To hop or not to hop: How to accurately describe the diversity of ion transport modes in solid polymer electrolytes

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For quite some time, it has been known that ion transport in solvent-free polymer matrices is different from that in inorganic solids or liquid solvents, as it takes place in a constantly evolving dynamic system of entangled polymer chains. However, different descriptions of the details of this process can be found throughout the literature, from the somewhat vague "ion transport coupled to segmental motion" [1] to "ions hopping along or between polymer chains" [2–4]. While these simple descriptions to some degree convey some of the intricacies of the ion transport processes, both descriptions are unfortunate simplifications that are insufficient to provide an accurate understanding of the actual submicrosopic processes that are the basis for ion movement in these systems.

In a sense, the ion transport in typical polymer electrolytes lies in between that of rigid ceramics and liquid solvents, and has the potential to cover the whole range of transport mechanisms between these extremes. This diversity can be captured using a more detailed classifications of the different transport modes, distinguishing between ion–solvent co-diffusion (vehicular transport), continuous transport and hopping [5]. But how prevalent are these different modes in relevant polymer electrolyte systems? From molecular dynamics simulations on poly(ethylene oxide):LiTFSI and poly(ε-caprolactone):LiTFSI electrolytes, we have applied and expanded on this model to quantify the ion transport mechanisms. Through this, we find that (1) the traditional models clearly understate the importance of the anions for the cation transport processes; (2) the distribution of transport modes is related to the polymer–ion coordination strength, and (3) ion hopping is essentially absent and is thus an unsuitable description of ion transport in soft polymer matrices.

References

[1] D. Bresser, S. Lyonnard, C. Iojoiu, L. Picard, S. Passerini, *Mol. Syst. Des. Eng.,* **4** (2019) 779–792.

[2] O. Borodin, G. D. Smith, *Macromolecules,* **39** (2006) 1620–1629.

[3] D. Devaux, R. Bouchet, D. Glé, R. Denoyel, *Solid State Ionics*, **227** (2012) 119–127.

[4] D. J. Brooks, B. V. Merinov, W. A. Goddard, B. Kozinsky, J. Mailoa, *Macromolecules,* **51** (2018) 8987–8995.

[5] C. Y. Son, Z. G. Wang, *J. Chem. Phys.,* **153** (2020) 100903.