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Electrolyte Optimization for Graphite Anodes toward Fast Charging

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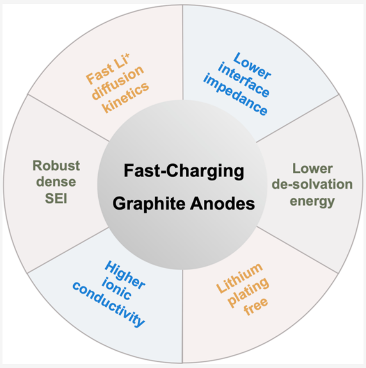
ABSTRACT: As the most advanced energy storage devices, lithium ion batteries (LIBs) have captured a great deal of attention and have been developed swiftly during the past decades. However, the improved fast-charging performance is more urgent than ever for time-saving and convenience, which is generally limited by the graphite anode. Recent studies have revealed that the fast-charging performance of graphite anodes is highly dictated by the properties of the electrolyte. Therefore, the investigations on fast-charging graphite based on designs of electrolytes are summarized from two aspects: solid electrolyte interphase (SEI) structures and solvated lithium ion structures. Finally, challenges and prospects for further research toward fast-charging graphite anodes are proposed.



1. INTRODUCTION

Over the few past decades, lithium ion batteries (LIBs) have become a research hotspot with the development of nonfossil and wireless society. However, the booming electric vehicle (EV) industry puts forward more stringent requirement for the battery performance, such as long cycling life, fast-charging ability and safety at a wide temperature range. Currently, one prominent shortcoming for EVs is the time-consuming charging from the empty to fully charged state compared to gasoline vehicles. Specifically, the anode is regarded as the limiting factor to battery safety and fast-charging performance due to its sluggish electrochemical reaction kinetics. In practical applications, graphite anodes dominate the market due to their low operating voltage (<0.1 V vs Li/Li^+), good cycling stability, and low cost. However, graphite anodes still suffer from inferior Li^+ intercalation kinetics, which corresponds to charging process in commercial LIBs, resulting in lithium plating under high current density especially at lower temperature conditions. For clarity, the concept of fast-charging corresponds to the specific requirement of 15 min recharging time (corresponding to a C-rate of 4C) which is proposed by the US Department of Energy.[1]

Recently, lots of effort has been paid to improve the fast-charging ability of graphite anodes through various ways including modifications of the graphite structure, employing composite materials, optimizing the charging procedures, developing advanced electrolytes, etc.[2−4] Among these approaches, electrolyte-related reports are of great effectiveness and convenience for achieving fast-charging LIBs. As shown in Figure 1A, the Li^+ intercalation into the graphite electrode mainly consists of four steps: (1) solvated lithium ions diffusion in the bulk phase of the electrolyte; (2) desolvation of solvated Li^+ at the solid electrolyte interface (SEI) to form naked lithium ions; (3) naked Li^+ passing through the SEI film; (4) charge transfer of graphite at the SEI−graphite interface; and (5) Li^+ diffusion within the graphite bulk. Previous studies have shown that interfacial reactions are the rate-determining steps (RDSs) of Li^+ intercalation into the graphite including steps 2, 3, and 4.[5−8] Wang et al. proposed three main principles for the development of fast-charging batteries including higher ionic conductivity, lower desolvation activation energy, and robust SEI.[9] Therefore, the properties of the graphite−electrolyte interface are crucial for the fast-charging performance of LIBs. To this date, numerous efforts have been made to promote Li^+ intercalation at the graphite−electrolyte interface.[10−12] Apart from surficial modification on graphite, it has been also demonstrated that the graphite−electrolyte interface can be finely optimized through rational design of electrolytes.

In this Review, we aim to provide an in-depth review on the interfacial engineering at the graphite−electrolyte interface. First, some critical principles and challenges will be discussed for electrolyte design. Next, relevant strategies will be reviewed based on two main purposes: (1) regulating the structure of SEI and (2) modifications on the solvation structures. It should be

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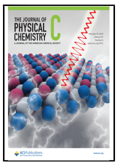

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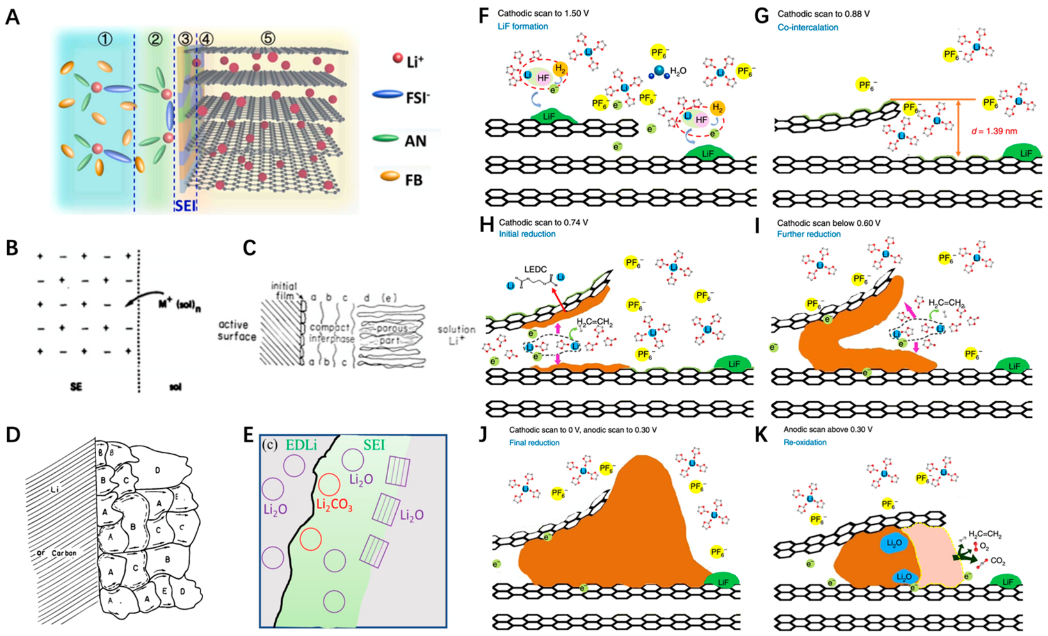

