Ion Transport through Perforated Graphene

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**Supporting Information**

ABSTRACT: We investigated the dependence of ion transport through perforated graphene on the concentrations of the working ionic solutions. We performed our measurements using three salt solutions, namely, KCl, LiCl, and K$_2$SO$_4$. At low concentrations, we observed a high membrane potential for each solution while for higher concentrations we found three different potentials corresponding to the respective diffusion potentials. We demonstrate that our graphene membrane, which has only a single layer of atoms, showed a very similar trend in membrane potential as compared to dense ion-exchange membranes with finite width. The behavior is well explained by Teorell, Meyer, and Sievers (TMS) theory, which is based on the Nernst–Planck equation and electroneutrality in the membrane. The slight overprediction of the theoretical Donnan potential can arise due to possible nonidealities and surface charge regulation effects.

Graphene is increasingly studied as a potential material for membrane applications, e.g., filtration, desalination, and electrodialysis. The material is highly robust, and being thin, it exerts minimum resistance to the fluid, 1 making it an attractive candidate for many membrane separation processes. It is also interesting to study the underlying physics governing the transport in a nanoporous single atomic layer membrane as new transport properties are expected to appear due to its unique structural and electrical properties. 2−6 When graphene is in its pristine state, it is completely impermeable, even for the smallest molecule helium. 18,20 However, when nanopores are created in a graphene sheet, it can become permeable and even ion-selective depending on pore-size. 3,5,9−12

To date, some studies have explored the ion-selective properties of graphene. 10,13−17 O’Hern et al. investigated the transport properties of ion bombarded graphene membranes supported on a polycarbonate substrate. The substrate had an average pore diameter of 200 nm so that these pores did not influence the ion transport through graphene. 18 The sizes of the graphene pores were tuned by using oxidative etching. Their study showed that the membrane was cation selective when the oxidative etching time was small, which resulted in small pores. The maximum membrane potential reported was around 3.5 mV, which is around 8 times lower than the theoretical Nernst potential at the reported concentration ratio of 3. The pore sizes of the graphene membrane in their study were in the subnanometer to nanometer range; however, they did not observe significant selectivity even for small pore sizes. This was possibly due to the concentration of the working solution being relatively high (0.5 M KCl/0.1667 M KCl), in which case the overall rejection capacity of the membrane would drop due to a decrease in the Debye length in the pores or a change in surface charge density. 19 A later study by Rollings et al., who created pores in graphene by applying ultrashort high voltage pulses, showed that a graphene membrane remains cation selective for pore diameters up to much larger sizes (∼100 nm). 20 In this case, the salt concentrations were much lower (1−100 mM max). They explored the selectivity of a single pore, whereas for practical application multiple pores are required.

A detailed investigation on the effect of solution concentration on membrane potential in these nanoporous graphene systems and therefore the selectivity has not been investigated to date. In this work, we perform a detailed experimental investigation of membrane potential difference across perforated graphene membranes versus solution concentration. Our findings show that the potential of 2D graphene membranes can be described by the Teorell, Meyer, and Sievers (TMS) theory, which is primarily used to describe the membrane characteristic of 3D dense ion-exchange membranes. 21,22 In the very low concentration range the membrane potential obtained was approximately 70% of the theoretical Nernst potential, which results from either some nonidealities in the theory or the presence of defects in the 2D graphene sheet. As in previous studies, we found graphene to be cation-selective and the loss in selectivity is consistent with a separation mechanism based on charged groups at the pore edges. 23

For conventional ion-exchange membranes, the theory of Teorell, Meyer, and Sievers (TMS) can be used to describe the resulting potentials between two different concentration reservoirs in the case of weakly or strongly charged membranes or different anion and cation diffusivities. 21,22,24,25 The former is related to the Donnan potentials in the system, while the latter to the diffusion potentials. The overall potential in TMS theory, which can be derived from the Nernst–Planck equations, is given by

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* Supporting Information
\[
\Delta \psi = -\frac{RT}{F} \ln \frac{C_2 \sqrt{C_R^2 + 4C_1^2} + C_R}{C_1 \sqrt{C_R^2 + 4C_2^2} + C_R} - \frac{RT}{F} \ln \frac{C_R^2 + 4C_2^2 + uC_R}{C_R^2 + 4C_1^2 + uC_R}
\]

