AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF PROTON TRANSPORT IN ANHYDROUS PROTIC IONIC LIQUIDS

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ABSTRACT

Protons diffuse rapidly in water due to their ability to undergo structural diffusion, where excess protons migrate through the system by sequentially hopping from hydronium to a neighboring water molecule. (This is also known as the Grotthuss mechanism, named for Theodor von Grotthuss, who first proposed the mechanism in 1806.) As a result of this mechanism, protons diffuse more rapidly than water or similarly sized cations such as sodium. Proton transfer is also important for the efficient function of hydrogen fuel cells (HFCs) and water electrolyzers (WEs). The most common proton exchange membranes (PEMs) used in HFCs and WEs are comprised of polymers containing a side chain with sulfonic acid groups, which, when hydrated with a sufficient amount of water, donate their protons to the aqueous layer through which they are then able to migrate via structural diffusion. Protons have also been shown to undergo hopping in other liquids, such as imidazole and phosphoric acid. Like water, imidazole and phosphoric acid are amphoteric, i.e. they can both accept and donate protons, and have been shown to form wires along which proton diffusion can occur.

In this work, we present the results of an *ab initio* molecular dynamics (AIMD) study of proton transport in novel imidazolium-based ionic liquids (ILs) containing varying amounts of excess imidazole.[1] Specifically, the systems studied here consist of 1-ethylimidazolium bis-(trifluoromethanesulfonyl)imide ([C_2Him][TFSI]) protic ILs, with mole fractions of imidazole (Im^0) of 0, 0.33, 0.50, and 0.67. We find that as the mole fraction of Im^0 increases, there is a pronounced increase in the number of proton transfer events, illustration the ability of Im^0 to participate in Grotthuss hopping. Importantly, we find that Im^0 forms robust wires along which protons diffuse, and an increase in the amount of added Im^0 results in the formation of longer wires and subsequently a greater increase in the charge diffusion constant relative to diffusion constants of other species. We will also present a detailed analysis of the proton hopping mechanism in these systems, including the relevant energies and timescales associated with proton transfer.

Lastly, we will briefly discuss ongoing computational work investigating proton transport in novel anhydrous polymer systems.

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References

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