Figure 1. (A) Scheme of the five steps of Li^+ intercalation into the graphite electrode. Reproduced with permission from ref 8, copyright 2022 Elsevier Ltd. (B) Scheme of the single crystal layer model of SEI structure. Reproduced with permission from ref 15, copyright 1979 ECS - The Electrochemical Society. (C) Scheme of the double layer model of SEI structure. Reproduced with permission from ref 16, copyright 2000 Elsevier Science S.A. (D) Scheme of the mosaic model of SEI structure. Reproduced with permission from ref 17, copyright 1997 ECS - The Electrochemical Society. (E) Scheme of the plum pudding model of SEI structure. Reproduced with permission from ref 18, copyright 2019 Microscopy Society of America. Schematic illustration of the interspatial formation chemistry during the very first lithiation. (F) In the presence of trace H_2O, HF starts to reductively decompose at 1.5 V to form LiF. (G) Solvated Li^+ with four EC molecules approaches the graphite edge and starts to cointercalate below 0.88 V. (H) EC reduction starts, generating both gaseous and organic lithium salts such as LEDC. (I) The further reduction of EC. (J) The final reduction of EC. (K) On reversal of the current to the anodic regime above 0.3 V, LEDC in nascent SEI start to be partially reoxidized. Reproduced with permission from ref 19, copyright The Authors.

noted that the ionic conductivity of the electrolyte will not be elaborated in this Review considering that it rarely serves as a rate-determining factor for fast-charging especially at room-temperature.[9] Last, future perspectives will be provided regarding to both fundamental research and practical applications.

2. OPTIMIZATION OF SEI STRUCTURE

2.1. The Role of SEI in Graphite Anodes. In 1970, the initial attempt to achieve reversible Li^+ intercalation for the graphite anode has ended in failure due to the continuous decomposition of propylene carbonate (PC) solvent and the exfoliation of graphite layers.[13] By contrast, the substitution of PC by ethylene carbonate (EC) results in reversible Li^+ (de)interactions in graphite, which is attributed to a more stable SEI formed at the interface.[14] Generally, SEI forms during the initial electrochemical reduction (lithiation) process. As the potential decreases, the reduction of electrolyte components (e.g., solvent, salts, and additives) takes place at the graphite surface before Li^+ intercalation. The reduction product generally consists of both organic components (e.g., Li semicarbonates ($ROCO_2Li$), Li decarbonates ($(ROCO_2Li)_2$), etc.) and inorganic components (e.g., Li_2CO_3, LiF, Li_2SO_4, Li_3PO_4, etc.). The typical thickness of SEI varies from several nanometers to tens of nanometers. An ideal SEI should be acquired of several properties: (1) Li^+ conductive while sufficiently electronically insulating to prevent the continuous decomposition of the electrolyte; (2) densely formed and physically stable (i.e., insoluble) in the electrolyte; (3) mechanically robust to tolerate the volume changes of active materials during cycling, especially in the presence of Si-based anode materials; (4) Li^+ selective to prevent other ions from passing through; (5) as thin as possible to reduce the diffusion path of Li^+. Considering the features of a SEI depend on its chemical components and physical structures, the development of fast-charging graphite anodes has been tied up with the in-depth study regarding to SEI structures and their corresponding formation process.

Although the concept of SEI has been proposed since the 1970s, the exact structure of SEI is still uneasy to reveal due to its fragility and instability during characterizations. In 1979, based on electrochemical tests and analysis, Peled et al. speculated that the SEI film may be a single crystal layer of Li^+ conductor (Figure 1B).[15] With the development of advanced analytical characterization techniques, Aurbach proposed the bilayer model of SEI which is composed of two connected layers including an inorganic compound-rich inner layer and an organic outer layer on the graphite surface (Figure 1C).[16] Then, the mosaic model of SEI was established by assuming the SEI film is composed of microphases of components (Figure 1D).[17] Recently, a cryogenic transmission electron microscope (cryo-TEM) has been employed to observe the SEI structure for more facticity. It is demonstrated that the crystalline microphases (as plums) are embedded in the matrix of the amorphous phase (as the pudding) in the SEI film (Figure 1E).[18] Actually, there is a growing awareness that the organic and inorganic components play different roles. It can be expected that a more vivid model will emerge with the rapid development of advanced characterization techniques.

