

Beyond Local Solvation Structure: Nanometric Aggregates in Battery Electrolytes and Their Effect on Electrolyte Properties

Zhou Yu, Nitash P. Balsara, Oleg Borodin, Andrew A. Gewirth, Nathan T. Hahn, Edward J. Maginn, Kristin A. Persson, Venkat Srinivasan, Michael F. Toney, Kang Xu, Kevin R. Zavadil, Larry A. Curtiss*, and Lei Cheng*



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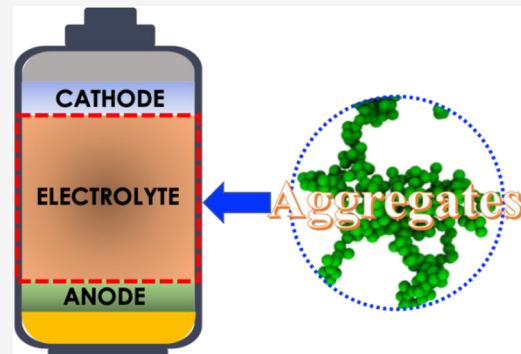
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ABSTRACT: Electrolytes are an essential component of all electrochemical storage and conversion devices, such as batteries. In the history of battery development, the complex nature of electrolytes has often been a bottleneck. Fundamental knowledge of electrolyte systems encompasses elucidation of structure–property relationships of the solution species. Recently, nanometric aggregates have been observed in several classes of electrolytes, including super-concentrated, redox-flow, multivalent, polymer, and ionic liquid-based electrolytes. Compared with the well-studied local solvation structures such as contact ion pairs and solvent-separated ions, these aggregates impose unique effects on the ion distribution and transport both within bulk electrolytes and at electrode/electrolyte interfaces. This Perspective highlights the discovery of the aggregates in various battery electrolytes and their impact on electrolyte properties. We also present an outlook for future studies of this emerging field of nanometric aggregates and the need for the development of new experimental and computational tools to study their properties.



Lithium-ion battery-powered devices are ubiquitous in modern society, spurred by ever-improving battery performance. However, many applications of energy storage devices, including Li-ion and next-generation batteries, still present major challenges at the level of materials and chemistries. Many of these challenges are related to the properties of the electrolyte materials or their interfacing with the emerging chemistries. Progress in the development of alternative and new electrolytes, such as salt-concentrated electrolytes, redox-flow electrolytes, multivalent electrolytes, and polymer electrolytes, is essential for advancing next-generation batteries.^{1,2} An emerging area of research on these electrolytes is the understanding of how the often found nanometric aggregates, i.e., beyond well-studied local ion solvation structure, affect the electrolyte properties.

The solvation structure of an electrolyte, originating from the solute–solvent interactions, has been extensively investigated during the past several decades to elucidate the origins of properties such as ion transport³ and redox characteristics.⁴ The focus of previous studies has been largely on solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and small aggregates (AGGs) that are composed of one ion

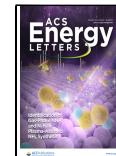
coordinating with more than one counterion such as shown in Figure 1a.⁵ Beyond these well-studied local solvation structures around dissolved ions, nanometric aggregates, which we refer to as n-AGGs, have recently been observed in various electrolyte systems where salt concentrations venture into the super-concentrated regime, poor solvents are used, or ions bearing multiple charges are introduced into the electrolytes. Different from the small AGGs composed of several ions, the n-AGGs are much larger, consisting of tens and hundreds of ions ($>\sim 1$ nm in dimension) as shown in Figure 1b, with some even forming heterogeneous ion-rich domain networks as shown in Figure 2.

Compared to the local solvation structure in electrolytes, the n-AGGs add more complexity to the electrochemical redox,

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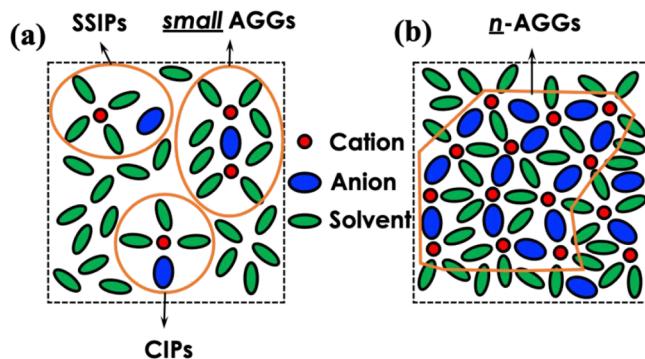


Figure 1. Schematic of solvation structures. (a) Solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and small aggregates (AGGs). (b) Nanometric aggregates (n-AGGs).

transport, and interfacial properties of electrolytes. For example, the n-AGG structures can modify the electronic structures of the solutions and thus the redox properties of the electrolytes. Strong ionic correlations within the n-AGGs can cause the transport properties of the electrolyte to deviate significantly from predictions based on the classical Stokes–Einstein and Nernst–Einstein equations. Furthermore, the n-AGGs may influence the electric double layers at interfaces as well as the interfacial reactions. In this Perspective, we first review the n-AGG structures found in various types of electrolytes and the driving forces for their formation. The effects of n-AGG structures on the microscopic and macroscopic transport properties, electronic structure, mechanical strength, and their structures at the interfaces are discussed. Finally, we present an outlook for future research needs to further establish the structure and property relationships of the aggregates, as well as the development of advanced experimental techniques and computational methods needed for these studies.

