Understanding the effect of trace solvent content on properties of polymer electrolytes through molecular dynamics simulations

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The rapid growth of mobile, portable, wearable, and flexible electronics leads to the increasing demand for energy storage devices using solid-state polymer electrolytes (PEs), which outperform liquid electrolytes in terms of safety, mechanical properties, and simplicity of device fabrication and packaging. However, processing PEs will always introduce solvent molecules that greatly affect the ionic conductivity and mechanical properties. For example, PEs prepared through solution-casting methods always have solvent residues. A trace amount of water molecules absorbed from the air is also inevitable. Recently, we demonstrated the controlled introduction of solvent molecules to PEs to balance the ionic conductivity and mechanical stiffness for structural energy storage applications. To better understand how solvent molecules behave and interact with other components in PEs, here we present the molecular dynamics simulation of a representative polymer electrolyte system with various water content. We use simulation results to determine the effect of trace water content before forming a liquid phase on ionic conductivity and mechanical properties. The insights into the molecular interactions in the PE system will help us design and optimize Pes' composition and processing for practical applications.

The simulation model of polymer electrolyte is built with polyethylene oxide (PEO) and lithium perchlorate ($LiClO_4$) with various water contents, in which the water molecule to lithium ion ratio ranges from 0 to 3. The electrolyte with each water content is simulated between two graphene electrodes to determine its ionic conductivity. Uniaxial deformation has been performed on the electrolyte to obtain the mechanical properties. All simulations were performed using the molecular dynamics simulation code LAMMPS with the CHARMM force field.

The results show that the ionic conductivity of the polymer electrolyte system increases significantly (up to one order of magnitude) with the increase of water content (up to 3 water molecules per lithium ion), even when the added water does not form a continuous liquid phase. The change of ionic conductivity with water content is correlated to the degree of association between different types of ions or molecules in the system, as evidenced by the evaluation of the radial distribution functions. As the association between polymer molecules and lithium ions reduces with increasing water, it becomes easier for the lithium ions to diffuse and resulting in higher ionic conductivity. It is also observed that the perchlorate ions' interactions with polymer molecules remain the same with different water contents, which shows different roles of lithium ions and perchlorate ions in ion conduction in this system. On the other hand, the modulus of elasticity of the polymer electrolyte does not change much with the increase of water, which agrees with the previous experimental work of our group. This means that the trace amount of water is strongly associated with other solid molecules or ions and is not affecting the stiffness of the system as long as no liquid phase is formed. The results will lead to novel strategies to design polymer electrolytes with both high ionic conductivity and good mechanical properties for flexible or multifunctional energy storage applications.