Mechanisms for generating selective ion transport and salt rejection in carbon nanotubes and graphene nanopores

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Carbon nanotubes and graphene nanopores have been suggested for use a wide range of purification and separation applications, from the desalination of sea water to the separation of liquids and gases. However, achieving the required high degree of selectivity among the molecules passing through the pores while maintaining rapid transport is a difficult challenge. Here we examine the physical mechanisms by which nanopores can distinguish between small ions, and reject salts while passing water, as an example of how selectivity and purification can be achieved. The simple principles described can be utilized to design novel nanoporous materials for the separation of a wide range of gasses, liquids and solutes.

Keywords: Purification, Water, Simulation, Fluidics, Nanostructure

Why are we interested in selectivity and rejection?

Materials composed of carbon nanopores have been proposed for use in a wide variety of applications including the desalination of salty water, the filtration of contaminated water, gas separations, chemical sensors, nanoscale pumps, energy conversion devices, components in high speed chromatography and many more. All of these uses take advantage of the extremely rapid flow of molecules that has been measured in carbon nanotubes and graphene. (1, 2) But, in addition, most of these applications also require the preferential transport of some molecules compared to others. For example, if nanoporous membranes are to be used for the desalination of salty water, it is essential that they are able to rapidly pass water while blocking the passage of ions. Similarly, any filtration or separation application relies upon selective passage of specific molecules through the pores, or the blockage of others. The feasibility of these applications is supported by experimental reports of divergent rates of transport of differing gasses (1, 3-7), liquids (2, 4) and ions

(8, 9) in carbon nanotubes and graphene nanopores, as well as rejection of ions (10, 11) and size selective transport of aqueous solutes. (12) However, utilizing these promising materials requires a careful understanding of how selective transport arises, so that it can be enhanced or targeted towards molecules of choice.

In recent years there has been a specific focus on understanding how ions can be removed from water or how the selective transport of ions can be achieved using carbon nanotubes and graphene. This is partly due to the simplicity of the molecules involved, partly due to the similarities with essential biological processes and partly due to the fact that ions themselves can flow through nanoporous materials at rates far exceeding that in conventional materials. (8, 9) Much of this work has centered on the use of molecular simulations, as they allow for the physical factors involved in transport to be dissected. However, as described below, the simplifications and approximations used in the simulations also allow for uncertainties to arise. Here we look into this literature to help explain the physical mechanisms involved in ion rejection and selectivity in carbon nanotubes and graphene. Not only can this aid in designing the materials to optimize the selectivity of the pores, it can help to determine how selection for other molecules can be achieved.

Ion rejection in narrow pores

The most obvious way to stop an ion passing through a narrow pore is to make the pore thinner than the size of the ion; that is to make use of size exclusion [Figure 1a]. While molecular sieving is useful for blocking the passage of larger ions such as ammonium, nitrate or sulfate, it is not so useful for small ions such as Na^+ or K^+ if you still want water to pass through the pore. Indeed, simulations have suggested that water will only pass through carbon nanotubes that are $\geq 3.5 \text{ \AA}$ internal diameter,* and only passes in intermittent fashion

* The diameter of nanotubes can be measured in many different ways including the effective internal diameter taking into account the size of the carbon atoms, the distance between the centre of opposing carbon atoms or the outside out the carbon density seen in electron micrographs. In this article we refer only to effective internal diameters.

through nanotubes with internal diameter $\leq 4.5 \text{ \AA}$ (13-15) Given that the diameter of Na^+ is $\sim 2 \text{ \AA}$, it would clearly be impossible to exclude this ion on the size of the bare ion alone while still allowing water to pass. Simulation studies have suggested, however, that Na^+ (and other ions) can be largely excluded from carbon nanotube pores as wide as $10 \text{ \AA}$, (14-17) clearly indicating that other factors prevent the passage of small ions.

