The Potential of Graphene Membranes

Ion Transport through Graphene Nanopores

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Mandakranta Ghosh

DISSERTATION

The Potential of Graphene Membranes:

Ion Transport through Graphene Nanopores

by Mandakranta Ghosh

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The Potential of Graphene Membranes: Ion Transport through Graphene Nanopores

DISSERTATION

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To Baba, Maa, Dadabhai and Rupal

“I mean, so hopefully soon there’s enough women and enough people of colour and enough of every group out there that feels that they get the recognition they deserve, and then we don’t have to talk about it anymore.”

Donna Strickland (Nobel laureate, 2018)

*Where the mind is without fear and the head is held high;
Where knowledge is free;
Where the world has not been broken up into fragments by narrow domestic walls;
Where words come out from the depth of truth;
Where tireless striving stretches its arms towards perfection;
Where the clear stream of reason has not lost its way into the dreary desert sand
of dead habit;
Where the mind is led forward by thee into ever-widening thought and action
Into that heaven of freedom, my Father, let my country awake.*
by Rabindranath Tagore (Nobel laureate, 1913)

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Scientific output

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Preface

This thesis is about ion transport through a very thin nanoporous membrane called graphene. Even though the pore sizes are bigger than the ion sizes, this single atomic nanoporous layer can selectively pass positive ions and block negative ions. This can be followed from the cover page of this thesis. The front cover has equal number of cations and anions which are trying to pass through the nanopores of the graphene. But as the membrane is cation selective, the back cover has mostly cations indicating selective transport. The thesis explains the transport mechanism. In this thesis I have tried to understand the ion transport at varied external factors such as type of ions, concentration, pH or external bias and used theoretical models to explain our experimental observations.

CHAPTER 1

Introduction

1.1 Background on separation techniques

Membrane filtration and separation are very important processes especially in water, food, dairy and chemical industries. These processes typically require ambient temperature, avoid harsh chemical reactions and are thus considered a green technique. Different industries and daily life applications such as water treatment to produce drinking water, industrial waste water treatment and food processes require the selectivity of membranes [1–3]. Ion separation and mineral recovery is an increasingly important aspect related to water treatment. Ion separation processes involving membranes concern reverse osmosis, nanofiltration, and (electro)dialysis. The first two processes typically involve a pressure gradient as driving force, whereas the latter is driven by concentration and potential gradients. The transport of ions through these membranes is governed by their interaction with the membrane phase, based on size and charge.

New generations of membranes are continuously researched specifically for smaller scale application, including bio-sensing and DNA translocation. With the steeply growing interest in 2D materials like graphene, studies regarding transport of ions through and between these atomically thin sheets are jointly increasing. The research objective described in this thesis is to engineer such a nano-porous membrane (based on 2D graphene) and investigate the corresponding ion transport through these pores. Before going into detail of this particular type of membrane, the essential concepts relevant for this area of research will be summarized.

There are different physical transport processes that occur in a membrane. The most important processes relevant for ion separation processes using membranes are (i) size exclusion, (ii) charge exclusion and (iii) dielectric exclusion [4].

- Size exclusion occurs when the pore size of the membrane is comparable or smaller than the species to be retained. Microfiltration (MF) membranes have relatively large pore sizes (0.1-10 μm) and are used to remove suspended particles or bacteria. To separate smaller species from 1-100 nm (e.g. proteins, viruses), ultrafiltration (UF) membranes are used. Nanofiltration (NF) membranes (1-10 nm) are used for removal of salt, amino acid, and dye [5]. A major industrially applied method for ion separation concerns reverse osmosis (RO), which requires a relatively higher pressure ($> 4 \text{ MPa}$) to overcome the osmotic pressure. The rejection mechanism in RO and NF is primarily based on a combination of size and dielectric exclusion [6–8].
- Ion exchange membranes (IEM) are used for demineralisation or deionisation of water, energy conversion and storage in fuel cells, redox flow batteries [9, 10]. The commercial membranes which are used for electrodialysis (ED) are typically dense polymeric membranes containing fixed charged groups in the membrane matrix. Depending on the valency of the fixed charged groups it can selectively pass cations or anions. Other than these commercial membranes, nano-porous materials such as solid state nano-pores in synthetic membranes (SiN_x , SiO_2), nano-porous graphene, graphene oxide multi layers, metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and hybrid membranes can act as ion selective membranes depending on the ion concentration. Biological nanopores such as protein α -hemolysin are found in cell membranes, acting as transport channels for ions or molecules in and out of cells [11–13]. The selection mechanism of these membranes can be based on size exclusion as well as exclusion based on double layer overlap and dielectric exclusion [14].
- Dielectric exclusion is an ion rejection mechanism observed in NF membranes

and typically dominates at < 1 nm and effective up to about 2 nm pore size [4, 14, 15]. This takes place at interfaces between media having different dielectric constants. The mutual interaction of ions at the surface and the induced bound electric charge at the interface leads to the dielectric exclusion. This also depends on pore geometry e.g. cylindrical pores have stronger exclusion compared to slit pores.

