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Ionic transport and pair formation in polymer electrolytes

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Salt-in-polymer electrolytes have interesting properties for practical use in batteries, smart windows, and electrochemical solar cells. However, a technological breakthrough is hampered by the relatively low mobility of the cations and a pronounced tendency to pair formation.

Common analysis (level 1) characterizes the degree of ion association in polymer electrolytes by the Nernst-Einstein deviation parameter Δ which quantifies the relative difference between the true ionic conductivity directly measured by electrical methods and the hypothetical maximum conductivity calculated from the individual ionic self-diffusion coefficients. Alternatively, the Haven ratio H_R may be used as key figure to specify the association degree. Despite their unambiguous definitions, Δ and H_R are global quantities with limited explanatory power. Similar is true for the cation transport number t^*_{cat} which relies on the same ionic diffusion coefficients usually measured by nuclear magnetic resonance or radiotracer methods.

In polymer electrolytes of low or moderate salt concentration neutral ion pairs dominate over higher-order aggregates. By evaluating this case in detail (level 2), more specific information can be extracted from the same body of experimental data that is used for the calculation of Δ, H_R and t^*_{cat}. This information concerns the individual contributions of pairs and free ions to the self-diffusion coefficient of cations and anions. Also the true cation transference number based on charged species only can be deduced. We present the basic theoretical framework and some pertinent examples dealing with ion pairing in systems based on poly(ethylene oxide) with inorganic salts or ionic liquids [1].

An even more extensive analysis (level 3) makes it feasible to split up each pair- and free-ion-specific contribution (or 'effective diffusivity') in a 'true diffusivity' and the relative abundance of the corresponding species. Such an extended approach requires assumptions about the basic type of temperature dependence of the true diffusivities and the reaction constant of ion pairing. This involves the introduction of parameters characterizing ionic mobility and association, such as Vogel-Tammann-Fulcher parameters as well as the enthalpy and entropy of pair formation. Within such a specific model, containing reasonable assumptions to reduce the number of free parameters, all experimental data can be simultaneously fitted using a least-squares routine [2].

References

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