

MS19-P12 Anion Packing and Cation Mobility in Potential Solid ElectrolytesYolanda Sadikin¹, Pascal Schouwink¹, Matteo Brighi¹, Radovan Černý¹

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The application of solid state batteries would be technologically more viable if operating temperatures were to approach values that do not require costly heating systems. Materials exhibiting superionic conductivity at ambient temperature are needed to solve such issues. These concerns can be addressed through materials research, especially through new crystalline phases. Complex hydride compounds are superior candidates for battery solid electrolytes, in view of their high energy density and excellent electrochemical stability, and their applications in batteries have been demonstrated.^[1] The complex hydride anions are susceptible to rotational disorder, hence, the so-called 'paddle-wheel mechanism'^[2] can be exploited to tailor superionic conductivity.

In compounds based on large complex anions, such as *closo*-boranes ($\text{B}_{12}\text{H}_{12}^{2-}$), the nearly spherical anions pack easily in *ccp*, *hcp* or *bcc* packing, creating conduction pathways built from continuous networks of tetrahedral and octahedral sites with their connectivity favorable for vacancy- and interstitially-driven cation mobility. The smaller cation (i.e. Li^+ and Na^+) is the mobile (conducting) species moving between the tetrahedral and octahedral sites.

The study of binary and ternary *closo*-borane compounds containing light alkali metals $\text{Na}_2\text{B}_{12}\text{H}_{12-x}\text{I}_x$ and $(\text{A}_1\text{A}_2)\text{B}_{12}\text{H}_{12}$ ($\text{A}_1 = \text{Li, Na, A}_2 = \text{Li, Na, K, Cs}$) will be presented with the aim of exploring possible routes to stabilize the suitable anionic packing, which stabilizes superionic phases at room temperature. The experimental approach includes anion modification via partial iodination of $(\text{B}_{12}\text{H}_{12})^{2-}$ anion, where H is substituted by I, and cation substitution, where the larger cation (K^+ , Cs^+) occupies the octahedral site and stabilizes the *closo*-borane framework with significant conducting pathways (*bcc* or *hcp*). The types of anion packing and connectivity of interstitial sites will be discussed as important features in designing superionic conductors based on *closo*-boranes. AC conductivities obtained from impedance spectroscopy show that *hcp*-packed metal *closo*-boranes exhibit superionic conductivity at lower temperatures than their cubic *ccp*-packed analogues, as observed in *h*- $\text{Na}_2\text{B}_{12}\text{H}_{12-x}\text{I}_x$ with σ_1 approaching 0.1 S cm^{-1} at 360K.

References:[1] A. Unemoto, M. Matsuo, S. Orimo, *Adv Funct Mater* 2014, 24, 2267.[2] A. Kvist, A. Bengtzelius in W. Van Cool, *Fast Ion Transport in Solids*. North Holland Pub. Co., Amsterdam, 1973, pp. 193-199.**Keywords:** superionics, *closo*-boranes, solid electrolyte, anion packing**MS19-P13** Ionic Liquids based on Crown Ethers as electrolytes for batteriesHervé Yao¹, Katharina M. Fromm¹

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Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and that are usually composed of an asymmetrical organic cation and a large charge-delocalized anion which is poorly coordinated. They are non-flammable, and thermally as well as electrochemically stable.

These properties make them very interesting for many applications including green solvents for synthesis, catalysis, and electrolytes for ionic and electronic devices¹. Crown ethers are able to strongly interact with alkali metal cations (Li^+ , Na^+ , K^+) and have been used as additives in battery electrolytes in order to increase the ionic conductivity of the latter and to prevent electrolyte decomposition²⁻³. However, few studies have been done on crown ethers in the field of electrolytes.

This is why we propose to integrate them covalently as an alkali cation carrier⁴⁻⁵ in the ionic liquid system. The aim of the project is thus to design and synthesize new Room Temperature Ionic Liquids (RTILs) based on crown ether moieties, to investigate their properties (flammability, thermal and electrochemical stability, conductivity, Li/Na-ion diffusion) and then to use them as electrolytes for rechargeable batteries. We will present their synthesis, structures and properties in this contribution.

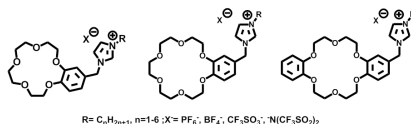
References:¹H. Ohno, *Electrochemical aspects of Ionic liquids*, John Wiley & sons, 2005²Abouimrane, A.; Alarco, P. J., *Journal of power source*, **2007**, 174, 1193-1196³Danil de Namor, Margot. A.; Abu Lebdeh. Y.; Davidson. I.; Armand. M., *Journal of Physical Chemistry*, **1994**, 98, 11796-11802⁴Shu, Z.X.; McMillan, R.S.; Murray, J.J., *Journal of the Electrochemical Society*, **1993**, 140, 101-103⁵Assuma, C.D.; Crochet, A.; Cheremond, Y.; Giese, B.; Fromm, K.M., *Angewandte Chemie International Edition*, **2013**, 52, 4682-4685

Figure 1. New Ionic liquids based on crown ether building blocks.

Keywords: Ionic liquids, electrolytes, battery, crown ether

MS19-P14 Can we predict Al ion conductors? A combination of crystallographic and energetic evaluation tools.

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Ionic conduction in crystalline oxides can be described as jumps of mobile ions between interconnected oxygen-coordinated crystallographic sites. Therefore, crystallographic evaluation tools can be utilised and combined into a high-throughput prediction method for crystalline ionic conductors. An energetic consideration in the end allows an in-depth analysis of the predicted ionic conduction process in order to verify the most-promising compounds.

Three approaches can be synergetically used to allow a time-efficient and consistent methodology for the identification of oxidic, crystalline aluminium ion conductors: Voronoi-Dirichlet partitioning (VDP) combined with data mining offers a fast high-throughput screening of crystallographic databases on the basis of a geometrical division of the crystal structure into domains assigned to each constituent of the structure, pointing towards possible void networks.

Bond-valence methodology (BVM) as a chemically motivated evaluation tool assists in the prediction process as the second step, determining the most probable migration ways by calculating bond-valence sums for each point in the crystal structure. Bond-valence energy landscape calculations then allow for an energetic estimation of jump energies.

The most promising structures are, eventually, fully electronically modelled by density functional theory (DFT) calculations *ab initio*. Calculating migration step energies subsequently enables a full assessment of jump energies from equilibrated structures as well as electronic conductivities and diffusion coefficients. As a very time-consuming method, DFT is applied as the final step.

This work presents the first results of the identification of promising oxidic Al-ion conductors involving all three approaches and their comparison.

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Keywords: Voronoi-Dirichlet, Bond-Valence, DFT, Ionic conductors, data mining