1.2 Ion exchange membranes (IEM)

Ion exchange membranes (and resins) are materials which allow selective transport based on the charge inside the membrane, and they are traditionally used for selective transport in processes such as electrodialysis, Donnan dialysis, electrolysis, fuel cells, sensing materials, medical applications.

Ion exchange membranes are thin films ($\sim 100 \mu\text{m}$) made of functional polymers containing ionic groups (such as $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}$, $-\text{COOH}$, $-\text{NH}_3\text{OH}$, etc) and are non porous [16, 17]. Depending on the nature of fixed charged groups, the membrane can be cation or anion selective. When the membrane contains negatively charged groups, they allow positive ions to pass through and block negative ions and are called cation exchange membranes. When the membrane contains cationic functional groups, they allow negative ions to pass through and block positive ions and are called anion exchange membranes. The selectivity of ions is expressed by the permselectivity (α_c). This quantifies the extent a membrane being selective for one type of ion and block the other. These membranes can be homogeneous or heterogeneous depending on the charge group distribution. This is given by the following equations,

$$\alpha_c(\%) = \frac{\text{Measured membrane potential}}{V_{\text{Theory}}} \times 100\% \quad (1.1)$$

$$V_{\text{Theory}} = \frac{RT}{zF} \ln \frac{c_1}{c_2} \quad (1.2)$$

In which R is the gas constant, T the temperature, z the ion valence, F the Faraday constant, c_1 and c_2 the concentrations of the two solutions across the membrane.

The hydrophilic nature of these membranes is such that water can permeate through the membrane together with the ions. The transport of ions through these material can be complex, due to the sorption and desorption of ions, defect formation due to chemical reaction or hopping of ions between the functional groups/solutions inside the membrane matrix [18].

1.2.1 Different transport processes with IEM

Electrodialysis (ED) is a demineralization technique in which ion exchange membranes are used. In this technique, a stack of alternating cation and anion exchange membranes are placed which are separated by spacers ($\sim 100 - 2000 \mu\text{m}$). Concentrated and desalinated streams are produced under the influence of an applied electrical potential or fixed current over the stack [9]. Diffusion dialysis is another method of separation which requires IEMs. In this case, the separation is driven by a concentration gradient and is used to recover acid or alkali from waste. Another method of selective separation of ions is called thermo-dialysis where a temperature gradient exist across an ion exchange membrane driving the transport [17]. The primary mechanism of ion selectivity of ion exchange membranes are due to a mechanism called Donnan exclusion of ions which will be discussed in section 1.3.

1.2.2 Ion transport phenomena in a charge selective interface

Studies on the ion transport through membranes mainly originated to explain transport phenomena in biological membranes. The transport of ions through charge selective interface, gives rise to various interesting phenomena such as permselectivity of cations or anions, generation of membrane potential, bi-ionic potential, ion conductivity, and water transport [17, 19, 20].

There are three driving forces which results in transport through charge selec-

tive interface. The three transport mechanism of ions through membranes are (i) electromigration, (ii) diffusion, (iii) advection. Electromigration of ions occurs due to an electric potential gradient ($\nabla\phi$). Diffusion occurs due to transport of ions due to concentration gradient (∇c), resulting in the ionic flow. Advection of ions takes place when there is a pressure gradient (∇p), and it is responsible for the fluid flow [21–23].

Electrodialysis combines all these transport phenomena. In electrodialysis, a stack of cation and anion exchange membranes are placed alternatively with a spacer material in between. In this process, a diluted and concentrated streams are separated by controlling the movement of ions by an externally applied potential difference ($\Delta\phi$). Advective ion transport is usually neglected through the ion exchange membranes [16, 17, 22].

To understand the ion transport phenomena let us consider a membrane in between two reservoirs having solutions with different salt concentration. Neglecting advective transport, the transport through this charge selective dense membrane is governed by the electrochemical (μ_i' J/mol) potential:

$$\mu_i' = \mu_i + zF\phi = \mu^o + RT \ln c_i + zF\phi_i \quad (1.3)$$

where z is the ion valence, F is the Faraday constant (C/mol), R is the gas constant (J/mol K), T is the temperature (K), and c_i is the ion concentration (mol/m³).

Now according to Donnan equilibrium, species present in contacting phases will have the same electrochemical potential once equilibrium is reached. This implies that for phases with concentrations c_1 and c_2 , their electrochemical potential will be equal:

$$\mu^o + RT \ln c_1 + zF\phi_1 = \mu^o + RT \ln c_2 + zF\phi_2 \quad (1.4)$$

This equation can be simplified and rewritten as,

$$\Delta\phi = \phi_2 - \phi_1 = \frac{RT}{zF} \ln \frac{c_1}{c_2} \quad (1.5)$$

In case of membranes, this equation basically represents the generation of a potential jump at the membrane/solution interface as a requirement of Donnan equilibrium theory. Another potential jump will be located at the other membrane side that is in contact with the solution on that side.

