

The Solvation Structure of Localized High Concentration Electrolytes

Wessel van Ekeren,^[a] Aram Hall,^[a] Katja Lahtinen,^[a] and Reza Younesi^{*,[a]}

The development of liquid electrolytes receives significant attention within the field of battery research. New concepts are emerging, and one of these groundbreaking ideas is localized high concentration electrolytes (LHCEs). The fundamental characteristic of this type of electrolyte is related to its solvation structure. However, despite the progress made, the solvation process and its relationship towards physicochemical and electrochemical properties are not yet fully understood. A

comprehensive understanding of LHCEs and their solvation structure requires further dedicated research and analysis. This concept review offers a thorough examination of the design principles governing LHCEs, elucidates methodologies for investigating solvation structures, connects these insights to interphase chemistry, and explores potential applications in future battery technology.

Introduction

Since the development of liquid electrolytes for rechargeable batteries, various solutions have been created to target different optimizations such as enhanced electrochemical performance, safety or stability versus metallic anodes. The solutions range from aqueous to non-aqueous and from dilute to high concentration liquid electrolytes. A different categorization could also be done based on the differences in the solvation structure, ranging from weak to strong solvating electrolytes.^[1] Investigating the impact of salt concentration and different solvents on both physicochemical and electrochemical properties has therefore become a focal point of research. The concept of high concentration electrolytes (HCEs) was for the first time demonstrated to prevent solvent co-intercalation in graphite,^[2] after which its use has been applied to different battery chemistries, and also to stabilize non-flammable alkyl phosphate based electrolytes.^[3] For non-aqueous liquid electrolytes, the threshold salt concentration to obtain a high concentration electrolyte is typically ~3.0 M, even though a strict definition does not exist.^[4] Above this concentration, the electrolyte solution is considered to be in the super-concentrated regime.^[5] However, such high salt concentrations have limited practical use because of high cost, high viscosity, sluggish kinetics, and poor wettability toward electrodes and separators.^[6] Therefore, a relatively new concept of localized high concentration electrolytes (LHCEs) was introduced by Zhang et. al.^[7] First, a high concentration of salt is dissolved in a (non-)aqueous solvent and subsequently a diluent is added to the HCE. From the solution point of view, the diluent is

considered to be inert to the solvation structure of the HCE. Such a diluent ideally should (1) have minimal salt solubility, (2) be miscible with the main electrolyte solvent, (3) be compatible with electrodes and (4) have lower costs than the main solvent and (5) contribute to enhanced electrolyte safety.^[8] Similar to the progress in non-aqueous liquid electrolytes, researchers have explored the use of a high concentration of salt in aqueous batteries, a concept which is known as Water-in-Salt (WIS).^[9] This type of electrolyte uses excessive amounts of salt, akin to HCE, and has similar drawbacks with the latter. Nevertheless, the primary advantage of WIS effectively mitigates parasitic reactions associated with water decomposition, thereby reducing hydrogen evolution. To overcome the drawbacks of WIS-like electrolytes, LHCEs have also been successfully studied in aqueous systems.^[10] There are reviews discussing the application of LHCEs in different battery chemistries and the impact of the electrolyte solvation structure on electrochemical performance,^[1,11] but here the focus is on the understanding of localized high concentration electrolytes and methods to fundamentally study their solvation structure. An overview of the development of highly concentrated electrolytes toward localized highly concentrated electrolytes is shown in Figure 1. Even though LHCEs are a promising type of liquid electrolyte to stabilize several battery chemistries, some challenges still exist. First of all, the LHCEs solvation structure and its relation to physicochemical and electrochemical properties is not fully understood. Secondly, the main diluents are limited to hydrofluoroethers and other non-fluorinated diluents are still unexplored. Light will be shed on the theory of LHCEs, the importance of understanding the solvation structure in relation to physicochemical and electrochemical properties and the future field development. Hereby it can be seen as a guide for rational electrolyte design to enhance electrochemical performance by tuning the solvation structure.

