

A quantum-chemical study on ion complexation in polymer electrolytes containing lithium aluminate salts

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Polymer electrolytes continue to attract scientific attention owing to their applications in fuel cells, lithium batteries, solid state electrochemical devices, sensors, displays, etc. This interest is further stimulated by continuous demand for cheap, stable and safe electrolytes of improved performance. An electrolyte of such a type consists of an inorganic salt dissolved in a polymer matrix, poly(ethylene oxide) (PEO) loaded with a lithium salt (e.g. LiClO_4) is a common example. Ion–ion and ion–polymer interactions play therefore a crucial role in determining electrolyte conductivity. Much of experimental research is focused on tuning such interactions in order to prepare an electrolyte with properties optimized for particular application. Theoretical studies aim at better understanding of ion complexation and transport processes to explain and, eventually, to predict the relationship between structure of the electrolyte and its properties.

In the present work¹ we have investigated a group of single-ion conducting electrolytes based on lithium aluminate salts which has been recently synthesized². Quantum-chemical calculations (including full geometry optimizations for salts and corresponding anions) as well as *ab initio* Molecular Dynamics (Born-Oppenheimer MD) simulations have been performed to obtain information about Li^+ coordination changes. We have calculated binding energies for Li^+ complexed at aluminate anions and compared them with experimentally measured electrolyte ionic conductivities. We have shown that these two quantities indeed correlate and theoretically estimated stabilization energies allow us to explain the conductivity differences.

¹A.Eilmes, P.Kubisiak, *Solid State Ionics* **2009**, 180, 934

²T.Fujinami, Y.Buzoujima, *J. Power Sources* **2003**, 119-121, 438