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Ion transport and sensing in porous graphene

Selective ion transport is a hallmark of biological ion channel behavior but is a major challenge to engineer into artificial membranes. We examine ion transport through graphene nanopores and found that, when the size of the pore is comparable to the size of the hydrated ions, the nanopore demonstrates strong nonlinear I-V behavior and has weak selectivity for K^+ over Cl^- ions [1]. Further, bare graphene nanopores yield measurable ion selectivity that varies over two orders of magnitude simply by changing the pore radius and number of graphene layers due to a enhanced water loss in the second hydration layer [2]. Measurement of selectivity and activation barriers from both first and second hydration layer barriers will help elucidate the behavior of biological ion channels. Moreover, for separation of ions from water, one can exchange longer, larger radius pores for shorter, smaller radius pores, giving a practical method for maintaining exclusion efficiency while enhancing other properties (e.g., water throughput) for filtration/desalination applications.

Additionally, we develop the first scaling theory for ion transport that enables all-atom molecular dynamic (MD) simulations to capture the access resistance, i.e., how the bulk electrolyte converges to the pore(s) [3,4]. This resistance is contextual, it depends on the presence of functional groups/charges and fluctuations, as well as the (effective) constriction geometry/dimensions. Addressing the context generically requires all-atom simulations, but this demands enormous resources due to the algebraically decaying nature of convergence with respect to the bulk size. Our finite-size scaling analysis – reminiscent of the treatment of critical phenomena – makes the access resistance accessible in MD. It suggests that there is a “golden aspect ratio" for the simulation that yields the infinite system result with a finite system. We employ this approach to resolve the experimental and theoretical discrepancies in the radius dependence of graphene nanopore resistance.

References

[1] S. Sahu, M. Di Ventra & M. Zwolak, Nano Lett. **17**, 4719 (2017)
[2] S. Sahu & M. Zwolak, Nanoscale, **9**, 11424 (2017)
[3] S. Sahu & M. Zwolak, arXiv:1708.03327 (2017)
[4] S. Sahu & M. Zwolak, arXiv:1711.00472 (2017)

Figures

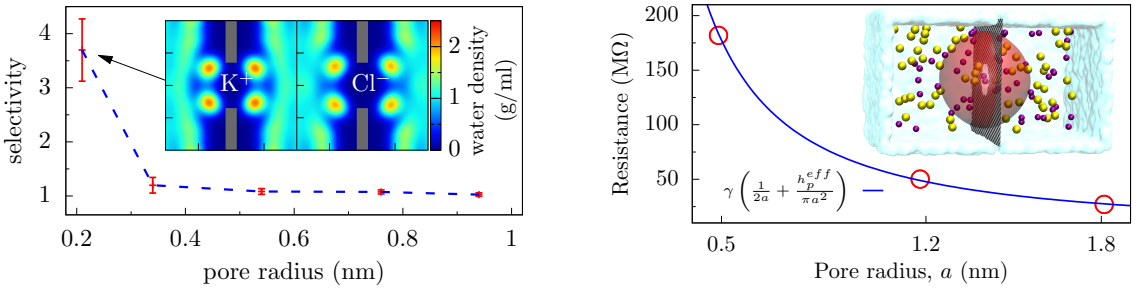

Figure 1: (Left panel) Selectivity (plot) and ion hydration (inset) in sub-nanoscale monolayer graphene pores. When the pore radius reaches the inner hydration layer, selectivity is observed do to partial removal of water molecules. (Right panel) Resistance versus pore radius (plot) and graphene membrane (inset). Using a novel scaling approach, we show that the radius dependence follows the continuum Maxwell-Hall form, which has both pore and access contributions.