[a] W. van Ekeren, A. Hall, K. Lahtinen, R. Younesi
Department of Chemistry – Ångström Laboratory, Uppsala University, Box
538, SE-751 21 Uppsala, Sweden
E-mail: reza.younesi@kemi.uu.se

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scopy is commonly employed to investigate the local vibration mode of molecules. The components of the solvation structure, *i.e.* anions, cations and (coordinated vs. uncoordinated) solvent molecules all differ in their bend, twist or stretch vibrations. The Raman spectrum of liquid electrolytes shows that the characteristic peak for free and solvent separated anions (SSIPs) may shift to a higher wavenumber when the anion is coordinated to one or multiple cations to form contact ion pairs (CIPs), or at higher salt concentrations even aggregates (AGGs).^[20,21] A standard Raman spectrum showing the impact of salt concentration and diluents on the formation of CIPs (cation-anion) and AGGs is illustrated in Figure 3 a). Here, it is shown that an increase in salt concentration results in higher amounts of coordinated dimethyl carbonate (DMC, 940 cm^{-1}) and stronger cation-anion interaction (720 cm^{-1} in 1.2 M blue shifted to 760 cm^{-1} in 5.5 M). The addition of the diluent (bis(2,2,2-trifluoroethyl) ether, BTFE) does not affect the DMC and BTFE coordination, but does weaken the cation-anion interaction, which explains the enhanced ionic conductivity and kinetic properties of LHCEs. However, care should be taken in analyzing the Raman spectra, since often only a limited range of wavenumbers are shown, whereby crucial information of overlapping peaks might be hidden, resulting in incomplete insights in the solvation structure. For instance, in a study of Yamada *et. al.* the abundance of free bis(fluorosulfonyl)imide (FSI⁻) anions was indicated by a vibration peak around 717 cm^{-1} .^[22] This peak is blue shifted to 730 cm^{-1} if the anions form CIPs and AGGs. However, since liquid electrolytes are getting more complicated due to the addition of multiple solvents and additives, the distinction of characteristic peaks becomes problematic. For instance, the flame retardant solvent triethylphosphate has a characteristic stretching P–O(C) peak around the same wavenumber as anion clusters of FSI⁻ (730 cm^{-1}). Therefore, the formation of CIPs and AGGs cannot be indicated in this

electrolyte and thus other techniques, such as FTIR or NMR, need to be used to provide more detailed insights.^[8]

Similar to Raman spectroscopy, FTIR is typically utilized for exploring the local vibrational characteristics of molecules. FTIR is a technique with rapid time scales, which allows a greater understanding of the solvation structure in terms of coordinated and uncoordinated solvents as well as providing insights into the solvation number (coordination number).^[23] In a study by Becht *et. al.* insights were shown on LiPF₆ in different carbonate solvents (propylene carbonate (PC), DMC and diethyl carbonate (DEC)).^[24] The information obtained from FTIR spectroscopy is similar to Raman spectroscopy, as can be seen in Figure 3 c) for a HCE and d) for a LHCE. In both FTIR spectra the characteristic peak around 1725 cm^{-1} is deconvoluted to show the characteristic peaks for solvated and free solvent molecules. Again, as for Raman Spectroscopy, it should be noted that meaningful deconvolution is critical for some solvents due to overlapping stretching bands. This issue seems more pronounced in FTIR compared to Raman spectroscopy. To further elucidate the solvation structure (more specifically the solvation number), NMR spectroscopy was applied.

The high-speed capability of FTIR spectroscopy allows us to distinguish between separate absorptions for uncoordinated and coordinated solvents. However, in the realm of NMR spectroscopy, the time scale is slower, and the exchange of solvents coordinated to cations occurs more rapidly than the NMR time scale can capture. The main advantage of NMR is to study the environment of different nuclei and observing clear chemical shifts when for instance salt concentrations are increased, solvent ratios are changed, or additives are added. NMR can be a complementary technique to analyze the surroundings of specific elements in the solvation structure (*i.e.* ⁷Li, ¹³C, ¹⁷O, ¹⁹F, ²³Na, ³¹P *etc.*). Hereby, the chemical shift of the nuclei upon changing for instance salt concentration or addition of additives provides information about the interactions in the solvation sheath (cation-solvent, anion-solvent, *etc.*). Usually, a co-axial tube is used to separate the reference solution, usually a deuterated solvent, from the electrolyte solution to prevent interaction with the solvation sheath. To gain understanding of the solvent chemistry mostly ¹H and ¹³C nuclei are studied. Especially in electrolytes with carbonate based solvents ¹³C can be useful to analyze the carbonyl group, which shows downfield chemical shifts upon enhanced coordination.^[25] Depending on the type of solvent, and especially for non-flammable solvents based on fluorine and phosphates, other nuclei can also provide insights, using respectively ¹⁹F and ³¹P NMR. The environment around the cation can be studied by analysing the cation nuclei, for instance ⁷Li, ²³Na or ³⁹K NMR. To study the solvent the main solvation interaction in liquid electrolytes ¹⁷O-NMR is powerful because it can provide information about the direct interaction of usually a double bonded oxygen of the solvent (*e.g.* carbonyl group in carbonate solvents) and the cation. However, ¹⁷O is a nucleus with a low NMR sensitivity bandwidth and a low abundance (0.038%), displaying lines over a very wide chemical shift range and requiring long sampling times.^[26] In light of progress in NMR technology, the attainment of reliable and