Formation of n-AGGs in Novel Electrolytes. The n-AGG formation in electrolytes has been studied both experimentally and computationally. Experimental techniques that directly probe nm scale structure in n-AGGs include small-angle neutron scattering (SANS)¹⁰ and small-angle X-ray scattering (SAXS).⁶ More widely used are experimental techniques that probe local structure, which include wide-angle X-ray scattering (WAXS),⁶ Fourier transform infrared spectroscopy (FTIR),^{11,12} Raman spectroscopy,³ X-ray absorption spectroscopy (XAS),¹³ and nuclear magnetic resonance (NMR) spectroscopy.¹³ While these do not directly probe the nm sizes associated with n-AGGs, they are sensitive to how the n-AGGs are related to the average local bonding environment of the ions. Computational studies, mainly based on molecular dynamics (MD) simulations and density functional theory (DFT), have provided structural information and insight into the driving forces for n-AGG formation. In addition, a thermodynamic model of reversible ionic aggregation and gelation has been developed recently which can capture the population of n-AGGs as a function of salt concentrations in electrolytes.^{14,15} The formation of n-AGGs is driven by the balance of the ion–ion and ion–solvent interactions. An intricate equilibrium among many types of interactions between solution species, such as electrostatic, hydrogen bonding, solvophobic, π – π stacking, and steric/volume exclusion, governs the formation of n-AGGs. Due to the high surface-to-volume ratio, the surface energy of the n-

AGGs with the solvent prevents the further increase of n-AGGs size or the salt precipitation.

In electrolytes with high salt concentrations, the static dielectric constant of the electrolyte tends to decrease and the electrostatic interaction between ions increases with the increase of the salt concentration,¹⁶ which facilitates the formation of the ionic aggregates such as those observed in aqueous electrolytes with high salt concentrations. The population of CIPs, including cation–anion and anion–anion pairs, becomes substantial when the concentration of LiTFSI aqueous electrolyte is higher than 3 m (mol/kg) based on IR spectroscopy and MD simulations.¹² Using FTIR spectroscopy and MD simulations, Lim and co-workers¹¹ observed hydrogen bonding between water and anions at high LiTFSI concentrations, and they postulated the formation of nanometric water channels intertwined with ion networks, which served to promote lithium ion conduction. Subsequent MD simulations by the same group using a refined model found that the tendency to form extensive water networks was diminished, but strong hydrogen bonding was still observed.¹⁷ The n-AGGs have been observed in the 21 m LiTFSI aqueous electrolyte, known as the representative water-in-salt electrolyte (WiSE), using MD simulations, neutron scattering, and spectroscopic techniques.^{6,10,12,18} Generally, water-rich and ion-rich aggregates are observed in the electrolyte, as shown in Figure 2a.⁶ The exact nature of these aggregate structures in terms of size and shape is not completely understood.^{12,18}

An electrolyte is an essential component in all electrochemical storage and conversion devices such as batteries, and it intimately interacts with other components in the device.

Electrolytes with multivalent ions or charge-localized small ions have a higher tendency to form n-AGGs compared to the electrolytes with monovalent or charge-delocalized large ions. As shown in Figure 2b, n-AGGs with tens of ion pairs occur when the concentration of $Mg(BH_4)_2$ is greater than 0.1 M (mol/L) in tetrahydrofuran (THF), dimethoxyethane (DME/G1), diglyme (G2), triglyme (G3), and tetraglyme (G4), and electrolytes with shorter-chain solvents have higher agglomeration tendencies based on MD simulations.⁷ For redox-flow electrolytes, recent work using SAXS and MD simulations found that the typical redox-active organic molecules (redoxmers), consisting of heterocyclic redox cores with polar pendant groups, such as dialkoxyarene, tend to form extended domains through interactions of nonpolar groups, such as *tert*-butyl, in the molecular structure and the exclusion of solvents, as shown in Figure 2c.⁸ Long-range domains composed of 2,1,3-benzothiadiazole (BzNSN) have also been observed using SAXS and MD simulations.¹⁹ The n-AGG formation in this case is driven by the π – π stacking interactions between the BzNSN molecules and steric or volume exclusion at a short distance.

In a relatively low dielectric constant polymer medium, the electrostatic interaction between ions is stronger than the ion–solvent interactions, and this favors the formation of n-AGGs. The extended n-AGGs have been observed in ionomers (e.g., Na^+ -neutralized poly(ethylene-*co*-acrylic acid) (PEAA) ionomer) using MD simulations, as shown in Figure 2d.^{9,20} For