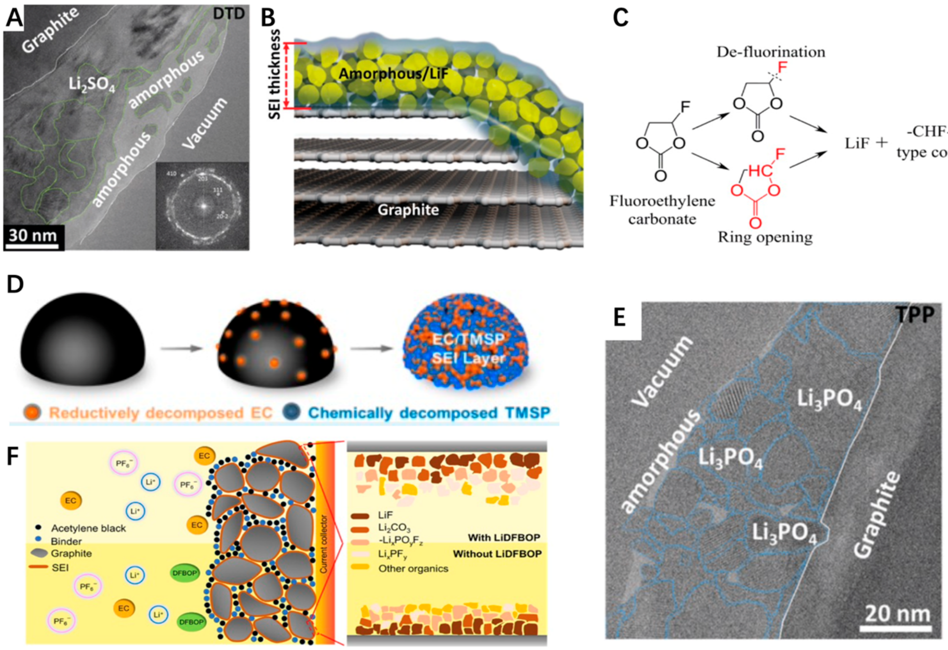

Figure 2. (A) Large-scale TEM image of the SEI in the electrolyte with DTD additive. Reproduced with permission from ref 25, copyright 2021 The Royal Society of Chemistry. (B) Schematic showing the as-formed percolating SEI in the electrolyte with FEC additive. Reproduced with permission from ref 25, copyright 2021 The Royal Society of Chemistry. (C) Scheme of possible reduction paths of FEC. Reproduced with permission from ref 31, copyright 2015 American Chemical Society. (D) Schematic showing the fundamentally SEI-forming mechanism for TMSP. Reproduced with permission from ref 40, copyright 2017 American Chemical Society. (E) Large-scale TEM image of the SEI in the electrolyte with TPP additive. Reproduced with permission from ref 25, copyright 2021 The Royal Society of Chemistry. (F) Scheme of the SEI structure of graphite in the electrolyte with LiDFBOP additive. Reproduced with permission from ref 45, copyright 2021 American Chemical Society.

Apart from revealing the structure of the SEI, the advanced analytical characterizations also effectively promote the investments on the formation mechanism of SEI. In order to realize the formation process of SEI in the 1 M LiPF$_6$ EC/DMC electrolyte, Pan et al. previously employed multiple characteristic methods to characterize the formation process of the SEI on graphitic electrode at the nanoscale, including electrochemical quartz crystal microbalance (EQCM), atomic force microscopy (AFM), differential electrochemical mass spectrum (DEMS), etc.[19] It was found that the process can be broken down to six steps: the reduction of HF produced by PF$_6^-$ and the trace H$_2$O (1.5 V, vs Li/Li$^+$) (Figure 1F); the cointercalation of Li$^+$-EC to the graphite layer (0.88 V, vs Li/Li$^+$) (Figure 1G); the reduction of EC blocking the entry of solvated Li$^+$ (0.74 V, vs Li/Li$^+$) (Figure 1H); the continuous reduction of EC (0.6 V, vs Li/Li$^+$) (Figure 1I); the final reduction forming the dense SEI (0.3 V, vs Li/Li$^+$) (Figure 1J); reoxidation of lithium ethylene dicarbonate (LEDC) (0.3 V, vs Li/Li$^+$, during oxidation) (Figure 1K). Afterward, Eichhorn et al. demonstrated that lithium ethylene monocarbonate (LEMC), which is formed through secondary chemical reactions rather than the direct electrochemical reduction in the battery environment, is the major organic component on graphite anode with 1 M LiPF$_6$ EC/DMC electrolyte instead of LEDC through rigorous and comprehensive characterizations including single-crystal and powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), elemental analysis, and solid-state/liquid 1*D*/2*D* nuclear magnetic resonance spectroscopy (NMR).[20]

2.2. Constructing an SEI Favorable for Li$^+$ Transfer.

Essentially, SEI components are the decomposition products of the electrolyte, including inorganic and organic species. It has been widely accepted that the inorganic components in SEI contribute to higher thermodynamical stability, mechanical robustness, structural compactness, and ionic conductivity, while the organic components in SEI provide its flexibility. Notably, most of the inorganic components of SEI (i.e., Li$_3$N, Li$_2$O, and Li$_2$CO$_3$) present a lower ionic migration barrier than Li alkyl carbonates (i.e., LEDC and LEMC).[21−23] Therefore, modulating the electrolyte composition is very important for optimizing the SEI structure.[24] Among all strategies to regulate the properties of SEI, one of the most cost-effective is taking advantage of electrolyte additives which refer to a small number of substances added to the electrolyte to improve the electrochemical performance of the battery. Generally, additives are "sacrificial" agents, which are more prone to undergo oxidation/reduction reactions than other electrolyte components.