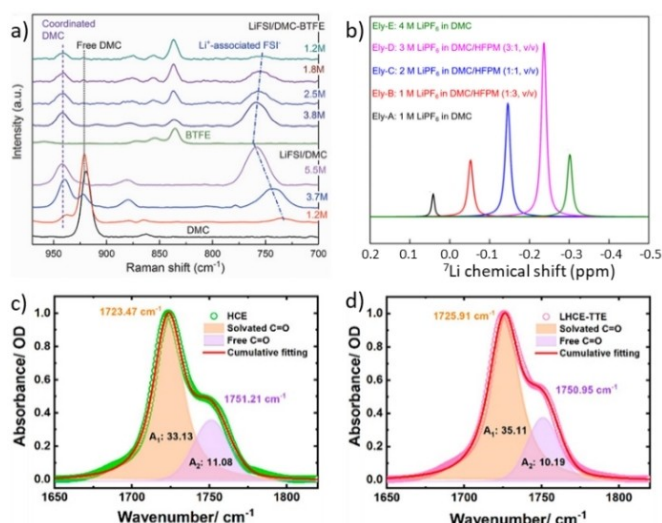


Figure 3. Typical spectra obtained to study solvation structure with a) Raman Spectroscopy, b) ⁷Li NMR, c) and d) FTIR. Figure reprinted with permission.^[6,7,27] Copyright 2018 John Wiley and Sons and Copyright 2022 American Chemical Society.

faster processing outcomes from non-enriched samples has become achievable due to high resolution NMR and could be promising in future research. Also, 2D NMR can determine correlations of bonds further from the first solvation shell, which could potentially provide information about the interaction of diluents (second solvation shell).

Another way to study the solvation structure, more focused on a global understanding of the liquid electrolyte structure, are SAXS and wide-angle X-ray scattering (WAXS). Though less frequently used SAXS has the capability to provide more comprehensive insights into the overall structure of the generated clusters and aggregates.^[12] This technique is capable of detecting the molecular distances of electrolyte components in the entire sample. The spacing between the anion clusters can be understood as a function of the salt concentration. Upon increasing the salt concentration, the distance between anions and anion clusters is usually shortened, and is indicated by a decreased q value (inverse of molecular distance \AA^{-1}). The measured q value can be related to the d spacing of the anion clusters according to $d = 2\pi/q$.^[12] The anion spacing can provide useful information with regards to the interactions within specific types of solvation take place and distinguish between SSIPs, CIPs and AGGs. It has been argued that deeper understanding of the formation of clusters can be identified with SAXS, where unreliable results may be obtained when fully relying on the peak position of Raman spectra.^[28] The Raman spectra are highly reliable for local coordination states, but does not provide direct information for long range order structures (formation of AGGs).

Ideally the techniques mentioned above are combined with computational studies to confirm certain interactions observed experimentally. Molecular level details of the solvation structure of liquid electrolytes can be addressed by computational studies, such as density functional theories (DFT) and *ab initio* molecular dynamics (MD).^[29] MD simulations are powerful to determine the bulk structures of electrolytes, such as cation solvation sheaths and the presence of free ions, SSIPs, CIPs and AGGs. Where MD might allow the generation and analysis of a large amount of different chemistries and configurations, the classical force fields used are failing in providing accurate descriptions of more complex systems because of non-standard interactions. Therefore, simulation results need further experimental verification. Also, DFT has recently attracted much attention, which allows for more precise descriptions of electronic structures and thus interactions between cations and anions.^[30] Even though DFT calculations can provide high-accuracy atomic- and molecular-level interactions, they are limited in probing electrolyte solvation structures due to high costs and limited size of the models. Nevertheless, the complementary use of computational studies is of utmost importance in order to understand specific interactions of components of the solvation structure. The effect of additives on the solvation structure, even though the amounts are typically rather limited, still can have a significant effect on the solvation structure. This was shown in an extensive study by Persson et. al.^[13] Here the effect of the SEI forming additive FEC (10 wt.%) on the solvation structure was investigated in the

rather standard LiPF_6 in EC electrolyte. It was shown that, using molecular dynamics, quantum chemical calculations, and FTIR measurements, the coordination number (CN) of FEC and cation Li^+ was varying between 5–6, slightly bigger than the previously advocated CN of 4. Also, the coordinated FEC-Li^+ has a 0.3 V higher reduction potential compared to the uncoordinated FEC, which has a similar reduction potential as EC-Li^+ . So, without understanding the solvation effect of the additive, the early onset of SEI formation would not be understood. It is important to consider that even small concentrations of additives might already alter the electrolyte solvation structure and thereby the reduction potential and SEI.