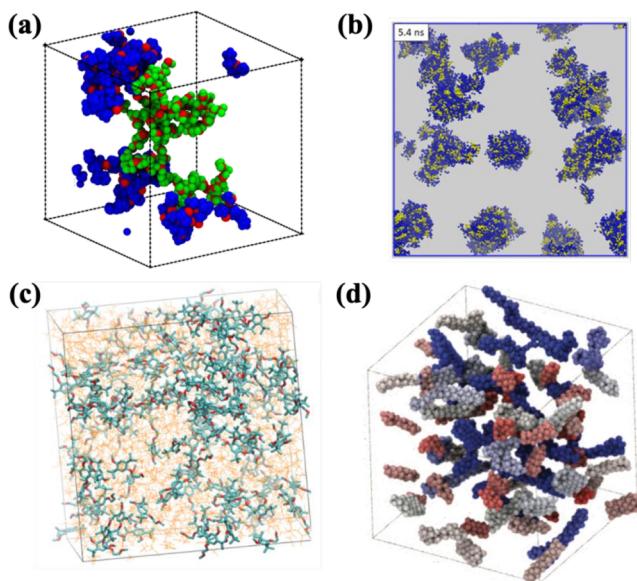


Figure 2. Nanometric AGGs in different electrolytes from MD simulations. Representative snapshot of (a) the largest water and ionic aggregates in 20 m LiTFSI in water⁶ (red, green, and blue balls denote Li ion, oxygen in water, and TFSI ion, respectively). Reprinted with permission from ref 6. Copyright 2020 American Chemical Society. (b) Salt aggregates in 0.4 M Mg(BH₄)₂ triglyme electrolyte⁷ (yellow and blue represent magnesium and boron, respectively, and solvent molecules are not shown for clarity). Reprinted with permission from ref 7. Copyright 2017 American Chemical Society. (c) Aggregates of 1 M dialkoxyarene redoxmer in acetonitrile⁸ (cyan, red, and orange denote carbon, oxygen, and solvent, respectively). Reprinted with permission from ref 8. Copyright 2020 American Chemical Society. (d) Long-range domains in ionomers with randomly spaced pendants⁹ with only charged beads and counterions (discrete aggregates are colored from red to white in order of increasing number of ions in the aggregate). Reprinted with permission from ref 9. Copyright 2012 American Chemical Society.

example, a lower fraction of ions was involved in the n-AGGs with the decrease of the charged bead density. Furthermore, the morphology and size of the n-AGGs were also found to vary with different locations (within or pendant to the backbone) and spacing between charged groups.⁹ Nanometric AGGs composed of hundreds of ions have also been found in LiTFSI poly(ethylene oxide) (PEO) electrolytes from an MD simulations study. Interestingly, the n-AGGs in these systems were found to carry negative charges, and the separated Li ions were solvated by PEO chains.²¹ Most recently, MD simulations predicted the formation of n-AGGs in electrolytes composed of LiTFSI or LiFSI salts in a dimethyl carbonate-terminated perfluorinated tetraethylene ether (i.e., C8-DMC); this was attributed to the poor solvating ability of the solvent.^{22,23} The examples discussed above show how n-AGGs structure can be commonly observed in both concentrated and low concentration electrolytes when the system is close to the solubility limit. In the context of battery electrolytes, increasing solution (salt or redoxmer) concentration is typically desirable because it corresponds to the increase of the charge carrier or active material concentrations. Next, we will discuss how these unique solvation structures impact the dynamical properties of the electrolytes.

Dynamics of n-AGGs. The dynamic properties of electrolytes are critical to the performance of batteries. High

ionic conductivity is needed for supporting the high current density required for fast charging or discharging rates. Ion motions in n-AGGs are expected to be strongly correlated; therefore, the transport does not simply obey the traditional theories as in conventional dilute liquid electrolytes. Exploring the effect of n-AGGs on ion dynamics is essential to understanding electrolyte performance. From the microscopic standpoint, cation diffusion has two components: vehicular and structural, as illustrated in Figure 3a. Vehicular motion represents an ion and its tightly bound solvation shell diffusing as one entity. It is usually considered the main ionic diffusion mechanism in dilute liquid electrolytes. Structural motion represents the diffusion of ions through successive ion dissociation/association exchange across different solvation shells. Although vehicular and structural motion often coexist, a particular electrolyte typically has one dominant diffusion mechanism. The characteristic diffusional length (L_{ij}^c) between the cation i and solvent or counterion j in the solvation shell determined by the self-diffusivity of cation i and the residence time of the solvent or counterion j in the first solvation shell is a useful metric to quantify the motion.²⁷ Large L_{ij}^c generally denotes more vehicular motion and vice versa. From the macroscopic standpoint, the diffusivity is typically quantified through the Einstein method, the conductivity can be estimated using the Nernst–Einstein relation, and the transference number can be calculated based on the self-diffusivity and charge of species to quantify the contribution of a given ionic species to the total electrical current of an electrolyte. These transport properties can be experimentally determined by pulsed-field-gradient (pfg) NMR, which neglects the correlated ion migration effects. However, binary diffusivities from the Maxwell–Stefan theory and Onsager theory begin to play a significant role in these transport properties at the concentrated regime where the ionic correlation cannot be ignored.²⁸ The correlated transport properties can be measured through advanced electrophoretic NMR-based (eNMR) analysis^{29–31} and a new method based on the concentrated solution theory.³²

Recently, nanometric aggregates have been observed in several classes of new electrolyte systems, including salt-concentrated electrolytes, ionic liquids, redox-flow electrolytes, multivalent electrolytes, and polymer electrolytes.