(1)

where \( R \) is the universal gas constant, \( T \) is the temperature, \( F \) is the Faraday constant, \( C_R \) is the fixed ion concentration in the membrane, \( C_1 \) is the high concentration, and \( C_2 \) is the low concentration solution. \( u \) is a term representing the different diffusion rates of cation \((u_c)\) compared to anion \((u_\text{a})\) in the membrane, given by

\[
u = \frac{u_c - u_\text{a}}{u_c + u_\text{a}} \tag{2}\]

The first term in eq 1 represents the Donnan potential, which is generated due to the ion partition between the solution and the charged membrane interface on both sides of the membrane. The second term is called the diffusion potential, which is generated due to the difference in diffusivities of cations and anions through the membrane. The total membrane potential \((\Delta \psi)\) can be derived from Donnan equilibrium and the basic Nernst–Planck equation.\(^{21}\) Equation 1 is valid for 1:1 salts. The equation for the 1:2 salts can be found in the work of Shang et al. and is provided in the Supporting Information.\(^{25}\)

At low concentration (when \( C_1 \) and \( C_2 \ll C_R \)), the Donnan potential is high and reaches the plateau of the Donnan dominated regime. However, with increasing concentration (when \( C_1 \) and \( C_2 \gtrsim C_R \)) and finite \( u \), the diffusion potential starts dominating.

The variation of potential with \( C_2 \) for different membranes (different value of \( C_R \)) and for the same salt (constant value of \( u \)) is shown in Figure 1a. We note that the Donnan dominated plateau and diffusion dominated plateau reach the same value for different \( C_R \) but the transition point from the Donnan plateau to the mixed potential (Donnan + diffusion) occurs at different concentrations. With a higher value of \( C_R \), the membrane reaches the Donnan plateau at a higher concentration. The potential curve for the same membrane (fixed \( C_R \)) but for different salts (different values of \( u \)) is shown in Figure 1b. In this case the curves reach the same Donnan plateau but different diffusion plateaus, as expected.

The holes in the graphene membrane are created by swift heavy ion (SHI) irradiation. The irradiation is performed at the IRRSUD beamline of the GANIL (Caen, France). During irradiation, only the graphene covered PET is bombarded with the help of a protecting shield. Xenon ions of 0.71 MeV/A are bombarded at a perpendicular angle. The fluence is \( 5 \times 10^8 \) ions/cm\(^2\), which implies that \( 5 \times 10^8 \) holes are created in 1 cm\(^2\).\(^{26}\) The membrane fabrication process is done in three main steps, which are illustrated in Figure 2. We use commercially available graphene (Graphena) grown by chemical vapor deposition (CVD) on a copper substrate. First, PMMA coated graphene is wet transferred to a clear, biaxially oriented, 13 μm thick PET support (Goodfellow). PET provides robustness to the membrane and covers intrinsic defects present in graphene. PMMA protects the graphene layer during the wet transfer onto the PET support layer. In the next step, the sample is irradiated with a heavy ion beam that creates pores in graphene and tracks in PET. The number density of holes that are created in graphene is about 1 per μm\(^2\), while the diameters of the holes varies between 1 and 10 nm.\(^{27}\) Finally, to create holes in PET at the track etched area, the membrane is immersed in an etching solution (3 M NaOH, 50 °C). The etching time is half an hour, which creates conical shaped pores in the PET having diameters of about 110 and 400 nm for the top and bottom, respectively. During the etching process, the PMMA again protects the graphene layer from the etching solution. After etching, the PMMA is removed by immersing the membrane in acetone for 45 min and a graphene/PET composite membrane is obtained. More details about the fabrication process can be found in the Supporting Information of our previously published paper.\(^{26}\) The holes in the PET being much larger, presumably do not influence the transport through graphene as the selectivity appears due to Debye layer overlap.

We measure the potential with a potentiostat (Autolab PGSTAT302N) across the membrane at various concentrations.\(^{28-31}\) The graphene membrane is first mounted between two holders with an aperture of 1 cm diameter and sealed with O rings. The membrane is then placed between two reservoirs containing two different concentrations, as shown in Figure 3.
During the measurement, equal volumes of solution are maintained in the reservoirs and the solution is continuously circulated. Also, the temperature of the ionic solutions is kept constant at 25 °C by circulating the solutions through a constant temperature bath. Calomel electrodes (SI Analytic, VWR) are used to sense the potential, correcting for the offset voltage between the two electrodes. During the experiment with the graphene membrane, we vary the concentration in each reservoir by keeping $C_1/C_2$ at a constant value of 5 (unless otherwise stated). The concentration for each solution is varied from 0.3 to 250 mM at the low concentration side. We measure the potential for three different salts, potassium chloride (KCl, 1:1), lithium chloride (LiCl, 1:1), and potassium sulfate (K$_2$SO$_4$, 1:2).