Ion exclusion from narrow carbon nanotubes can be largely explained as a consequence of dehydration barriers. (14, 16) In bulk solution, ions attract a ‘shell’ of surrounding water molecules due to the electrostatic interaction between the charge on the ion and the water dipole [Figure 1b]. Although water molecules in the shell exchange over time, this so called ‘hydration sphere’ effectively increases the size of the ion. If a pore is smaller than the size of the hydration sphere then it will not fit inside unless there is a rearrangement in the hydration sphere itself. To do this, water molecules can adjust their geometry around the ion allowing it to squeeze into *slightly* smaller spaces at a small energy cost. Alternatively, water molecules can be removed from the hydration shell, reducing the effective size of the hydration sphere and allowing the ion to fit into a smaller pore. But, removing each water comes at an increasing energetic cost. (15, 18) Thus, unless there is a compensating attraction between the ion and the pore itself, the dehydration barrier can prevent ions from entering the pore. Narrow hydrophobic pores, such as carbon nanotubes, tend to allow only a discrete number of water chains to form through the interior of the pore. (~ 1 chain in a $4.7 \text{ \AA}$ diameter pore, ~ 2 in a $5.9 \text{ \AA}$ pore, 4 in a $7.5 \text{ \AA}$ pore (14, 19)). Thus, as shown in **Figure 1b**, when the ion enters the narrow pore many water molecules may have to be removed from the hydration shell. In addition, the attraction between a bare hydrophobic pore and the ion is small as there are no permanent charges in a pristine carbon nanotube to generate strong electrostatic interactions in this situation. Thus, the dehydration barrier can effectively prevent ions from passing through the pore.

To give a concrete example of this, the number of water molecules in the first hydration shell of Na^+ is plotted in **Figure 2a** as a function of the position of

the ion within carbon nanotubes of different diameter. In the narrowest pore shown, the number of water molecules in the first hydration shell is significantly less than in bulk. The corresponding energy barrier for the ion to enter the pore is indicated in **Figure 2b**, highlighting the large energetic cost for ion transport in narrow pores caused by partial dehydration. The inability to overcome this energetic barrier is the reason why ions do not pass through these narrow pores unless a very large driving force is applied (salt rejection decreases as the driving force increases. (17)) Even if the number of water molecules in the first hydration shell in the pore is not significantly different to that in bulk, an energy barrier can remain due to rearrangement of the hydration sphere or removal of more distant water molecules. (15) As the dehydration barrier gets smaller, the chance of an ion overcoming it due to thermal motion or a driving force increases and so the ion rejection declines with increasing pore diameter as seen in **Figure 2c**. Once the pore is wide enough that water does not have to rearrange or be stripped from the hydration sphere, ion rejection from dehydration is lost.

Blockage of ions through dehydration barriers can be overcome if there are attractive ion-pore interactions. For example, near complete ion rejection was seen in simulation studies of graphene nanopores when the rim of the pore was essentially hydrophobic (contained only hydrogenated edges). But, increasing the polarity of the pore rim with hydroxyl groups reduced the salt rejection (except in very narrow pores) as ion-pore interactions began to compensate the dehydration barriers. (20)

While molecular dynamics simulations have predicted a high degree of ion rejection in pore up to 10 Å diameter due to dehydration barriers, so far it has been difficult to reproduce this experimentally. Fornasiero et al measured ion rejection in sub 2nm diameter carbon nanotubes, but this was attributed to electrostatic effects due to its dependence on pH and ion concentration, (10, 11) and ions have been measured to pass through < 1.4nm nanotubes under an electric field.(8) The disparity between simulation and experiment could come from many causes. Firstly, simulations are typically conducted on one or a few simple pristine nanotubes, whereas the experiments are conducted using a

large number of nanotubes that are likely to include a variety of sizes and chemical functionalization. The presence of a few wide pores, pores with favourable electrostatic interactions with the ions, or membrane defects could allow for ion transport, even if narrow pristine pores block ion flow. It is also possible that the simulations are overestimating the degree of ion rejection due to simplifications in the models used. Chief among these is likely to be the inter-atomic potentials used in these most models that do not allow for electronic polarization, and therefore cannot adequately model the stabilisation of ions in the pores and cation- π interactions from movement of electrons in the extended aromatic nanotubes. There can also be a disparity of many Å in terms of how the tube diameters are measured in simulation and experiment making a direct comparison difficult.

Another way to prevent ions from passing through nanotubes is to make use of repulsive electrostatic interactions. For example, the presence of charged groups at the entrance of narrow pores will effectively exclude the oppositely charged ions from entering the pore as indicated in **Figure 1c**. (21, 22) But while dehydration acts to prevent the passage of *both* cations and anions, charged functional groups will *attract* one ion species into the pore. Whether or not the passage of this ion type is slowed or sped up is difficult to predict – more rapid transport is expected due to the increased local concentration of the ion, but slower passage can arise if the ion remains bound to the charged group for a prolonged time. The presence of neutral but polar groups also produces complex behavior, but in general is not enough to prevent one ion type from passing through the pore. However, zwitterionic groups at the pore mouths have been shown to be tremendously effective at preventing ion transport, with simulations showing the passage of both Na^+ and Cl^- is blocked in nanotubes up to 16.9Å diameter due to electrostatic repulsion of both ion types.(23) Rejection of both cations and anion has also been demonstrated in experimental measurements of zwitterion functionalized CNT/polyamide nanocomposite membranes. (23)