Ionic transport in salt-concentrated electrolytes (e.g., 4.12 M NaFSI–DME electrolyte) containing n-AGGs has been studied. Based on MD simulations, the coordinated ligand exchange at a time scale of tens of picoseconds is responsible for Na ion diffusion within n-AGGs, which implies that the ionic diffusion is dominated by structural motion as shown in Figure 3b.²⁴ In equimolar NaFSI sulfolane (SL) electrolytes, Na⁺ ions can diffuse through the exchange of the ligands (solvent and anion) via structural motion, which contributes to a high transference number (i.e., ~0.8).³³ In WiSE, ~20–40% Li ions are fully solvated by water molecules, which most likely diffuse via the vehicular motion as in the dilute condition due to the similarities in solvation structures.^{10,11,34} The dissociation of a Li ion from a TFSI anion in n-AGGs occurs faster than the break-up process of the n-AGGs, which implies Li

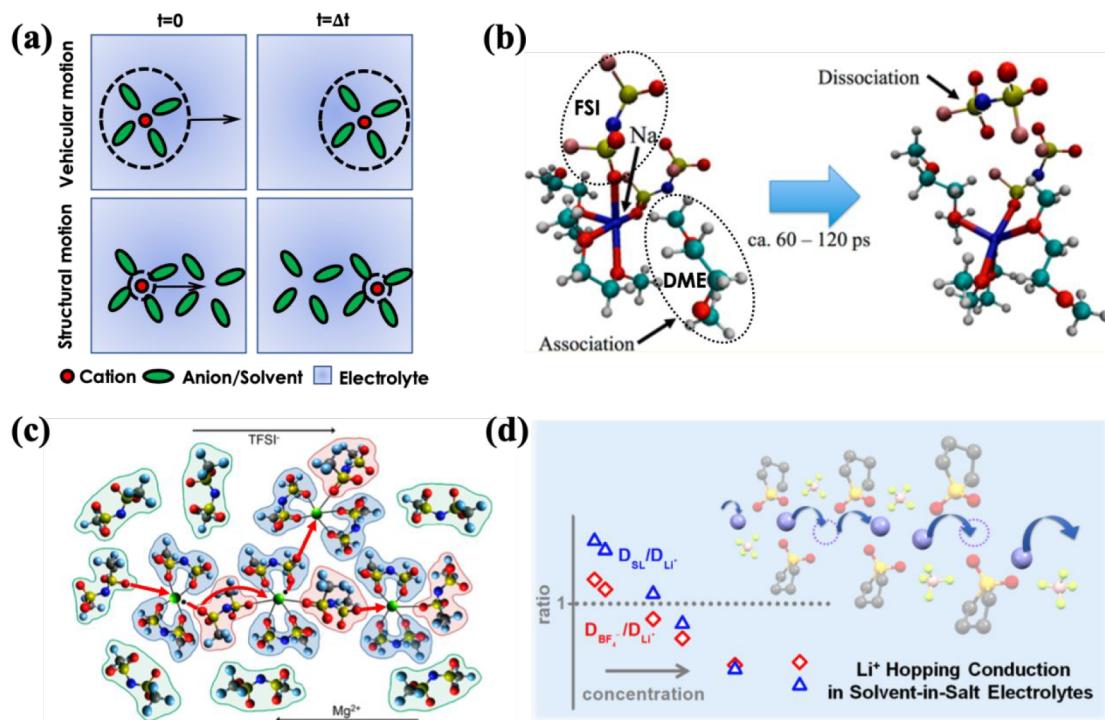


Figure 3. (a) Schematic of vehicular and structural motion from $t = 0$ (left panel) to $t = \Delta t$ (right panel). (b) Snapshot of the ligand exchange in 4.12 M NaFSI–DME electrolytes.²⁴ Initially, one Na ion is coordinated by two DME molecules and two FSI ions. After ca. 60–120 ps, one FSI ion from the initial solvation shell dissociates with the Na ion, and another DME molecule enters the solvation shell. Reprinted with permission from ref 24. Copyright 2018 American Chemical Society. (c) Structural motion in the Mg²⁺-IL electrolytes.²⁵ The red arrows indicate the ion dissociation and association process with the diffusion of Mg²⁺ ion. The black arrows indicate the overall direction of ion movement. Reprinted with permission from ref 25. Copyright 2014 American Chemical Society. (d) The ratios of self-diffusion coefficients of Li⁺ (D_{Li^+}), BF₄⁻ ($D_{BF_4^-}$), and sulfolane (D_{SL}) and the Li⁺ hopping conduction in solvent-in-salt electrolytes.²⁶ Reprinted with permission from ref 26. Copyright 2018 American Chemical Society.

ions can diffuse along with TFSI⁻ ions in n-AGGs via the structural motion in WiSE.⁶ In addition to the transport mechanistic studies, a Green–Kubo-based approach was developed to calculate a full Stefan–Maxwell diffusivity matrix³⁵ and define the correlated transference number³⁶ that accounts for the ionic correlation effect. The correlated transference number was found to be ~0.33 in 20 m LiTFSI WiSE electrolytes,⁶ in contrast to the uncorrelated transference numbers of ~0.65 and ~0.70 calculated using the Einstein method and measured by pfg-NMR experiments, respectively.^{6,10} The correlated transference number of ~0.33 is also much higher than that in the equimolar LiTFSI and G4 with a concentration of 4.5 m (i.e., ~0.06).³⁷ One possible explanation for this is the two heterogeneous domains formed in the WiSE electrolyte, n-AGGs and water-rich domains, with the latter corresponding to fast ionic conductivity,⁶ whereas in the equimolar LiTFSI and G4, all ions are in a similar solvation environment that is highly associated and correlated with the solvent. Other methods, such as those based on mutual diffusions, would also be useful for capturing the high correlation of ions in n-AGGs.^{35,38,39} This comparison illustrates that in some cases n-AGG formation could be beneficial for improving Li⁺ transport and transference number.

