

Elucidating proton permeation and hydrogenation behaviour in graphene-based materials from DFT calculations

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Two-dimensional materials (e.g., graphene and h-BN) offer a prospect of membranes that combine negligible permeability to gases with high proton conductivity, and could outperform the polymer-based existing proton exchange membranes used in various applications including fuel cells [1],[2]. Besides the well-investigated pristine graphene, there are hundreds of known two-dimensional materials that have not been explored from a permeability perspective. Hence, to guide the design and selection of promising 2D-structures, Density Functional Theory (DFT) calculations have been used as a high-throughput computational method for a first screening based on descriptors related to the permeability of the 2D-membranes [3]. Focus has been paid to functionalized graphene structures such as graphene oxide (GO) and fluorographene, to graphene-derivatives including non-metallic substitutions such as B, N, P, etc., and to other reported one-atom layer structures such as silicene, germanene and phosphorene. Simulations have been validated with experimental results (when available) and used as a guide for the rational selection of the best 2D materials for this application.

Results demonstrate that chemical functionalization can be used to enhance proton transparency without compromising gas impermeability. In particular, the enhancement is attributed to microscopic corrugations of the underlying graphene lattice, which are caused by functional groups bonded to the graphene surface [4]. In addition, surface hydrogenation has a similar enhancement effect in the studied materials. Furthermore, it was found a tendency to lower energy barriers for structures having larger pore sizes in their 6-atom rings (see Figure 1). For instance, boron substitution facilitates permeation, also attributed to a distortion induced by B atoms with larger atomic radii and an elongation of the B-C bond length; conversely, nitrogen atoms were identified as unfavourable for proton transport due to the distortion in carrier mobility. The revealed molecular-insights could expand the potential application of such 2D-materials in hydrogen-related technologies.

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References

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Figures

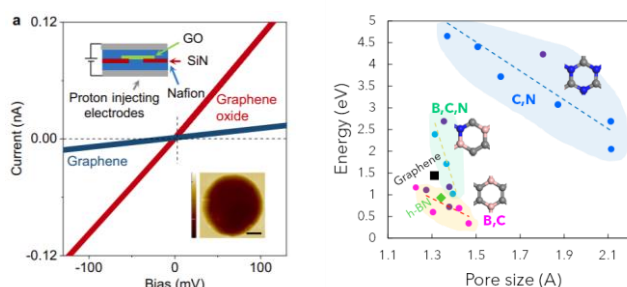


Figure 1: (left) Comparison of proton permeation (I-V characteristic) for graphene and GO monolayers. (right) Calculated DFT energy barriers of graphene-derivative structures, and correlation with the relaxed pore size of the permeated ring.