Ion selection in pristine and functionalized nanotubes

Selection in bare hydrophobic pores

Differing dehydration barriers for different ions can lead to the passage of one ion being favoured over another. The size of the dehydration barrier for an ion depends upon how tightly it holds the surrounding water molecules and how many must be removed to enter the pore. In general, large ions hold more water in the hydration shell than small ones, simply because there is more space around these ions in which to pack water molecules. However, small ions bind each water molecule more tightly because the water can reside closer to the ion yielding a stronger electrostatic attraction.

All ion types must be largely dehydrated to enter a very narrow pore. For example in a $<5 \text{ \AA}$ diameter pore, no ion can contact more than 2 water molecules as only a single water chain fits inside the pore as shown schematically in **Figure 3a**. Thus, small ions are impeded the most as there is a greater energy cost in removing their tightly bound water. This leads to the slightly counterintuitive consequence that a narrow hydrophobic pore (with limited pore-ion interactions) will favour the passage of large ions over small ones (15, 24) Indeed this is exactly the situation in biological potassium channels that favour the passage of the larger K^+ over the smaller Na^+ despite being extremely narrow (although ion-pore interaction also play a role in this highly polar pore). In contrast, small ions can fit through wider pores with a near complete hydration shell, and so these face a smaller dehydration barrier than large ions (**Figure 3b**). Thus a wider pore is likely favour the passage of small ions over large ones. (15) Once the pore is much wider than the size of the hydration sphere then selectivity is lost.

The different dehydration barriers faced by ions is essential for explaining which ions will pass through carbon nanopores and polymeric water filtration membranes. For example, fluoride, (F^-) and nitrate (NO_3^-) are common anionic contaminants in drinking water. Fluoride is small, but tightly holds the water in its hydration shell. It is effectively removed from water by nanofiltration and reverse osmosis membranes even though these contain pore sizes much larger than the diameter of fluoride itself. Nitrate is much harder to remove from water, because there is only a very small dehydration penalty for this

larger, weakly hydrated ion to enter the porous filtration membrane. (25-27)
Hydration based ion selectivity has also been directly measured in intrinsic defects pores in graphene (28) and in isolated sub 2nm graphene nanopores. (29, 30)

Selection in functionalized pores

Most carbon nanopores contain some degree of chemical functionalization caused by oxidation, defects or intentional chemical modification. In these cases, there are a huge range of factors that can generate ion selectivity in addition to dehydration. Indeed, the literature elucidating selectivity in biological pores is extensive and a large variety of physical mechanisms have been discussed. Although we often think of biological pores being more complex than synthetic nanopores, comprehending selection in the latter is complicated by the fact that in general we don't have precise control or knowledge over what functional groups will be present at exactly what position in the pore - unlike in biological pores.

Perhaps the simplest way to generate selective ion transport in a nanopore is to add charged groups to the pore walls. As noted above, the presence of charged groups has been shown in simulations to aid the passage of oppositely charged ions, while hindering the passage of like charged ions (**Figure 4a**). (21, 22)
The same principles have been realized experimentally (4, 31-33), showing that charged groups can create cation/anion selection even in quite wide pores. Charged pore walls can be obtained not only by adding fully charged functional groups, but also by creating polarity in a net neutral pore. For example, Sint et al (24) used computational models to show that the addition of fluorine atoms on the rim of graphene pore creates a large polarity in the sheet and a negatively charged pore rim (**Figure 4b**), such that only cations will pass through the pore. Similarly, the presence of hydrogen atoms at the rim has the opposite effect, favouring the passage of anions (**Figure 4c**). In this case discrimination among the ions was further modulated by the ion size due to the dehydration barriers as described above, with the larger ions being favoured in the narrow pores studied. An inherent selectivity of K^+ over Cl^-

has been measured experimentally for graphene nanopores up to 2nm in diameter. (30) It is proposed that this originates from oxygen containing groups existing on the graphene surface (from partial oxidation) that carry a negative charge at neutral pH that attract cations and repel anions.

