CHEMISTRY OF MATERIALS

COMMENTS

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Comment on "Mixed Grotthuss and Vehicle Transport Mechanism in Proton Conducting Polymers from Ab initio Molecular Dynamics Simulations"

In their recent publication, Ludueña, Kühne, and Sebastiani[1] propose a new mechanism of proton transport in hydrated poly(vynil phosphonic acid) (PVPA) based on first principles molecular dynamics simulations. However, we believe that there are a number of misconceptions and inconsistencies leading to incorrect conclusions presented in this article, which we would like to clarify.

(1) PVPA does not show any significant proton conductivity under anhydrous conditions, but for a hydration number of $\lambda([H_2O]/[R{-}PO_3H_2]) \approx 0.8$, a moderate conductivity ranging from $\sim 10^{-4}$ S/cm at room temperature to $\sim 10^{-2}$ S/cm at 100 °C was reported.[2] As for all ionic conductivity processes, the temperature dependence is a clear signature of a thermally activated process behind the charge transport. At the same time, the hydration number of $\lambda \approx 0.8$ can only be kept at a high water pressure (p_{H_2O} = 1 atm at 120 °C). In brief, PVPA is not an anhydrous proton conductor, but it shows moderate proton conductivity with high thermal activation enthalpy at $\lambda \approx 0.8$. Moreover, since this conductivity is very close to the conductivity of the ion exchanged K^+-form, it most likely stems from the mobility of hydronium (H_3O^+) ions.[2] For the hydration levels used in the present work (λ = 0.125 and 0.5) the expected conductivities should be even lower. Therefore, the simulations on this system should also not show any significant diffusive proton dynamics in thermal equilibrium or drift velocities in the direction of small electric fields well within the linear response regime (for which diffusion and mobility may be related through the Nernst–Einstein relation).

(2) The dynamics, as seen by the authors, is probably a result of the magnitude and kind of applied external driving force. In particular, it is not a thermally activated process, since in the words of the authors, the simulations *yield similar rates for most temperatures* or have *mild temperature dependence* only showing marked dependence on the magnitude of the externally imposed force. We are convinced that the selected methodology by applying large directional forces on the protons in order to model the transport in the real fuel cell is changing the nature of the transport process and therefore leads to wrong conclusions. As mentioned before, the proton dynamics responsible for the conductivity is purely due to the thermal motion of particles, and normally, the electrochemical potential gradient (small compared to the variations of the internal potentials), whether in a fuel cell or a conductivity cell, just leads to a small drift velocity on top of the much faster random diffusion resulting in a proton flux (see any standard electrochemistry textbook[3]). Moreover, it is also clear that the concentration gradient of charged particles (in this case protons) in condensed matter cannot be the driving force behind these processes, simply because the local electroneutrality condition does not allow for any significant concentration gradient.[3] Second, the application of an external force (if small) would only be meaningful if the physical protons were the actual charge carriers and their charges, as seen by the electric field, were constant. However, if the protons of neutral moieties and protonic defects interchange, as it is the case in, for example, water, H_3PO_4, and imidazole, this assumption is no longer valid. Besides this, the magnitudes of forces as used by the authors require more careful attention. As mentioned in the paper, an application of forces of ~200 pN leads to the breakage of P–O bonds, which are some of the strongest in the system. Nevertheless, the chosen force resulting in any noticeable proton dynamics is 30 pN, which is still extremely high and is surely artificially biasing all the chemical bonds involving hydrogen. In a practical comparison, this kind of force on a particle having unit charge would correspond to ~1.6 kV of applied external bias on a sample having 10 μm thickness (electric field strength of $\mathcal{E} \approx 1.6$ MV/cm). These considerations lead us to the conclusion that proton conductivities as obtained from these simulations are purely a result of the external biasing on the system and do not represent any realistic situation.

(3) Another point we would like to raise is, that in contrast to most of the first principles molecular dynamics simulations on protonic defects in water, where the protonic defects have to be introduced extrinsically due to the very low degree of self-dissociation, the situation in phosphonic/phosphoric acid systems is rather different. Here, the charge carriers responsible for the conductivity are generated intrinsically (high-degree of self-dissociation[4] and protonation of the residual water). Therefore, the introduction of excess protons into the simulation box, as was done by the authors, does not reflect this situation in any way. On the contrary, this might create an artificially high energy state and incorrect representation of the proton conduction mechanism.

(4) In addition to other minor inconsistencies in this work, in our mind the normalization of the conductivity is deeply flawed: the authors estimate the theoretical charge carrier concentration in their system by using the pK_a value of H_3PO_4, which actually describes the acid dissociation equilibrium in a highly diluted aqueous solution. This assumption neglects the fact that the described system has very low water content, that phosphonic (as well as phosphoric) acid has a very pronounced amphoteric character (high Brønsted-Lowry acidity and basicity constants), and that the main source of charge carriers in the dry state is the self-dissociation, or in this particular slightly humidified state, additionally the protonation of water molecules forming H_3O^+ ions. Basically, it means that there are at least two reactions involved and their equilibrium constants are not trivially related to the acidity of phosphoric acid.

We are convinced that a fundamental understanding of these processes and materials is absolutely crucial for further progress in this field. Unfortunately, the facts suggest that the particular case presented in this paper is not a good example of a system

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showing fast intrinsic proton transport, and the authors were forced to apply very crude measures in their simulations, which, we believe, eventually lead to wrong conclusions as well as the concept of a new *carrier-mediated Grotthuss mechanism*.

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