Additives containing sulfur are commonly used for improving the performance of graphite. 1,3,2-Dioxathiolane-2,2-dioxide (DTD) has been wildly used for its higher reduction potential (1.3 V vs Li/Li$^+$) than EC (0.95 V vs Li/Li$^+$) and SEI forming ability to suppress the cointercalation of solvent molecules and exfoliation of graphite layers. Recently, applying the cryo-TEM, Gu et al. found that lithium sulfate (Li$_2$SO$_4$) crystallites with a particle size of several nanometers to tens of nanometers are intercalated between the SEI layers, forming a dense Li$_2$SO$_4$-rich SEI with high ionic conductivity, which may facilitate the rate performance of the graphite anode (Figure 2A).[25] Besides, many other additives containing sulfur are also investigated, such as 1,3-propane-sultone (PS),[26] prop-1-ene-1,3-sultone (PES),[27] vinyl ethylene sulfite (VES),[28] etc. Similarly, PS can also serve as a SEI film former to facilitate the generation of a uniform and stable SEI during the first cycle, suppressing consequent reduction of the electrolyte. While PES and VES have an even higher reduction potential over PS which derives from the additional unsaturation bond in their molecules. Yang et al.

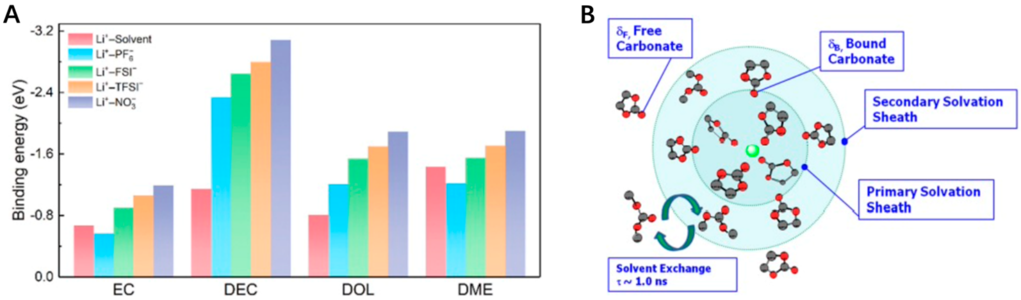

Figure 3. (A) Comparison of Li^+-PF_6^-/FSI^-/$TFSI^-$/NO_3^- and Li^+-solvent binding energies in EC/DEC/DOL/DME electrolytes. Reproduced with permission from ref 49, copyright 2019 Wiley-VCH. (B) Schematic illustration of Li^+-solvation sheath in nonaqueous electrolytes and the various ^{17}O nuclei in their coordination states with Li^+. Reproduced with permission from ref 50, copyright 2013 American Chemical Society.

found that, by combining the functional groups of sulfite and vinylene, the VES additive effectively helps to form a compact SEI composed of $ROSO_2Li$, Li_2SO_3, Li_2S, and Li_2O.[29] With the help of the well-formed SEI, the cointercalation of PC molecules can be effectively avoided.

Besides, fluorine-containing additives are well developed for forming a designed SEI film on the graphite anode because they usually possess relatively lower lowest unoccupied molecular orbital (LUMO) energy and lower highest occupied molecular orbital (HOMO) energy.[30] Fluoroethylene carbonate (FEC) is the most famous additive of this kind. The reduction potential of FEC (1.37 V vs Li/Li^+) is much higher than that of the EC solvent, leading to the prior decomposition during the initial lithiation of graphite anodes. As a result, as formed LiF and Li_2O can improve the density, robustness, and chemical/electrochemical stability of the SEI film and help to construct a sturdy shell on the graphite surface (Figure 2B).[25] As for the decomposition mechanism of FEC, there is still debates without an admitted conclusion (Figure 2C).[31,32] One point of view proposed that FEC decomposes to LiF through intermediate products of vinylene carbonate (VC) and HF. Another one holds that FEC is electrochemically reduced via ring opening reaction leading to the formation of lithium poly(vinyl carbonate) ($(CH_2{-}CHOCO_2Li)_n$), LiF, and partially fluorinated dimers. Despite the controversy about the formation process of LiF, the fluorine-containing organic−inorganic composite SEI results in an improved electrochemical stability across a wide voltage range and electron-insulating ability, while still allowing facile Li^+ transport.[33,34] Besides, the artificial SEI containing LiF has also been demonstrated to increase the electrochemical stability of Si-based anodes.[35,36] Apart from FEC, other additives containing fluorine also show good SEI film-forming effects, such as 4-fluorophenylacetate (4-FPA), 1,2-bis(difluoromethylsilyl)ethane (FSE), allyl tris(2,2,2-trifluoroethyl) carbonate (ATFEC), etc. Due to the fluorine substitution, 4-FPA exhibits preferable reducibility to phenylacetate (PA) and tends to build up a more protective SEI for graphite to prevent the cointercalation of PC and the exfoliation of graphite.[37] In addition, the existence of fluorine in SEI is an effective way to enhance the thermal stability of the electrode,[38,39] which can be realized by adding proper amounts of FSE or ATFEC.

Organic additives containing phosphorus are also effective to enhance the fast-charging performance of graphite electrodes. One of those typical additives is tris(trimethylsilyl) phosphate (TMSP) which reacts chemically with radical anion intermediates derived from the electrochemical reduction of the carbonate solvents to generate a stable SEI layer and contributes to the better cycling stability and higher Coulombic efficiency (CE) (Figure 2D).[40] Similarly, triphenyl phosphate (TPP) is also effective in forming a dense and compact lithium phosphate (Li_3PO_4)-dominated SEI (Figure 2E).[25]

