Covalent benzenesulfonic functionalization of graphene and graphene nanopore for enhanced and selective proton transport

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A fundamental understanding of the proton transport through a graphene and graphene nanopore is essential for developing innovative two-dimensional proton exchange membranes. We computationally explore ways to enhance proton transport using a combination of ReaxFF Molecular Dynamics, Metadynamics, and Density Functional Theory (DFT). We identified consistent improvements in proton permeability, in terms of activation barrier and selectivity, for the benzenesulfonic functionalized graphene (incl. nanopores) compared to other functional moieties such as -OH and COOH for example. The benzenesulfonic functionality dynamically acts as proton-shuttle by establishing a favorable hydrogen-bond network, resulting in an effective proton transport channel. The discovered optimal balance between the proton permeability and selectivity is a key ingredient for efficient proton exchange membrane applications. Both the benzenesulfonic functionalized graphene and graphene nanopore exhibits a theoretically estimated areal proton conductivity that surpasses even the state-of-the-art Nafion. Ergo, these models exhibit formidable potential as candidates for the future advancement of graphene-based membranes in energy conversion devices.

References

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Figures

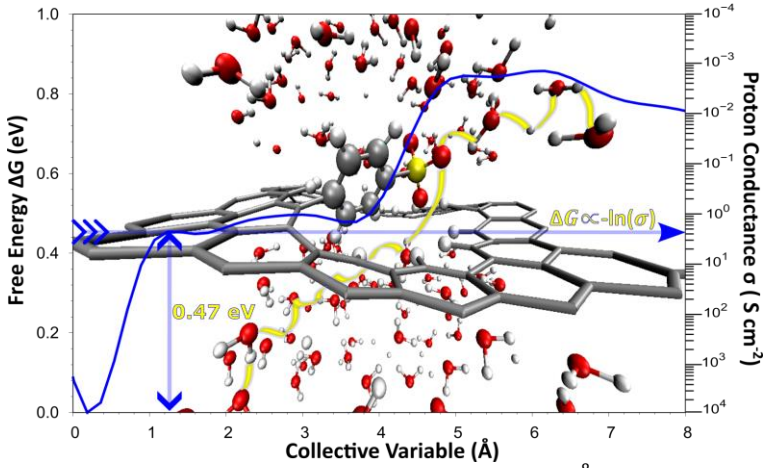

Figure 1: Free energy ΔG profile (eV) along the Collective Variable (Å) for the proton transport through a benzenesulfonic functionalized graphene nanopore solvated in water, over 1 ns of ReaxFF-MD Metadynamics simulation. Estimated proton conductance σ (S cm^{-2}), in logarithmic scale, is proportional to the Gibbs free energy barrier ΔG (eV) for proton diffusion, using the Nernst-Einstein equation.