Transport in ionic liquid and multivalent electrolytes containing n-AGGs have also been studied. In Mg(TFSI)₂/Pyr₁₄TFSI electrolyte, the Mg ion was suggested to move via structural diffusion through exchange among the adjacent [Mg_n(TFSI)_m]^{(m-2n)-} clusters shown in Figure 3c,²⁵ while MD

simulations indicated a substantial vehicular contribution to Mg²⁺ transport due to long Mg-TFSI residence times that becomes even more pronounced if Mg²⁺ is replaced with Zn²⁺, which does not form n-AGGs at moderate metal cation concentrations.⁴⁰ Using MD simulations, the effects of n-AGGs on the diffusivity of cations in Mg(BH₄)₂-based electrolytes have been explored. The appearance of n-AGGs composed of Mg and BH₄ ions significantly reduces the self-diffusivity of Mg ions in the electrolytes. The motion of Mg ions is restricted within or around these n-AGGs. Given that the clusters are relatively immobile and surrounded by solvents, the local motion of the Mg ion barely contributes to long-range charge transport.⁷ In a representative alkali-metal ionic liquid-based electrolyte (i.e., Na[FSI]/[Pyr₁₃][FSI]), when the number ratio of Na and FSI ions is lower than 0.3, the drift of Na ions, with their negative solvation shells composed of FSI ions through vehicular motion, contributes to a small or even negative transference number. However, with increasing Na ions in the system, n-AGGs appear, and the diffusion of Na ions through the n-AGGs relies on the structural motion, which contributes to a positive and higher transference number of Na ions.³⁹ In highly concentrated LiBF₄ sulfolane electrolytes (SL/LiBF₄ ≤ 3), the diffusion of Li ions is faster than that of BF₄⁻ anions and SL solvent. Results from Raman spectra and MD simulations indicate that this faster diffusion of Li ions is due to the hopping conduction of the Li ion through the BF₄⁻ anion and the SL solvent functioning as ligands, as shown in Figure 3d.²⁶

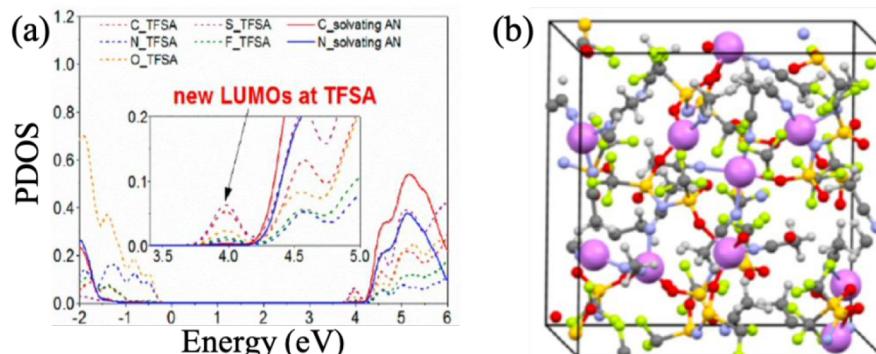


Figure 4. (a) Projected density of states (PDOS) and (b) representative snapshot calculated in *ab initio* MD simulations in 4.2 M LiTFSI acetonitrile electrolytes.⁴² Purple, dark gray, light gray, red, blue, yellow, and green balls represent Li, C, H, O, N, S, and F atoms, respectively. Reprinted with permission from ref 42. Copyright 2014 American Chemical Society.

The interchain and intrachain hopping transport mechanisms are well-known in polymer electrolytes. The high conductivity of the PEO system originates from a percolated network composed of O from PEO serving as solvation sites.⁴¹ When n-AGGs form in highly concentrated LiTFSI PEO electrolytes, the Li ions have a weaker correlation with the motion of the PEO chains, and Li ions coordinated only by TFSI ions are up to 40% less mobile than those coordinated by PEO chains.²¹ The conduction of Li ions as part of negatively charged aggregates will counteract the motion of the positively charged isolated Li ions, which contribute to the low or even negative transference number considering ionic correlation.²¹

Intuitively, ion motions in the n-AGGs are limited because the bulky aggregate structures are relatively immobile. The appearance of n-AGGs in electrolytes usually leads to the transition from vehicular to structural motion and slows down the diffusivity and decreases conductivity. However, the ultimate limiting current of the electrolytes is determined by transport properties beyond self-diffusion and ionic conductivity. Transference number, which is shown to be highly affected by the transport mechanism and ion correlation, is another important transport property that can be manipulated and offers a route to improving the energy and power density of the batteries. The effect of n-AGGs on the correlated transport properties is still not well understood.

