Mechanism of Proton Permeation Through Graphene Monolayer

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Research from The University of Manchester has shown that graphene is permeable to protons while hindering other single-charge ions, such as Lithium [1, 2], which is a breakthrough in developing graphene as a 2D membrane for fuel cell application. In this study, we modelled the proton permeation through a pristine graphene monolayer to bring to light the mechanism of permeation that has been hypothesized: i) direct penetration, ii) flipping penetration, and iii) H3O+ penetration. [3] Mechanism 3 is less likely to occur due to the large size of the hydronium ions, leading to a high energy barrier for it to pass through the graphene ring. Besides, our study includes the permeation flux of proton influenced by the electric field at a temperature range between 300 K and 350 K. All Molecular Dynamics (MD) with ReaxFF force field simulations are conducted using the LAMMPS package.

Our results demonstrate that the permeation of proton through graphene follows Mechanism 1 and Mechanism 2, with Mechanism 2 having a higher occurrence than Mechanism 1. Hydrogenation of graphene is observed as proton shuttles via vehicular and Grotthus's hopping mechanism through the reservoir under the influence of an electric field. Our results agree with the experiment on single-gated graphene. [2] Due to the high tendency of hydrogenation on the graphene, Mechanism 2 is the most probable and observed at higher frequencies in our simulation, where protons are adsorbed on the graphene atom before flipping to the other side through the graphene ring. The results of Mechanism 2, as the most probable pathway for proton permeation, also hold at higher temperatures up to 350 K. During permeation, the graphene ring expands, leading to a larger ring size with a broader bond distribution (see Figure 1b). The larger ring size does not have a significant impact on the proton permeation mechanism, as protons are more likely to be trapped within the hydrogenation well as they approach the graphene. With increasing temperature, a higher flux (see Figure 1a) of proton permeation is observed. This could be attributed to the lower charge density on the graphene plane (see Figure 1c) having a weaker electrostatic interaction with the proton and the thermal energy added to the proton to escape the hydrogenation well. Besides, it is also observed that most permeations occur in saturated areas with hydrogen. These results again agree with previous DFT reports [4, 5] that show a higher local saturation of hydrogen on graphene reduces the energy barrier for proton permeation. In this study, we demonstrate the permeation mechanism of protons through defect-free graphene and the influence of temperature on the flux of proton permeation.

References

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Figures

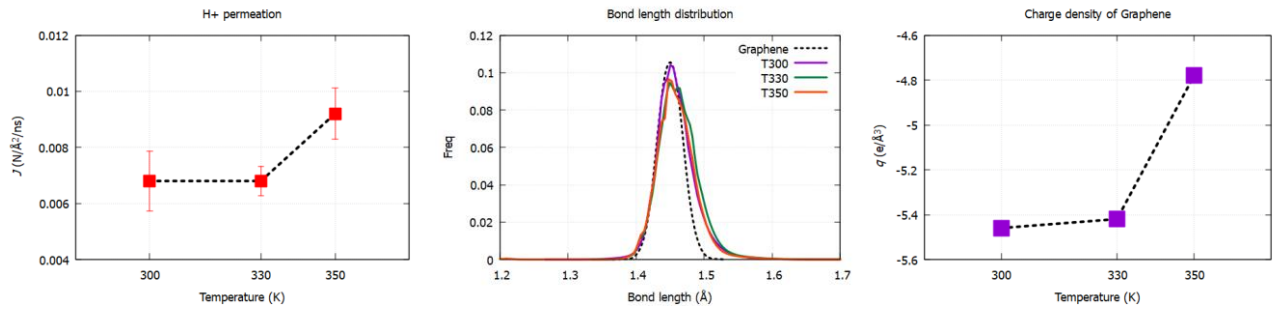

Figure 1: a) Permeation flux of proton. b) Bond distribution of Graphene. c) Charge density on Graphene XY plane.