

Solvation structure in dilute to highly concentrated electrolytes for lithium-ion and sodium-ion batteries

Gustav Åvall,^a Eibar Flores,^{a,b} Steffen Jeschke,^a and Patrik Johansson^a

^a *Dept. of Physics, Chalmers University of Technology, 412 96, Gothenburg, Sweden*

^b *Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

E-mail: gustav.avall@chalmers.se

Highly concentrated electrolytes have recently attracted attention after reports of non-volatility, enhanced kinetics, and reversible LIB operation using graphite and lithium metal anodes, demonstrated for various salts and solvents [1-3]. These improvements are attributed to the electrolyte structure that promotes electrode passivation, prevents solvent co-intercalation into graphite, and facilitates (de)lithiation via a different lithium de-solvation mechanism [4].

In order to gain further insight into how these properties arise we studied the solvation structure of Li/NaPF₆ in both acetonitrile and propylene carbonate over a wide range of salt concentrations via semi-empirical computational chemistry. The first cation solvation shell is primarily characterized by the cation-solvent and cation-anion distances and angles, but the sampling of several large ensembles enable a general statistical analysis. We find these shells to be well-defined and solvent rich for dilute electrolytes, but at elevated concentrations anion rich and disordered, displaying a large multitude of stable solvation structures (Fig. 1). We hence can connect the observed improved liquidus range and the altered de-solvation mechanism and transport properties to this flexibility of the first cation solvation shell [5].

Comparing the Li- and Na-based electrolytes as well as the two different solvents applied the concentration dependence is stronger in the Na-based electrolytes, suggesting even more pronounced beneficial properties, even at more moderate concentrations. In addition, the solvent has a clear impact, *e.g.* the calculated angle distributions differ greatly between the solvents with PC having a propensity for bidentate coordination, distorting the solvation shell.

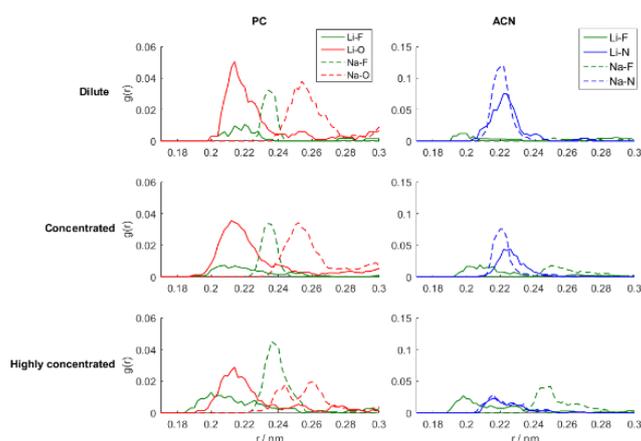


Figure 1. Computed radial distribution functions.

References:

- [1] L. Suo, Y.-S. Hu, H. Li, M. Armand, L. Chen, *Nat. Commun.* 4 (2013) 1481
- [2] Y. Yamada et al., *ACS Appl. Mater. Interfaces.* 6 (2014) 10892–10899
- [3] Y. Yamada, A. Yamada, *J. Electrochem. Soc.* 162 (2015) A2406–A2423
- [4] Y. Yamada, M. Yaegashi, T. Abe, A. Yamada, *Chem. Commun.* 49 (2013) 11194–11196
- [5] E. Flores, G. Åvall, S. Jeschke, P. Johansson, *Electrochim. Acta*, 233 (2017), 134-141