Future Field Development: Opportunities and Challenges

The solvation structure of localized high concentration electrolytes is the key element of their concept. The understanding of the solvation structure is gaining more and more attention, especially in relation with the interphase chemistry. However, care has to be taken when interpreting experimental results, especially when peaks of spectroscopy are overlapping. So, it is important to understand the limitations of each technique and how complementary techniques (both experimental, as well as computational studies) should be applied to understand the fundamentals of the solvation structure. The choice of method to analyze the solvation structure must be decided based on the evaluation of the electrolyte components. The solvation structure can be studied as bulk property, where the focus is on solvent-ion and solvent-solvent interactions. A combination of techniques, such as experimental and computational, is required to provide detailed insights in the solvation structure and link it to electrochemical performance. Even though consensus seemed to be reached about the solvation structure of LHCEs, future work should be done to provide more detailed insights on how the interactions take place between anions, cations and solvents. In particular the effect of new types of diluents and their correlation to the electrolytes' electrochemical properties are interesting avenues to optimize the solvation structure. Also, neutron diffraction of liquid electrolytes is a promising technique which could provide insights on the environment of specific nuclei. The techniques and theory described in this concept review provides pitfalls and pathways to apply the concept of solvation structure and LHCEs to further electrolyte development, as well as fundamental understandings of interfacial chemistries.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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- [1] P. Xiao, X. Yun, Y. Chen, X. Guo, P. Gao, G. Zhou, C. Zheng, *Chem. Soc. Rev.* **2023**, *52*, 5255–5316. <https://doi.org/10.1039/d3cs00151b>.
- [2] W. R. McKinnon, J. R. Dahn, *J. Electrochem. Soc.* **1985**, *132*, 364–366. <https://doi.org/10.1149/1.2113839>.
- [3] R. Gond, W. van Ekeren, R. Mogensen, A. J. Naylor, R. Younesi, *Mater. Horiz.* **2021**, *8*, 2913–2928. <https://doi.org/10.1039/D1MH00748C>.
- [4] G. A. Giffin, *Nat. Commun.* **2022**, *13*, 1–6. <https://doi.org/10.1038/s41467-022-32794-z>.
- [5] O. Borodin, J. Self, K. A. Persson, C. Wang, K. Xu, *Joule* **2020**, *4*, 69–100. <https://doi.org/10.1016/j.joule.2019.12.007>.
- [6] F. Ren, Z. Li, J. Chen, P. Huguet, Z. Peng, S. Deabate, *ACS Appl. Mater. Interfaces* **2022**, *14*, 4211–4219. <https://doi.org/10.1021/acsami.1c21638>.
- [7] S. Chen, J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, J. G. Zhang, *Adv. Mater.* **2018**, *30*, 1–7. <https://doi.org/10.1002/adma.201706102>.
- [8] W. W. A. van Ekeren, M. Albuquerque, G. Ek, R. Mogensen, W. R. Brant, L. T. Costa, D. Brandell, R. Younesi, *J. Mater. Chem. A* **2023**, *11*, 4111–4125. <https://doi.org/10.1039/D2TA08404J>.
- [9] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, *Science* **2015**, *350*, 938–943. <https://doi.org/10.1126/science.aab1595>.