Electronic, Mechanical, and Interfacial Properties. The n-AGGs in electrolytes can also affect their electronic, mechanical, and interfacial properties. The unique solvation structures of the ions in the n-AGGs result in changes to the orbital or band energies. For example, through the analysis of the projected density of states (PDOS) calculated in an *ab initio* MD simulation, a pioneering study by Yamada et al. found that the lowest unoccupied molecular orbital (LUMO) of the TFSI⁻, due to its unique solvation environment of interacting with multiple Li⁺, shifts to an energy level that is lower than that of the solvent, as shown Figure 4a.⁴² A similar shift of the LUMO has also been observed in a representative localized salt-concentrated electrolyte, 1.2 M LiFSI/DMC-BTFE, where the n-AGG structures are present.⁴³ As a result of lowered LUMO of anions, the reductive decomposition of salt occurs before the solvent, leading to the formation of the anion-derived solid electrolyte interphase (SEI), which was shown to reduce the interfacial resistance⁴⁴ and prolong the cycle life of a battery.⁴⁵ Similar observations have been made in other concentrated electrolytes such as LiTFSI in dimethyl sulfoxide.⁴⁶ The n-AGGs and the unique solvation structure

feature of anions coordinating with more than one cation can be clearly observed from the solution structure shown in Figure 4b. These examples highlight that the formation of n-AGGs changes the electronic structure and thus the redox stability of electrolyte components, resulting in a change in SEI composition.

The formation of n-AGGs can change the electronic structure and thus the redox stability of electrolyte components, resulting in a change in solid electrolyte interphase composition.

Since high mechanical strength is one of the key performance metrics for using a polymer as a solid-state electrolyte to enable Li metal anodes, n-AGG–rheology relationships in polymer electrolytes have attracted research attention. The effects of the n-AGGs on stress relaxation and uniaxial tensile deformation have been investigated using coarse-grained MD simulations.⁴⁷ Specifically, with the decrease of the spacing of ions along the chain, the morphology of the electrolyte transitions from discrete small aggregates to percolated n-AGGs. The n-AGGs in the system make ion rearrangements facile, thus reducing the relaxation time of chains, which in turn results in low viscosity. However, the n-AGGs increase the overall cohesion of the material; therefore, the mechanical strength increases, especially at high strain rates.⁴⁷ The coarse-grained MD simulations showed that the rheological properties of polymer electrolytes are affected by the size and shape of n-AGGs, which can be tailored by changing the spacing and position of ions along the polymer chain.

The interfacial studies on electrolytes with n-AGGs have mainly focused on structural changes near the interface including the electric double layer (EDL), although they have not considered possible electrochemical reactions that could occur in batteries. Using ultramicroelectrode measurements and potential-dependent atomic force microscopy (AFM), it was found that at the interface of WiSE and gold, [Li(H₂O)_x]⁺[TFSI]⁻_y ion pairs can accumulate at positive potentials within a 6.4–6.7 Å layer, while [Li(H₂O)_x]⁺ is enriched at negative potentials, forming a 2.8–3.3 Å layer, as illustrated in Figure 5a. This observation is consistent with the vibrational spectroscopy showing that anions and cations within hydration shells are enriched at positive and negative

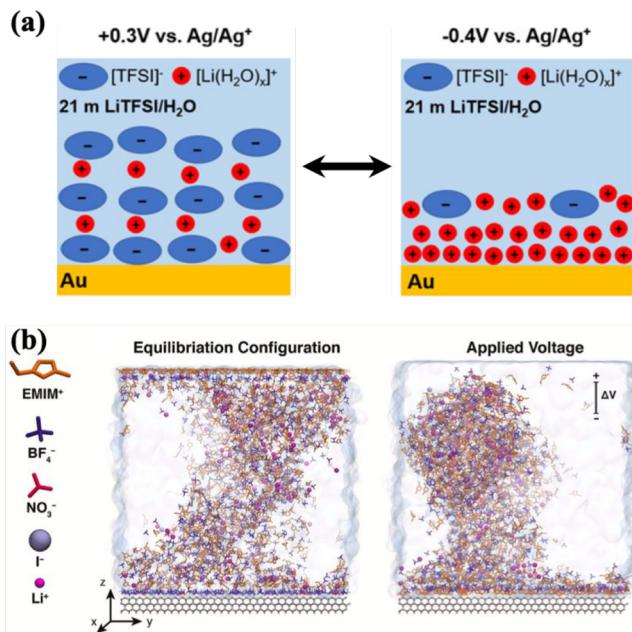


Figure 5. (a) Schematic of a double layer of WiSE at surfaces applied with different potentials.⁴⁸ Reprinted with permission from ref 48. Copyright 2020 American Chemical Society. (b) Representative snapshot of Li–O₂ electrolytes (1 M LiI, 1 M LiNO₃, and 0.2 M O₂ in [EMIM][BF₄]/TEGDME (vol:25/75)) at the interface with or without external voltage bias. The solvent molecules (TEGDME) are not shown for clarity.⁴⁹ Reprinted with permission from ref 49. Copyright 2021 Elsevier.