In addition, some lithium salts (e.g., lithium bis(oxalate)-borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), lithium bisoxalatodifluorophosphate (LiBODFP), and lithium difluorophosphate ($LiPO_2F_2$)) containing boron or phosphorus elements have also been reported as additives or major lithium salts to promote the performance of graphite anodes by tuning the SEI layer. In general, SEI containing boron has enhanced interfacial stability on the anode surface.[41−43] However, the use of LiBOB salt is hindered by its negative effects on increasing the impedance and polarization of the graphite electrode. While LiDFOB can help to form a SEI with relatively low impedance which effectively suppresses the lithium plating at high current density and low temperature.[44] As for the additives containing phosphorus element, such as lithium tetrafluoro oxalato phosphate (LiTFOP), LiDFBOP, and $LiPO_2F_2$, they are reported to provide a Li_3PO_4 involved inorganics-rich SEI layer and help to improve thermal stability of batteries (Figure 2F).[45,46] For example, $LiPO_2F_2$ can build a stable SEI to enhance the rate performance and cycling stability of graphite anodes even under high-loading conditions which is ascribed to the relative low interface impedance.[47] Meanwhile, the side reactions at the electrode−electrolyte interface can also be inhibited with the help of stable SEI formed by $LiPO_2F_2$, resulting in a prolonged cycling life of the battery.[48]

3. OPTIMIZATION OF SOLVATION STRUCTURE

3.1. Solvation Structure of Li^+. Solvation reactions occur when the salt dissolves into solvents. In aqueous solutions, the cations are surrounded by water molecules as the primary solvation sheath. And anions exist in the outer layer. Similarly, nonaqueous electrolyte of LIBs is prepared by dissolving lithium salts into organic solvents, where lithium salts dissociate into lithium ions and corresponding anions. In general, both solvent and anion can serve as ligands to coordinate with Li^+ through ion−dipole or ion−ion interactions, the actual solvation structure depends on the competitive coordination between them (Figure 3A).[49] In dilute electrolytes, Li ions are usually solvated by strongly solvating polar solvents and most anions are excluded from the solvating sheath (Figure 3B).[50−53] As a result, the high desolvation energy would cause problems such as sluggish charge transfer, cointercalation of solvent, etc.

In addition, since the primary solvation sheath is the precursor of SEI, the solvation structure would lead to solvent-derived interfacial chemistry.[54,55] For instance, the essential role of EC

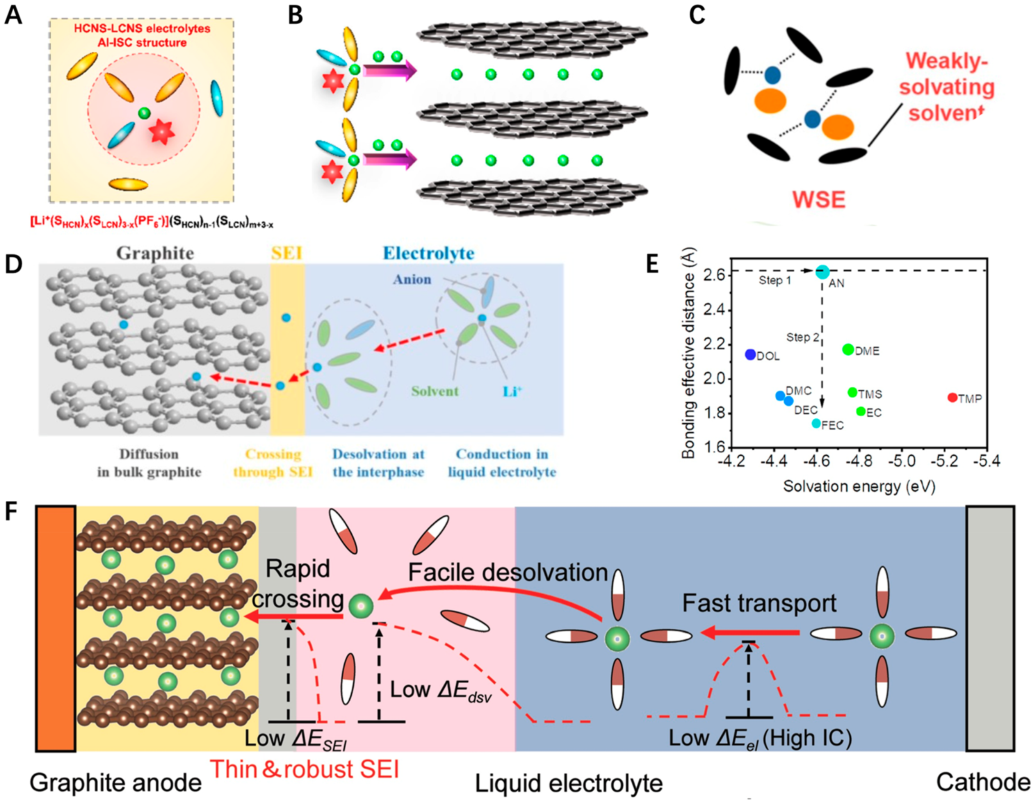

Figure 4. (A) Simplified solvation models and structure formula of the HCNS-LCNS electrolytes. Reproduced with permission from ref 58, copyright 2021 American Chemical Society. (B) Schematic diagrams of the stability of the electrolytes with the AI-ISC structure toward the graphite electrode. Reproduced with permission from ref 58, copyright 2021 American Chemical Society. (C) Schematic showing the solvation structure of WSE electrolytes. Reproduced with permission from ref 11, copyright 2020 Wiley-VCH GmbH. (D) Schematic illustration of Li^+ diffusion process from electrolyte to electrode, with an energy-consuming desolvation step. Reproduced with permission from ref 12, copyright 2022 Wiley-VCH GmbH. (E) The two-step selection of fast-charging solvents depending on the calculated Li^+ solvation energies (*x*-axis, color) and bonding effective distances (*y*-axis, size). Reproduced with permission from ref 59, copyright 2022 American Chemical Society. (F) Schematic of fast-charging for the graphite anode considering all steps that the electrolyte affects Li^+ transport from cathode to anode during charging. Reproduced with permission from ref 9, copyright 2022 Wiley-VCH GmbH.

for graphite anodes originates from its preferential solvation ability and reduction behavior which creates an EC-derived SEI to support reversible Li^+ intercalation in graphite. However, at high charging rates, the EC-derived SEI suffers from severe instability due to the organics-dominated interface, which results in poor fast-charging performance.