Our goal is to investigate the cation selectivity of 2D perforated graphene membranes and how this varies with salt concentration and type. The selectivity is estimated by measuring the potential across the membrane generated due to charge imbalance and scaled to the theoretical Nernst potential ($\Delta\psi_N = (RT/F) \ln(C_1/C_2)$).

In Figure 4, the membrane potential scaled to the Nernst potential ($\Delta\psi$) plotted against different concentrations. Solid squares are the values for KCl, the open circles are the values for K$_2$SO$_4$, and the open triangle denotes the values of LiCl. The relative standard deviation of measurements is approximately 1%.

At low salt concentration, where the fixed ion concentration in the membrane is much higher than the solution concentration, the ability to reject the co-ions by the graphene membrane is high (approximately 70% of the theoretical Nernst potential). This is similar to the ratio found by Rollings et al. for a single nanopore in a graphene membrane with KCl in a ratio of 100:1, where a reversal potential of approximately $-100$ mV was measured vs a theoretical Nernst potential of approximately $-115$ mV. When the concentration of the solution increases, the difference between $C_R$ and $C_1$ decreases, which decreases the rejection of the co-ions by the membrane and the diffusion potential starts contributing to the membrane potential. At very high salt concentrations, there is no rejection of co-ions by the membrane and the diffusion potential dominates due to the difference in diffusivities of co-ions and counterions through the membrane.

We have also performed our experiment with PET foils irradiated with the same fluence ($5 \times 10^8$ ions/cm$^2$) and having the same SHI setting and etched in conditions (3 M NaOH, 50 °C, half an hour) similar to that of the composite membrane without any graphene on top of it. For these PET-only membranes we did not observe any selectivity during the experiment. This implies that the ion selectivity is due to the nanoporous graphene membrane.

In our case, we see that the plateau value in the low concentration region is smaller than the Nernst potential. This is possibly due to larger pores in the graphene structure compared to the Debye length, which is on the order of 10 nm for the lowest concentration investigated. In order to express the deviation of the measured potential vs the ideal Nernst case,
we introduce a factor $\alpha$ to the Donnan potential term in the TMS theory.

$$\Delta \psi = \alpha \Delta \psi_{\text{Donnan}} + \Delta \psi_{\text{Diffusion}}$$  \hspace{1cm} (3)

We fit the experimental data shown in Figure 4 with the modified TMS model (eq 3) with the fitting parameters, $\hat{C}_R$, $\alpha$, and $(\bar{u}_+ / \bar{u}_-)$. The third parameter is introduced here because the value of this ratio of diffusivity through the membrane, in principle, can differ from the diffusivity ratio in the bulk.

The lines in Figure 4 represent the experimental data with the modified TMS model for the three individual salt solutions. The results are for a single membrane (sample 1) tested multiple times. The measurement errors are, on average, approximately 1%. The curves show very similar patterns. At low concentrations, all of them reach a plateau at similar potentials, whereas the membrane potentials at very high concentrations are different for the three different salts. The potential at high concentrations is solely dependent on the diffusion potential of the salt, which is different for the three different salts we use. The diffusion potential for KCl is approximately zero, while that for LiCl is negative. For both salts, a clear transition from the Donnan to diffusion dominated regime is evident. For KCl both K$^+$ and Cl$^-$ ions have similar diffusivities in the bulk, which results in the diffusion potential tending to zero. For LiCl, we measure a negative diffusion potential because Cl$^-$ ions move faster than Li$^+$ ions, which is consistent with their bulk behavior. Unlike for KCl and LiCl, we could not measure the potential at very high concentration for K$_2$SO$_4$ due to its low solubility in water; however, the trend shows that it has a positive diffusion potential at higher concentrations. This is consistent as K$^+$ moves faster than SO$_4^{2-}$ ions in the bulk and therefore should result in a diffusion potential tending to a positive value.