potentials, respectively.⁴⁸ The nanoheterogeneity of a WiSE electrolyte close to a negatively charged mica surface was studied using combined surface force measurements and AFM.⁵⁰ It was found that various nanostructures with the size range of 1.0–6.0 nm coexist in the WiSE electrolyte, whose size increases with concentration. However, close to the surface, the structural size is less dependent on concentration, revealing the significant influence of the surface on the nanostructure.⁵⁰ A recent study used synchrotron X-rays to produce electrons at the solid/electrolyte interface to mimic reductive environments and simultaneously probe the structure of surface films to monitor the decomposition products of LiTFSI WiSE electrolyte. It was found that the primary decomposition product at the interface is LiF, consistent with the reaction mechanisms of contact ion-pairs, while the decomposition product of water was not observed.⁵¹ This work provided indirect evidence that the salt-rich solvation structure dominates near the interfaces. In a recent study of the Li–O₂ battery, it was found that, when an external voltage bias is applied, the n-AGGs in the electrolyte (i.e., 1 M LiI, 1 M LiNO₃ in [EMIM][BF₄]/TEGDME (vol: 25/75)) with 0.2 M dissolved O₂ become more extended in the EDL due to the reorientation and rearrangement of the electrolyte with the electric field (see Figure 5b). Since O₂ has a high tendency to stay in the solvent-rich domain, the reorientation and rearrangement of the n-AGGs modify the accessibility of the O₂ at the reactive interface.⁴⁹ These examples demonstrate that n-AGGs play an especially strong solvation structure-directing role at electrified interfaces. This affords a potentially powerful design tool that can be used to control the accessibility of specific species to the electrode surface and thus control critical interfacial properties such as charge-transfer kinetics

and electrochemical stability. Understanding the degree to which these properties can be manipulated represents a key research opportunity for n-AGG electrolytes.

Outlook. Computational and experimental studies have shed light on the structures of n-AGGs and their influence on physicochemical properties of electrolytes. Nevertheless, there is much that is still not understood about the structure–property relationships of electrolytes with n-AGGs. For example, the exact morphology of the n-AGGs (e.g., domain, channel, and chain-like small aggregates) in WiSE is under debate,^{6,10,11,18} which ultimately affects the contributions of the different aggregate structures to the overall ionic transport properties. In nonaqueous organic redox-flow development, most studies thus far focused on the materials and electrochemical studies at millimolar concentrations. The effects of the n-AGGs on the electrochemical and transport properties of redoxmers and conducting ions at technologically more relevant concentrations (>1 M) will need to be elucidated to ultimately allow the design (e.g., redox molecules with functional groups that encourages or discourages aggregation) and optimization (e.g., choice of salt and concentrations) of the system. Meanwhile, there have only been a small number of studies of n-AGGs at interfaces where they can have a significant effect on the structure of the EDL, ion desolvation processes, and irreversible decomposition of the electrolyte, as well as the formation mechanism, composition, and structure of the resultant SEI. In addition, in the case of chemical transformation batteries based on precipitation–dissolution chemistries such as Li–O₂ and Li–S, little is known as to how n-AGGs may affect the charge and discharge reactions at the interfaces. A recent simulation study of Li–S electrolytes showed clustering and aggregation of the polysulfide reaction intermediates in localized high-concentration electrolytes, which we speculate to be responsible for the quasi-solid-state reaction mechanism observed previously.^{52,53} Smart design of electrolytes to control the aggregation of reaction intermediates might provide a viable path to optimize precipitation–dissolution reactions; the intermediate species will stay relatively immobile near the electrode surface while avoiding forming large solid-state particles, helping to improve the reaction kinetics. Finally, there is a need to establish the design principles to control n-AGGs formation so they can be avoided or targeted to improve the performance of the battery electrolytes. Since the next-generation electrolytes will be expected to meet multiple performance metrics simultaneously, including fast ionic conductivity, high chemical/electrochemical stability, etc., understanding and controlling how n-AGGs affect various properties in the bulk and at the interfaces becomes imperative.

Future studies of this emerging field require the development of experimental and computational tools to better characterize and manipulate these aggregate structures to take advantage of their unique properties.

Advanced molecular and experimental techniques can help to provide a new understanding of the effect of n-AGGs on electrolyte properties. In the computational field, the accuracy of potential energy functions and the efficiency of simulations

are two key points for advanced MD simulations. Although MD simulations with generic force fields can often capture the basic physics of these electrolytes, there are still some well-known limitations. The development of the machine learning force field breaks the dilemma of accuracy versus efficiency to some extent.^{54–57} Enhanced sampling in MD simulations, such as umbrella sampling, metadynamics, etc., is an effective way to accelerate the thermodynamics calculation through adding bias potentials to the Hamiltonian.⁵⁸ These methods will be very useful for n-AGGs studies. Furthermore, explaining the macroscopic transport properties, especially the negative transference number in the electrolytes with n-AGGs through theoretical derivation from the Maxwell–Stefan theory, is an emerging research hotspot.

Recent experimental advances will provide a better understanding of the role of n-AGGs on electrolyte structural and transport properties. For example, conventional SAXS and SANS lack elemental specificity in terms of identifying the ionic species present in the n-AGGs. The use of resonant SAXS⁵⁹ or a combination of SAXS and SANS can provide elemental specificity and offer the prospect to obtain more detailed insight into the n-AGGs structures that can be directly compared to MD simulations. From the transport perspective, X-ray photon correlation spectroscopy (XPCS) is an emerging technique that has been shown to probe transport properties in polymer electrolytes,⁶⁰ with future time scales potentially reaching down below a microsecond. XPCS of the n-AGGs may provide data on the dynamics of the domain fluctuations, which are intimately tied to the transport properties.