Therefore, in order to realize fast-charging graphite anodes, it is effective to optimize electrolyte solvation structures, facilitate beneficial interfacial chemistry, and construct favorable SEI.[56]

3.2. Rational Selection of Solvent System. Tuning the intrinsic solvating power of solvents is an effective approach toward favorable interfacial chemistry. Reducing the solvating power of solvents can theoretically allow more anions to coordinate with Li^+. Compared to the conventional tetrahedral solvation structure of Li^+, the anion-induced solvation structure of Li^+ has a higher energy level of LUMO, leading to better reduction stability of solvent molecules.[57] And the entry of film-forming anions into the solvation of Li^+ could facilitate the formation of anion-derived SEI, which can decide the electrochemical stability and the ion migration kinetics at the interface. Regulating the Li^+ solvation structure of electrolytes is able to tune electrochemical compatibility with graphite electrodes. Cao et al. introduced the low-coordination-number solvents (LCNSs) into the high-coordination-number solvent electrolytes (HCNS) to induce anions into the primary solvation shell of Li^+, forming the anion-induced ion−solvent-coordinated (AI-ISC) (Figure 4A). The HCNS-LCNS electrolytes with the AI-ISC structure exhibit enhanced interfacial stability and reversibility of the graphite anode (Figure 4B).[58] Besides, Zhang et al. have demonstrated a weakly solvating electrolyte (WSE) by using a nonpolar but salt-dissolving solvent (i.e., 1,4-dioxane). WSE exhibits a peculiar solvation structure in which ion pairs and aggregates prevail under a standard salt concentration (Figure 4C). It is shown that the competitive coordination between solvents and anions controls the transition from solvent-derived interfacial chemistry to anion-derived interfacial chemistry. As a result, the anion-derived SEI exhibits superior interfacial charge transport kinetics and high stability, enabling fast-charging and long-term cycling of graphite anodes.[11] In addition, Xia et al. designed an electrolyte with a weakly solvated solvent (ethyl trifluoroacetate, ETFA, 70% in vol) to facilitate the desolvation, together with a high permittivity and film-forming cosolvent (fluoroethylene carbonate, FEC, 30% in vol) to synchronously satisfy the ionic conductivity (Figure 4D). The synergetic effect from the weakly solvating electrolyte and well-optimized SEI layer enabled graphite anode with a fast-charging ability up to 6C. Meanwhile, excellent reversible capacity of 183 mAh g^{-1} was achieved at low temperature of −30 °C.[12]

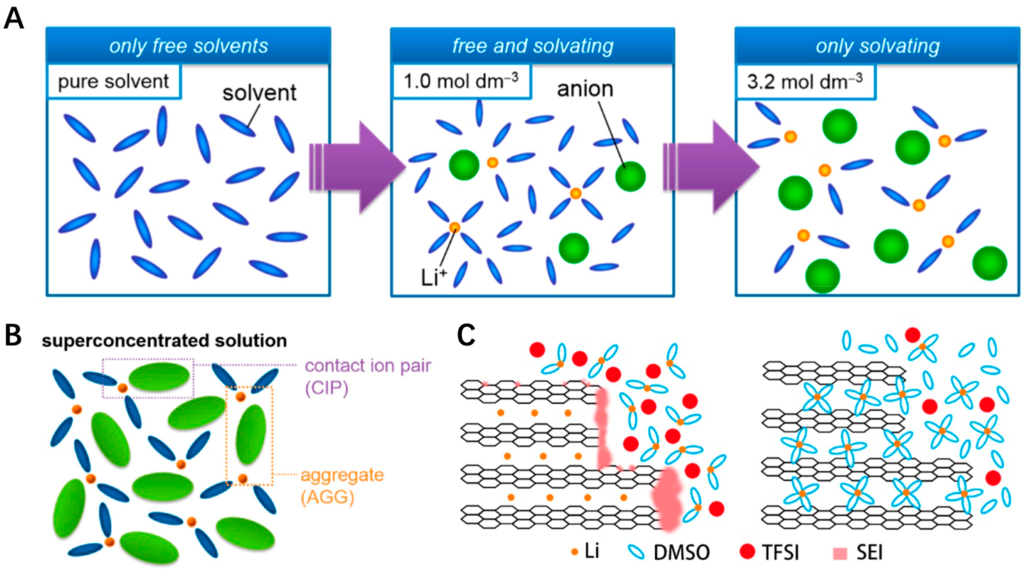

Figure 5. (A) Schematic of coordination structure in dilute and high-concentration electrolyte (HCE). Reproduced with permission from ref 64, copyright 2014 American Chemical Society. (B) Representative environment of Li$^+$ in a HCE (i.e., 4.2 mol dm^{-3}). Reproduced with permission from ref 63, copyright 2014 American Chemical Society. (C) Model diagram of the interface reactions of the graphite electrode with high-concentration DMSO-based electrolyte and dilute DMSO-based electrolyte. Reproduced with permission from ref 65, copyright 2015 American Chemical Society.