For KCl and LiCl we use the equation for a 1:1 salt whereas for K$_2$SO$_4$ we use the TMS model for a 1:2 salt. The least-squares estimates of the fitting parameters and 95% confidence interval of the fitting parameters for the three different salts are shown in Table 1. We obtain similar $\hat{C}_R$ values for KCl and LiCl whereas $\hat{C}_R$ value for K$_2$SO$_4$ is much lower. The lower value of $\hat{C}_R$ for K$_2$SO$_4$ is possibly due to charge regulation effects or insufficient data points at high concentration. As mentioned, the low solubility of K$_2$SO$_4$ in water limited the experimental range for this salt.

The value of correction factor ($\alpha$) varies from 0.58 to 0.76 for the three salts. The bulk values of $\bar{u}_+ / \bar{u}_-$ for KCl, LiCl, and K$_2$SO$_4$ are 1.04, 1.97, and 0.54 respectively. The table shows that the fitted values of $\bar{u}_+ / \bar{u}_-$ (0.99 ± 0.05, 1.64 ± 0.08, 0.43 ± 0.03) do not differ much from the bulk values, which implies that there is a relatively small change in the diffusivity ratios of cations and anions when they diffuse through a membrane like graphene consisting only a single layer. For dense ion-exchange membranes, the diffusivity ratio of ions in the membrane can vary by a large degree. For an example, in Nafton-117 the diffusion coefficient of K$^+$ is around half of its bulk value.

The variation of potential with concentration can be physically understood from the concept of an electric double layer for charged membranes. The terminated carbon bonds at the pore edges in graphene membranes contain some fixed negative functional groups likely due to partial oxidation. These ionic groups are likely created during the bombardment process or during the etching step. At a very low ionic concentration, the Debye layer is large, which blocks the pores for co-ions, leading to Donnan exclusion and a high membrane potential. When the concentration of ionic solution is high, the Debye layer thickness becomes small compared to the pore radius. Additionally, the pore charge density can be affected by the bulk concentration via surface charge regulation.

Figure 5 shows the variation of membrane potential scaled to the Nernst potential with varying concentration for two different KCl salt concentration ratios. For both cases, at low concentration the membrane potential reaches a plateau. This implies that with the increase in concentration ratio, the selectivity remains the same. We note that when the concentration at the higher concentration side of the membrane is increased (for $C_1/C_2 = 10$), the transition from the Donnan dominated regime to the diffusion dominated regime happens at lower concentration ($C_2$), as shown in Figure 5. This implies that it is the high concentration side of the solution that determines the transition from the Donnan dominated regime to the diffusion dominated regime in the membrane potential versus concentration plot.

To check the reproducibility of the membrane behavior, we have used three similar membranes prepared by the same fabrication method and performed our membrane potential measurements with potassium chloride for a $C_1/C_2$ ratio of 5. The average membrane potential for the three samples is shown in Figure 6. The standard deviation for measurement represents the sample to sample variation.

We have fitted the data for each sample with the modified TMS model and have obtained the best-fit parameters, which are shown in the Table 2. We note that the values of $\hat{C}_R$ are different between samples. This implies that variation among the samples can arise due to the difference in the amount of fixed charge groups introduced during the fabrication process. We have fitted the data from the three sample altogether with the modified TMS model to check the variability of membrane...
charge, possibly due to variation in the pore-size distribution and coverage of charged functional groups in the nanopores. Our detailed observation of variable cation selectivity of graphene membranes with concentration motivates further studies of ion transport through nanoporous graphene membranes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b02771.

Pictures of the material and experimental setup, experimental results for PET membranes without any graphene on top, TMS equation for 1:2 salt, and TEM image of graphene pore (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science 2008, 321, 385–388.
(2) Hu, S.; Loxada-Hidalgo, M.; Wang, F. C.; Mishchenko, A.; Schedin, F.; Nair, R. R.; Hill, E. W.; Boulchadolcov, D. W.; Katsnelson, M. I.; Dyke, R. A.; et al. Proton Transport Through One-Atom-Thick Crystals. Nature 2014, 516, 227–230.
(3) Cohen-Tanugi, D.; Grossman, J. C. Water Desalination Across Nanoporous Graphene. Nano Lett. 2012, 12, 3602–3608.
(4) Jang, D.; Ibrobo, J.; C.; Laoui, T.; Karnik, R. Water and Solute Transport Governed by Tunable Pore Size Distributions in Nanoporous Graphene Membranes. ACS Nano 2017, 11, 10042–10052.
(5) Celebi, K.; Buchheim, J.; Wyss, R. M.; Drou几年ian, A.; Gasser, P.; Shorubalko, I.; Kye, J.-I.; Lee, C.; Park, H. G. Ultimate Permeation Across Atomically Thin Porous Graphene. Science 2014, 344, 289–292.
(6) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional Gas of Massless Dirac Fermions in Graphene. Nature 2005, 438, 197.
(7) Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Impermeable Atomic Membranes from Graphene Sheets. Nano Lett. 2008, 8, 2458–2462.
(8) Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes. Science 2012, 335, 442–444.
(9) Huang, L.; Zhang, M.; Li, C.; Shi, G. Graphene-Based Membranes for Molecular Separation. J. Phys. Chem. Lett. 2015, 6, 2806–2815.
Mirzayev, R.; Kozubek, R.; Lebius, H.; Karlu Meyer, J.; Lebius, H.; Band Krasheninnikov, A. V.; et al. Creating Nanoporous Graphene with Applications Permeability in a Cation Exchange Membrane. Biophys. J. 2017, 114, 511–518.