Controlling the selectivity among the cations or anions is challenging and remains mostly the realm of simulation studies trying to mimic biological pores. The most common ion pair studied in this context is Na^+ and K^+ , as discrimination between these similar ions is critical in the biological setting. Selecting for K^+ over Na^+ is easier than the reverse as the lower dehydration cost of transporting K^+ can be utilized. Biological potassium channels contain carbonyl groups lining the pore that attract cations and generate selection for K^+ over Na^+ that can be up to 1000:1.(34) This arrangement has been mimicked in carbon nanotubes (**Figure 4d**) (35), but surprisingly did not yield selection for K^+ over Na^+ . A similar approach in graphene nanopores (**Figure 4e**) did yield K^+ selectivity but nowhere near to the extent seen in the biological pores,(36) indicating how precise control over the geometry of the functional groups is essential to gain the high degree of selections seen in biological potassium channels. This is reinforced by the fact that small modification in the arrangements of carbonyl groups in the carbon nanotubes can shift the selection towards either Na^+ or K^+ .(35)

Biological Na^+ selective channels contain highly polar or charged groups that favourably bind smaller ions over large ones simply because small ions can move closer and so have stronger electrostatic interactions.(37) But, copying this selectivity in a synthetic pore requires careful control over pore geometry. Na^+ selection could only be achieved if the charged pore was small enough to ensure that single file transport was ensured, such that Na^+ ions passing through the pore block the passage of other ions (**Figure 4f**). (36, 38) If this is not the case, the stronger binding of Na^+ simply slows its passage without blocking K^+ , allowing for faster transport of K^+ than Na^+ . The fact that selection between Na^+ and K^+ (and presumably other similar ion pairs) is difficult to predict and requires fine control over the location and type of

chemical modification means that rationally designing such selectivity into synthetic nanopores is a significant challenge.

Challenges

While simulation studies of simple pores have helped dissect the physical mechanisms yielding ion rejection and selectivity in carbon nanopores, a challenge remains to be able to replicate many of the simplified situations in the experimental setting. Indeed, it still remains difficult to make direct comparisons between simulation and experiment due to the differences in the systems being studied. This is critical if the inter-atomic interactions in the simulations are to be carefully parameterized. There are also important differences between transport in elongated carbon nanotubes and anatomically think graphene nanopores that have not been fully discussed here. For example, more complete dehydration and extensive electrostatic interactions are possible in a nanotube, whereas an ion passing through graphene is likely to remain partly in contact with bulk water and can only have electrostatic interactions close to the graphene plane. Recently, slit pores between graphene sheets have also emerged as an interesting material for filtration applications and allow a new variety of pore geometries to be explored. Exploiting the potential of these remarkable materials in purification and filtration applications requires harnessing the physical principles reviewed here and uncovering any addition factors that can influence transport, as behavior at the nanoscale is often surprising.

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Figure Captions

Figure 1. Physical mechanisms of ion rejection. (a) Size exclusion, in which the ion is larger than the size of the pore, (b) dehydration barriers created by the necessity to remove water from an ion to enter the pore, and (c) electrostatic repulsion between the ion and the pore.

Figure 2. Origin, size and consequences of dehydration barriers. (a) Coordination number of Na^+ as it enters a narrow ($4.7\text{\AA}$), medium ($5.9\text{\AA}$) and wide ($7.5\text{\AA}$) carbon nanotube. (b) Free energy barrier experienced by Na^+ as it enters a narrow, medium and wide carbon nanotube. (c) Rejection of Na^+ and Cl^- versus diameter for bare carbon nanotube pores. Data in (a) and (b) replotted with permission from (14), data in (c) replotted with permission from (17).

Figure 3. Dehydration based ion selectivity pristine nanotubes. (a) In narrow pores all ions must be largely dehydrated to enter the pore. Thus, the larger ions with smaller hydration free energies can enter most easily. (b) In a medium diameter pore the larger ions still require dehydration, while smaller ions can enter with a near complete hydration shell. Thus, the passage of smaller ions is favoured.

Figure 4. Chemically functionalized pores that generate ion selectivity. (a) Tip functionalized carbon nanotubes that can generate anion vs cation selectivity or enhance salt rejection. (21) (b) A cation selective F-N terminated graphene pore and (c) an anion selective H-terminated graphene pore. (24) (d) A carbonyl lined carbon nanotube with Na^+/K^+ selectivity that depends on the precise positions of the functional groups. (35) (e) A K^+ selective carbonyl lined graphene pore and (f) a carboxylate lined Na^+ selective pore. (36)

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Figure 1

Figure 2

Figure 3

Figure 4