamental interactions in electrolytes and further changes the physical and chemical properties. For example, alkali metals have different electrode potential trends in water and propylene carbonate solutions.⁴⁹ On the other hand, organic electrolytes react with electrodes and produce complicated interfaces, including solid-state organic and inorganic compounds, but these newly formed interfacial structures are less considered in classical models. New electrochemical models concerned with reactive electrodes and organic electrolytes are highly required for Li battery research.

(3) *Structure–Function Relationships.* Multiscale calculations are powerful to reveal the microstructure and obtain the fundamental physical/chemical properties of electrolytes, but the correlation between the structure and battery performance is still very hard to determine because of the intrinsic gaps between theoretical models and complicated experimental conditions. The electrolyte compounds have a great synergetic effect with each other, which is hard to consider in routine models at several-angstrom/nanometer scale. High-accuracy calculations based on large-scale models are supposed to

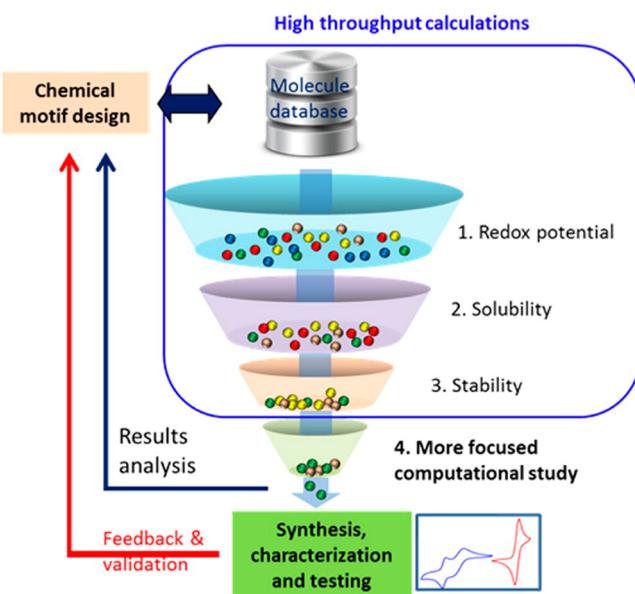


Figure 11. Schematic of high-throughput calculations on electrolytes. Reproduced from ref 47. Copyright 2014 American Chemical Society.

tors, such as the redox potential, solubility of salts, and chemical and thermal stability, can be adopted to narrow the candidate range according to specific applications. The well-established approach accelerates the search for optimal electrolyte materials and greatly reduces the time and expense costs compared with conventional trial-and-error methods.

A large and effective database is needed prior to the construction of a high-throughput screening diagram. However, some material properties are still very expensive to obtain by high-level quantum-chemical calculations, such as the ionic conductivity and band gap. Machine learning methods afford the possibility to build structure–property relationships. Training a reliable model based on the current data enables

provide new insights into the structure–function relationship of Li battery electrolytes. Besides, the emerging machine-learning methods afford a new research paradigm to understand the structure–function relationship based on a huge data set.

With a comprehensive and deep understanding of the fundamental interactions and the structure–function relationship, highly stable and promising electrolytes can be rationally designed to achieve safe high-energy-density Li batteries. The general principles demonstrated in Li batteries are reasonably expected to be applied to other battery systems and even universal electrochemistry in solutions.

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Author Contributions

The manuscript was written through contributions of both authors. Both authors approved the final version of the manuscript.

Notes

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