As far as the inorganic film-forming ability is concerned, the FEC-derived solvation structure of Li$^+$ is essential for realizing fast-charging graphite anodes. And, on the basis of quantum chemistry calculations (Figure 4E), the largest bonding effective distance implies the greatest ion-hopping-assisting potential for acetonitrile (AN). Owing to the similar solvation energies, it is convenient to adjust the solvation configurations using FEC and AN as solvent. Therefore, Fan et al. developed a fast-charging electrolyte (1 M LiPF$_6$–FEC/AN, 7/3 by vol) enabling 20C graphite anodes. By tuning the solvent ratios, they revealed the hopping-assisting nature of AN and proposed the solvation frequency as a proxy to quantify the Li$^+$-hopping efficiency among different solvation configurations, thereby creating an FEC-dominated sheath and AN-rich environment. The superior fast-charging performance of the 7FEC/3AN electrolyte is attributed to both the low-resistance SEI and the high interfacial ionic conductivity.[59] Recently, Fan et al. also developed other fast-charging electrolytes; 1.8 M LiFSI in 1,3-dioxolane (DOL) enabled the graphite electrode to achieve an extremely high capacity of 315 and 180 mAh g^{-1} at 20C and 50C, respectively. It has been demonstrated that the low desolvation energy of Li$^+$ in electrolyte endows a fast interfacial kinetics, and an ultrahigh-rate graphite anode with a decent cycling stability can be achieved by simultaneously improving the ionic conductivity of the electrolyte and forming a uniform and LiF-rich SEI at the surface of the graphite. In brief, the design principles of solvation structures of the fast-charging electrolytes can be exhibited in Figure 4 which includes low desolvation energy (ΔE_{dsv}) of Li$^+$, high ionic conductivity, and the ability to form thin and robust SEI on graphite surfaces (Figure 4F).[9]

3.3. Tuning Lithium-Salt Concentration.

3.3.1. High-Concentration Electrolyte. The coordination structure of Li$^+$ can also be regulated by developing high-concentration electrolyte (HCEs) (usually >3 mol dm^{-3}) to meet the demands for advanced LIBs such as high-voltage cathodes, dendrite-free Li metal anodes, fast-charging graphite anodes, etc.[60] As a benchmarking breakthrough, the achievement of HCE can be attributed to the altered Li$^+$ aggregation (i.e., Li$^+$-solvent and Li$^+$-anion coordination environments). As discussed above, polar solvent molecules tend to coordinate with Li$^+$, weakening the association between Li$^+$ and anions in conventional diluted electrolytes (e.g., 1 mol dm^{-3}). The evolution of solvent structures for a typical HCE at various Li-salt concentrations are shown in (Figure 5A). With the increase of salt concentration, the anions tend to have priority in competing with solvent molecules, which forms a regulated coordination structure of Li$^+$ and finally changes the interfacial chemistry.[61] The typical solvated structure of Li$^+$ in HCEs is shown in (Figure 5B). The anion-derived coordinated structure generates in the primary solvation sheath of Li$^+$ forming a myriad of contact ion pairs (CIPs) as well as agglomerates (AGGs).[62]

Yamada et al. first reported the concept of HCEs and found enhanced reductive stability and fast-charging character in lithium bis(trifluoromethanesulfonyl)amide (LiTFSA)-AN electrolyte. In this HCE, the frontier orbital characters in solution are modified and the LUMOs shift from AN to TFSA$^-$ anions. Consequently, the anions are predominantly reduced to form an anion-derived SEI which is the origin of the high reversibility and fast-charging ability of graphite electrodes (250 mAh g^{-1} at 5C).[63] Based on the same criterion, they have presented various HCEs in different organic solvents without EC, including sulfoxides (e.g., dimethyl sulfoxide (DMSO)), ether (e.g., tetrahydrofuran (THF)), and sulfone. It is concluded that the anion-based SEI as well as unique solution structure should be the origin of the universal working of a graphite electrode in various HCEs.[64] The SEI formation on the graphite electrode in LiTFSI/DMSO electrolyte of different salt concentrations was investigated via in situ AFM, confirming that the interfacial reactions at the electrode surface were significantly affected by the salt concentration. It was observed that, in dilute electrolyte, solvated Li$^+$ continuously intercalated into graphite layers, causing serious interfacial decomposition of electrolyte accompanied by deterioration of the structure of graphite surface. In contrast, in the concentrated electrolytes, passive films formed at the step edges and the defects on the electrode surface, allowing Li$^+$ intercalation with high