AUTHOR INFORMATION

Corresponding Authors

Lei Cheng – Joint Center for Energy Storage Research (JCESR) and Materials Science Division, Argonne National Laboratory, Lemont, Illinois 60439, United States; orcid.org/0000-0002-3902-1680; Phone: +1-630-252-8377; Email: leicheng@anl.gov

Larry A. Curtiss – Joint Center for Energy Storage Research (JCESR) and Materials Science Division, Argonne National Laboratory, Lemont, Illinois 60439, United States; orcid.org/0000-0001-8855-8006; Phone: +1-630-252-7380; Email: curtiss@anl.gov

Authors

Zhou Yu – Joint Center for Energy Storage Research (JCESR) and Materials Science Division, Argonne National Laboratory, Lemont, Illinois 60439, United States; orcid.org/0000-0003-3316-4979

Nitash P. Balsara – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States; Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0002-0106-5565

Oleg Borodin – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Battery Science Branch, Energy Science Division, Sensor and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland 20783, United States; orcid.org/0000-0002-9428-5291

Andrew A. Gewirth – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont,

Illinois 60439, United States; Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States; orcid.org/0000-0003-4400-9907

Nathan T. Hahn – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Material, Physical and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States; orcid.org/0000-0001-6187-4068

Edward J. Maginn – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States; orcid.org/0000-0002-6309-1347

Kristin A. Persson – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; Department of Materials Science, University of California, Berkeley, California 94720, United States; orcid.org/0000-0003-2495-5509

Venkat Srinivasan – Joint Center for Energy Storage Research (JCESR) and Argonne Collaborative Center for Energy Storage Science, Argonne National Laboratory, Lemont, Illinois 60439, United States; orcid.org/0000-0002-1248-5952

Michael F. Toney – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309, United States; orcid.org/0000-0002-7513-1166

Kang Xu – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Battery Science Branch, Energy Science Division, Sensor and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland 20783, United States

Kevin R. Zavadil – Joint Center for Energy Storage Research (JCESR), Argonne National Laboratory, Lemont, Illinois 60439, United States; Material, Physical and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, New Mexico 87185, United States; orcid.org/0000-0002-3791-424X

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsenergylett.1c02391>

Notes

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

The authors declare no competing financial interest.

Biographies

Zhou Yu was a postdoctoral appointee at Argonne National Laboratory before moving to Los Alamos National Laboratory in November 2021. His research interests focus on understanding and predicting physicochemical properties of advanced energy materials using simulation and theory-driven approaches.

Nitash P. Balsara is the Charles W. Tobias Professor in the College of Chemistry at UC Berkeley. His research interests lie at the interface between polymer science and electrochemistry.

Oleg Borodin is a scientist in the Electrochemistry Branch of the Army Research Laboratory. His research interests are multiscale modeling of materials for energy storage applications such as batteries and capacitors.

Andrew A. Gewirth is the Peter C. and Gretchen Miller Markunas Professor in the Department of Chemistry at the University of Illinois at Urbana–Champaign. His research interests are in the study of the structure and reactivity of surfaces and interfaces.

Nathan T. Hahn is a scientist at the Material, Physical and Chemical Sciences Center at Sandia National Laboratories. His research interests include various aspects of materials synthesis and characterization for electrochemical applications.

Edward J. Maginn is the Keough-Hesburgh Professor in the Department of Chemical and Biomolecular Engineering at the University of Notre Dame. His research interests focus on developing a fundamental understanding of the link between the physical properties of materials and their chemical constitution.

Kristin A. Persson is a Professor in Materials Science and Engineering at UC Berkeley with a joint appointment as Faculty Staff Scientist at Berkeley Lab. Her research interests include materials in extreme pH environments, novel multivalent electrode and electrolyte materials, novel photocatalysts for water splitting and CO₂ reduction, and new polar materials.

Venkat Srinivasan is the director of the Argonne Collaborative Center for Energy Storage Science and deputy director of the Joint Center for Energy Storage Research. He is interested in moving technologies to market, focused on batteries, to accelerate technology commercialization.

Michael F. Toney is a Professor in the Department of Chemical and Biological Engineering at the University of Colorado Boulder. His research interests focus on incisively characterizing and understanding the physics and chemistry that underlie the functioning of materials for sustainable energy as well as synthesis pathways.

Kang Xu is currently a Lab Fellow and Team Leader at the U.S. Army Research Laboratory and an Adjunct Professor at the University of Maryland. His research interests focus on synthesis and characterization of electrolyte materials and fundamental understanding of chemistries, dynamics, and kinetics of electrode/electrolyte interphases.

Kevin R. Zavadil is a Distinguished Member of the Technical Staff in the Material, Physical and Chemical Science Center at Sandia National Laboratory. His current research interests include solvation structure, interfacial speciation, and electrode interphase forming reactivity of electrolytes for rechargeable multivalent metal ion batteries.

Larry A. Curtiss is a Distinguished Fellow at Argonne National Laboratory. His research interests are in the development of new quantum chemical methods and their applications to understanding and discovery of new materials. (<https://www.anl.gov/profile/larry-a-curtiss>)

Lei Cheng is a chemist in the Materials Science Division at Argonne National Laboratory. Her research interests include first-principles computational studies of energy storage materials and heterogeneous catalysis. (<https://www.anl.gov/profile/lei-cheng>)

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