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Strongly Correlated Ion Dynamics in Plastic Ionic Crystals and Polymerized Ionic Liquids

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Abstract

 Understanding the mechanisms controlling ionic conductivity is critical for the development of the next generation of batteries and supercapacitors. This paper discusses the significant role played by ionic correlations in conductivity of concentrated ionic systems. Our studies of an organic ionic plastic crystal reveal that correlations in ions dynamics suppress conductivity by 25-100 times in comparison to the expected uncorrelated ionic conductivity estimated from the Nernst-Einstein relationship. Additional analysis also demonstrates that ionic correlations suppress conductivity in polymerized ionic liquids and gel by ~10 times. Thus, ionic correlations, usually neglected in many studies, play a very important role in conductivity of concentrated ionic systems. These results cannot be explained by a diffusion of ion pairs because all these systems are essentially single ion conductors. In contrast, strongly correlated motions of mobile ions with the same charge (cation-cation or anion-anion correlations) are the major mechanism suppressing the ionic conductivity in these systems. On the basis of these results, we emphasize that charge transport rather than ion diffusion is critical for electrolyte performance and suggest the potential design of plastic crystals and polymer electrolytes with enhanced ionic conductivity.

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