CHEMISTRY OF MATERIALS

COMMENTS

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

The preceding comment by Vilčiauskas and Kreuer[1] raises several concerns regarding computational aspects of our first-principles molecular dynamics study[2] on microscopic proton transport mechanisms in a phosphonic acid based polymer (PVPA).

We are glad that our work on proton conductors has attracted interest and has stimulated this discussion with experimental colleagues from the field. The specific computational methods which we used and which are addressed by the comment may indeed appear surprising from an experimental point of view. Thus, we will clarify in the following why the specific computational protocols were used, which is the type of results that can be derived, and why we believe that our conclusions do hold.

As an initial general remark, we want to point out that when theoretical/computational methods are applied to a given physical phenomenon, the specific approach often differs from the common experimental approach to the same problem. This implies that the actual experimental conditions may not be reproduced quantitatively in a simulation, and such reproductions are actually often not even intended.

The first paragraph "(1)" of the comment repeats an observation that was actually reported in our paper: the introduction of small bias forces does in fact not lead to any sustained proton drift velocities which are comparable or even larger than the numerical noise of our simulations.

The first specific remark "(2)" of the comment discusses the steering force that we applied to all acidic protons in the system. This external force serves as a driving force needed to accelerate the actual ion conduction process, that is, proton hops, which are (activated) rare events. In an unbiased MD simulation, these jumps would happen at best way too infrequently (see point "(1)") to obtain reliable statistics from a 50 ps trajectory, hence the name "rare event".

It is correct that the absolute magnitude of this force is high when it is seen as a macroscopically applied force. However, it is small compared to the normal canonical oscillations of the instantaneous forces acting on the atom due to their chemical environment (i.e., vibrations of covalent bonds). We have explicitly verified that the external forces are about 2 orders of magnitude smaller than the physical forces. Therefore, our driving force can indeed be seen as a (small) bias force which only accelerates the proton hopping processes. We are confident that the actual mechanism of the proton conduction process is not significantly altered.

The third point "(3)" concerns the matter of adding excess protons to the hydrated phosphonic acid polymer. Instead of this, the comment suggests to wait until spontaneous autodissociation $2\ R{-}PO_3H_2 \rightarrow R{-}PO_3H^+ + R{-}PO_3H_3^-$ happens in the MD simulation. While at first glance the latter approach appears physically more straightforward, there are several severe shortcomings of this suggestion.

1. In a real hydrogen fuel cell, there *are* excess protons which are provided by the dissociation of the fuel (H_2). In reality, it must be those excess protons which are transported, because a dissociated acid molecule would still be neutral and would not lead to effective long-range ion transport.
2. In our setup, the quantification of directed ion transport is achieved by means of a simple collective variable Q, which is based on atomic positions only. In a neutral system (without excess protons), it would be considerably more involved to observe and to numerically characterize how far an "effective proton" has migrated due to the bias force. One of the problems is that all (acidic) protons are equal; that is, it is not possible to distinguish the "regular" protons in a hydronium ion (H_3O^+) from the "excess" proton. Therefore, it is necessary to define a quantity which treats all those protons equally but still quantifies the effective transport through the system.
3. When using excess protons, we obtain much better statistics regarding the evolution of our collective charge transport variable $Q(t)$. It is a misconception to believe that in a neutral system, spontaneous dissociation would have happened on any reasonable time scale. In fact, in a trial run, we did not observe any real autodissociation on the normal ab initio time scale (100 ps), only very short-lived oscillations of the acidic OH bonds.

There is an additional point "(4)" raised in the comment, which is related to the charge carrier renormalization that we applied. Our correction factor is based on the equilibrium constant of the phosphonic acid dissociation constant (eq 3), which contains the concentrations of the acid, its base, H^+/hydronium, and water. Normally, the conventional use of acid/base equilibria implies a high dilution in water, which is why the water concentration is normally taken as fixed, $[H_2O] = 1\ g/cm^3$. We are very well aware of the fact that this is not the case in our system, which is why we have used the appropriate concentration(s) of water in our simulation cells instead. The equilibrium constant reflects the free energy difference of the reaction, renormalized by the temperature. In principle, it does not depend on the concentration of the reactants. In our case, this is certainly only approximatively true, but we are not aware of any better numerical estimation for the reaction free energy difference in the "slightly humid" phosphonic acid polymer (i.e., very low water concentration $[H_2O] \ll 1\ g/cm^3$). This is why we believe that our correction factor is at least semiquantitative.

Hence, in summary we believe that the methods and protocol we used, as well as the conclusions we drew, are adequate and reflect the main physics of the microscopic motion of protons in

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PVPA. Therefore, we do not see any necessity to alter any of our conclusions.

Guillermo A. Ludueña,[†] Thomas D. Kühne,[‡] and Daniel Sebastiani*,[†,§]

[†]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

[‡]Institute of Physical Chemistry and Center of Computational Sciences, Johannes Gutenberg University Mainz, Staudinger Weg 9, 55128 Mainz, Germany

[§]Physics Department, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

AUTHOR INFORMATION

Corresponding Author

*daniel.sebastiani@fu-berlin.de

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