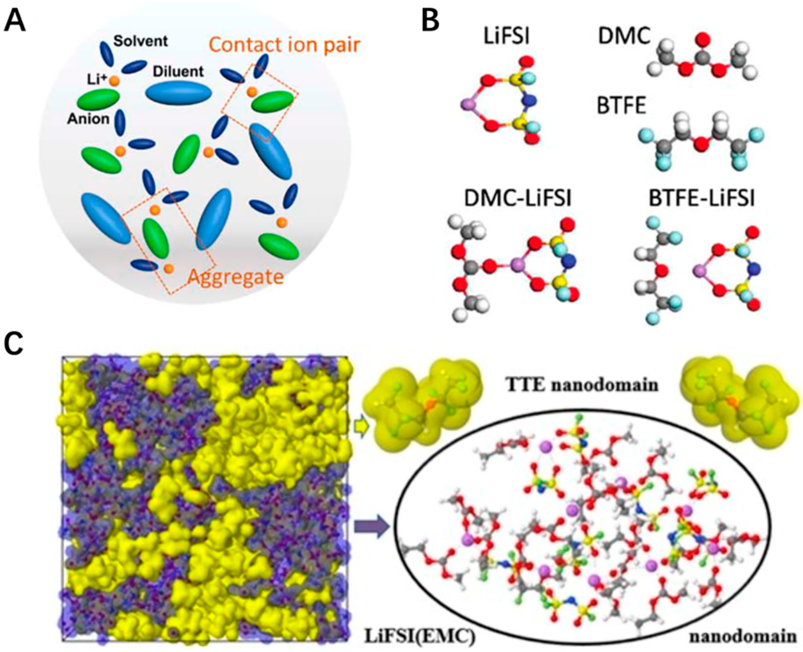

Figure 6. (A) Schematic of coordination structure in localized high-concentration electrolytes (LHCEs). Reproduced with permission from ref 69, copyright The Authors. (B) Optimized structures of electrolyte components, and the solvent−salt pairs of DMC-LiFSI and BTFE-LiFSI. Reproduced with permission from ref 70, copyright 2018 WILEY-VCH. (C) Electrolyte structure of the 2.0 M LiFSI-EMC/TTE from MD simulations at 25 °C showing the TTE-rich and LiFSI(EMC)$_{1.6}$ nanodomains. Reproduced with permission from ref 71, copyright 2022 Wiley-VCH GmbH.

reversibility and low resistance (Figure 5C).[65] Briefly, with the help of HCEs, the batteries could show superior electrochemical performance especially when operated at extreme conditions including high rates.

3.3.2. Localized High-Concentration Electrolytes. Recently, Zhang et al. proposed the concept of the localized high-concentration electrolyte (LHCE) which is also intended to form CIPs and AGGs in the solvated structure of Li$^+$ as same as in the HCEs (Figure 6A) but exhibit more favorable properties including low viscosity, high ionic conductivity, and low cost. Note that HCEs are the foundation of LHCE functionality; therefore, the purpose of diluting an HCE is to reduce the overall salt concentration in the LHCE but retain the highly concentrated salt-solvent clusters as they are in the HCE. Many efforts have been made to develop LHCEs, leading to a flourishing research field of low-temperature LIBs (working under −20 °C and below).[66−68]

Diluents are essential in LHCEs, and it has been demonstrated that several hydrofluoroethers (HFEs) can be used as diluents for many HCEs, such as bis(2,2,2-trifluoroethyl) ether (BTFE) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE). Computation calculations show that, compared to the solvent−salt pairs of DMC-LiFSI, HFE (e.g., BTFE) is not coordinated to Li$^+$ in the HFE-LiFSI pair but instead outside the primary solvent sheath of the Li$^+$ (Figure 6B), indicating the completely different behavior of HFE diluent from that of the solvent DMC.[69,70] Therefore, Wang et al. designed an exemplary electrolyte of 2.0 M LiFSI-EMC/TTE in which a presence of the TTE-rich and LiFSI(EMC)$_{1.6}$-rich domains is observed through molecular dynamics (MD) simulations (Figure 6C). A Li$^+$ cation has the highest affinity to carbonyl oxygens Oc(EMC) followed by the oxygens from FSI$^-$. The high ratios of AGGs and CIPs are confirmed which is beneficial for the formation of anion-derived interfaces at the anode and the formation of thin inorganic-rich SEI. The graphite anode in the above electrolyte exhibits good rate performance at 3C at room temperature, and the full cell is able to operate in a wide temperature range from −40 to +50 °C which is attributed to simultaneously reduced resistance and activation energies in both Li$^+$ transport in electrolyte−electrode interfaces and charge transfer process.[71]

4. CONCLUSIONS AND PERSPECTIVES

Range anxiety and time-consuming charging have been more and more urgent issues to be solved for EVs. To achieve fast charging, the sluggish lithiation process for the graphite anode should be promoted, where the desolvation process and the transfer through SEI for Li$^+$ appear to be rate-controlling steps. Here, electrolyte optimization strategies to construct an SEI favorable for Li$^+$ transfer and to regulate the solvation structure toward fast charging have been summarized. As for SEI optimization, the option of proper film-forming additives is one of the essential cost-effective strategies. With regard to the solvated structure regulation, rational option of solvents and concentration tuning work very well. Although great progress has been made, further efforts should be made to address the following issues.

1. Although there are now many means to characterize the structure and solvation structure of SEI, more advanced characterization tools are still needed. First of all, the structural information on SEI cannot be obtained by a single characterization tool such as XPS, SEM, TEM, cryo-TEM, energy dispersive spectroscopy (EDS), electron energy-loss spectroscopy (EELS), and secondary ion mass spectrometry (SIMS). Therefore, how to use them concertedly to get a full picture of SEI remains a challenge. Besides, due to the sensitivity and fragility of SEI, appropriate measures should be taken to reduce the deviation of the test. Moreover, we need to develop more

in situ characterization methods to characterize the dynamic processes of SEI formation.

2. In addition, it has been shown that the development of a novel electrolyte could be further accelerated with the aid of calculation and simulation methods including ab initio molecular dynamics (AIMD) simulations, density functional theory (DFT) calculations, multiphysics simulations, etc. Especially, DFT calculations are effective for finding favorable additives while AIMD simulations are beneficial for revealing the solvated structure in electrolytes.

3. As we mentioned before, the formation of SEI and the adjustment of the solvation structure are interrelated, and it is also important to take a simpler and more effective approach to optimize both of them at the same time. For instance, some SEI forming agents can also serve as the main solvent in the electrolyte.

4. Finally, we need to note that the electrochemical performance of graphite in a full cell is different from its performance in a half-cell. The difference in the fabrication and electrochemical protocols for coin cells and pouch cells may lead to a significant discrepancy in the SEI formed on the graphite surface. Therefore, it is necessary to minimize the gap between academic fields and industry.

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