- [10] S. Chen, Q. Nian, L. Zheng, B. Q. Xiong, Z. Wang, Y. Shen, X. Ren, J. Mater. Chem. A **2021**, *9*, 22347–22352. <https://doi.org/10.1039/d1ta06987j>.
- [11] Z. Tian, Y. Zou, G. Liu, Y. Wang, J. Yin, J. Ming, H. N. Alshareef, *Adv. Sci.* **2022**, *9*, 1–29. <https://doi.org/10.1002/advs.202201207>.
- [12] K. Qian, R. E. Winans, T. Li, *Adv. Energy Mater.* **2021**, *11*, 1–22. <https://doi.org/10.1002/aenm.202002821>.
- [13] T. Hou, G. Yang, N. N. Rajput, J. Self, S. W. Park, J. Nanda, K. A. Persson, *Nano Energy* **2019**, *64*, 103881. <https://doi.org/10.1016/j.nanoen.2019.103881>.
- [14] Y. Yamada, A. Yamada, *J. Electrochem. Soc.* **2015**, *162*, A2406–A2423. <https://doi.org/10.1149/2.0041514jes>.
- [15] D. Brouillette, D. E. Irish, N. J. Taylor, G. Perron, M. Odziemkowski, J. E. Desnoyers, *Phys. Chem. Chem. Phys.* **2002**, *4*, 6063–6071. <https://doi.org/10.1039/b203776a>.
- [16] X. Ren, S. Chen, H. Lee, D. Mei, M. H. Engelhard, S. D. Burton, W. Zhao, J. Zheng, Q. Li, M. S. Ding, M. Schroeder, J. Alvarado, K. Xu, Y. S. Meng, J. Liu, J. G. Zhang, W. Xu, *Chem* **2018**, *4*, 1877–1892. <https://doi.org/10.1016/j.chempr.2018.05.002>.
- [17] K. Xu, Y. Lam, S. S. Zhang, T. R. Jow, T. B. Curtis, *J. Phys. Chem. C* **2007**, *111*, 7411–7421. <https://doi.org/10.1021/jp068691u>.
- [18] X. Cao, P. Gao, X. Ren, L. Zou, M. H. Engelhard, B. E. Matthews, J. Hu, C. Niu, D. Liu, B. W. Arey, C. Wang, J. Xiao, J. Liu, W. Xu, J. G. Zhang, *Proc. Natl. Acad. Sci. USA* **2021**, *118*, 1–9. <https://doi.org/10.1073/pnas.2020357118>.
- [19] Y. S. Hu, H. Pan, *ACS Energy Lett.* **2022**, *7*, 4501–4503. <https://doi.org/10.1021/acseenergylett.2c02529>.
- [20] D. W. James, R. E. Mayes, *J. Phys. Chem.* **1984**, *88*, 637–642. <https://doi.org/10.1021/j150647a058>.
- [21] J. S. Daubert, T. Afroz, O. Borodin, D. M. Seo, P. D. Boyle, W. A. Henderson, *J. Phys. Chem. C* **2022**, No. ii. <https://doi.org/10.1021/acs.jpcc.2c03805>.
- [22] Y. Yamada, M. Yaegashi, T. Abe, A. Yamada, *Chem. Commun.* **2013**, *49*, 11194–11196. <https://doi.org/10.1039/c3cc46665e>.
- [23] K. D. Fulfer, D. G. Kuroda, *J. Phys. Chem. C* **2016**, *120*, 24011–24022. <https://doi.org/10.1021/acs.jpcc.6b08607>.
- [24] D. M. Seo, S. Reiningger, M. Kutcher, K. Redmond, W. B. Euler, B. L. Lucht, *J. Phys. Chem. C* **2015**, *119*, 14038–14046. <https://doi.org/10.1021/acs.jpcc.5b03694>.
- [25] L. Yang, A. Xiao, B. L. Lucht, *J. Mol. Liq.* **2010**, *154*, 131–133. <https://doi.org/10.1016/j.molliq.2010.04.025>.
- [26] J. Peng, L. Carbone, M. Gobet, J. Hassoun, M. Devany, S. Greenbaum, *Electrochim. Acta* **2016**, *213*, 606–612. <https://doi.org/10.1016/j.electacta.2016.07.144>.
- [27] Y. Wu, A. Wang, Q. Hu, H. Liang, H. Xu, L. Wang, X. He, *ACS Cent. Sci.* **2022**, *8*, 1290–1298. <https://doi.org/10.1021/acscentsci.2c00791>.
- [28] K. Qian, S. Seifert, R. E. Winans, T. Li, *Energy Fuels* **2021**, *35*, 19849–19855. <https://doi.org/10.1021/acs.energyfuels.1c03328>.
- [29] N. Yao, X. Chen, Z. H. Fu, Q. Zhang, *Chem. Rev.* **2022**, *122*, 10970–11021. <https://doi.org/10.1021/acs.chemrev.1c00904>.
- [30] E. Flores, G. Åvall, S. Jeschke, P. Johansson, *Electrochim. Acta* **2017**, *233*, 134–141. <https://doi.org/10.1016/j.electacta.2017.03.031>.

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