(21) Tanaka, Y. Ion Exchange Membranes: Fundamentals and Applications; Elsevier: Amsterdam, Netherlands, 2015.

(22) Sata, T. Ion Exchange Membranes: Preparation, Characterization, Modification and Application; The Royal Society of Chemistry: Cambridge, U.K., 2004.

(23) Goswami, A.; Acharya, A.; Pandey, A. K. Study of Self-Diffusion Coefficient and Ion Conductivity of Monovalent and Divalent Cations in Nafion-117 Ion-Exchange Membrane. J. Membr. Sci. Res. 2016, 2, 1234–1241.

(24) Galama, A. H.; Post, J. W.; Hamelers, H. V. M.; Nikonenko, V. V.; Biesheuvel, P. M. On the Origin of the Membrane Potential Arising Across Densely Charged Ion Exchange Membranes: How Well Does the Teorell-Meyer-Sievers Theory Work? J. Membr. Sci. Res. 2016, 2, 128–140.

(25) Shang, W. J.; Wang, X. L.; Yu, Y. X. Theoretical Calculation on the Membrane Potential of Charged Porous Membranes in 1–1, 1–2, 2–1 and 2–2 Electrolyte Solutions. J. Membr. Sci. 2006, 285, 362–375.

(26) Madau, L.; Schumacher, J.; Ghosh, M.; Ochedowski, O.; Meyer, J.; Lebus, H.; Band’Etat, B.; Toimil-Molares, M. E.; Trautmann, C.; Lammertink, R. G. H.; et al. Fabrication of Nanoporous Graphene/Polymer Composite Membranes. Nanoscale 2017, 9, 10487–10493.

(27) Vázquez, H.; Ahlgren, E. H.; Ochedowski, O.; Leino, A. A.; Mirzayev, R.; Kozubek, R.; Lebus, H.; Karlsson, M.; Jaksic, M.; Krasheninnikov, A. V.; et al. Creating Nanoporous Graphene with Swift Heavy Ions. Carbon 2017, 114, 511–518.

(28) Gunn, R. B.; Curran, P. F. Membrane Potentials and Ion Permeability in a Cation Exchange Membrane. Biophys. J. 1971, 11, 559–571.

(29) Wills, G. B.; Lightfoot, E. N. Transport Phenomena in Ion-Exchange Membranes. Ind. Eng. Chem. Fundam. 1966, 5, 114–120.

(30) Cassady, H. J.; Cimino, E. C.; Kumar, M.; Hickner, M. A. Specific Ion Effects on the Permeselectivity of Sulphonated Poly(Ether Sulfone) Cation Exchange Membranes. J. Membr. Sci. 2016, 508, 146–152.

(31) Geise, G. M.; Cassady, H. J.; Paul, D. R.; Logan, B. E.; Hickner, M. A. Specific Ion Effects on Membrane Potential and the Permeselectivity of Ion Exchange Membranes. Phys. Chem. Chem. Phys. 2014, 16, 21673–21681.

(32) Petr, Vanýsek CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 2005.

(33) Holloway, R.; Schumacher, J.; Pandey, A. K. Study of Self-Diffusion of Monovalent and Divalent Cations in Nafion-117 Ion-Exchange Membrane. J. Phys. Chem. B 2001, 105, 9196–9201.

(34) Riley, J. Colloid Science: Principles, methods and applications; Wiley: Chichester, U.K., 2010.