The flux of ions is proportional to the negative gradient of the electrochemical potential. Differentiating equation 1.3 with respect to x , where x represents the transport direction perpendicular to the membrane, the gradient of the electrochemical potential can be expressed as,

$$\frac{d\mu_i'}{dx} = RT \frac{d \ln c_i}{dx} + z_i F \frac{d\phi}{dx} \quad (1.6)$$

The ionic molar flux, in solution and membrane is represented by J_i (mol/m² s). The molar flux by definition is the product of molar concentration and velocity. This velocity is the product of the mobility and the total driving force. The driving force for ion transport in this case is the negative electrochemical potential gradient. The ionic flux is thus given by,

$$J_i = -\frac{u_i}{F} c_i \frac{d\mu_i'}{dx} \quad (1.7)$$

where u_i is the electric mobility (m²/V s), which is related to the ion diffusion coefficient, D_i (m²/s) by the electrical mobility equation

$$D_i = \frac{RT}{z_i F} u_i \quad (1.8)$$

Combining equations 1.6, 1.7 and 1.8, we get

$$J_i = -\frac{D_i}{RT} c_i \left(\frac{d \ln c_i}{dx} + z_i F \frac{d\phi}{dx} \right) \quad (1.9)$$

Rewriting this equation gives the common form of the Nernst-Planck (NP) equation.

$$J_i = -D_i \left(\frac{dc_i}{dx} + c_i \frac{z_i F}{RT} \frac{d\phi}{dx} \right) \quad (1.10)$$

As mentioned earlier, depending on applications, the advective term which is a multiplication of concentration (c_i) and velocity (v_i) is neglected in the NP equation. The advective term in the wall normal direction (through the membrane) is usually very small compared to the ion diffusion and migration terms.

1.3 Theory of membrane potential

When two electrolyte solutions of different ionic concentrations are separated by an ion exchange membrane, an electric potential is generated across the membrane which is called the membrane potential. If the solutions contain the same co-ions but different counter-ions then the potential generated is called the bi-ionic potential.

The membrane potential, specially for biological membranes is typically calculated using the Goldman-Hodgkin-Katz (GHK) voltage equation [24–27]. This equation is applicable for multiple permeating monovalent species and it takes into account the permeability of each specie. The GHK equation can be derived from the NP equation. For single type permeating monovalent ions, GHK reduces to the Nernst equation. The limitation of the GHK model for the application of ion exchange membranes is that it does not take into account the effect of fixed charge of the membrane or the effect due to divalent ions. Another model which is also used is the space charge model (SCM) which was introduced by Osterle and co-workers [28, 29]. This describes the electrolyte transport through a charged capillary pore. This model considers gradients in radial and axial direction. The most widely used theoretical approach to describe the membrane potential is the

Teorell-Meyer-Sievers (TMS) theory [16, 17, 22].

1.3.1 Teorell-Meyer-Sievers (TMS) theory

TMS theory is based on the Donnan equilibrium theory and Nernst-Planck equation [16, 17, 22]. This model is one dimensional (1D) which means the gradient of ion concentrations are unidirectional across the membrane. The fixed charge is uniformly distributed inside the membrane. Figure 1.31 shows a cation exchange membrane which has a fixed ion concentration $\bar{c}_R$. The membrane is placed between two different concentration electrolyte reservoirs, high concentration electrolyte c_1 on one side and low concentration electrolyte c_2 on the other side. In a cation exchange membranes, cations can be transported across the membrane while anions are mostly blocked. The membrane potential is generated because of the equilibrium in the electrochemical potential.

Figure 1.1 — The concentration profile inside ion exchange membrane separated by two electrolyte reservoirs with concentrations c_1 , c_2 . The concentrations for positive, negative and fixed ion concentration inside the membrane are denoted by $\bar{c}_+$, $\bar{c}_-$, $\bar{c}_R$.

The transport of ions due to advection is neglected in this theory assuming that there is no water transport. In equation 1.10, we note that F/RT is the inverse of the thermal voltage. Thereby a dimensionless potential can be defined as $\Psi = \phi F/RT$. The NP equation can be arranged as

$$J_i = -D_i \left(\frac{dc_i}{dx} + c_i z_i \frac{d\Psi}{dx} \right) \quad (1.11)$$

The TMS theory is based on zero current density across the membrane in an equilibrium situation which from Equation 1.11 gives

$$\frac{1}{c_i} \frac{dc_i}{dx} = -z_i \frac{d\Psi}{dx} \quad (1.12)$$

Due to the difference in the concentration of ions inside the membrane compared to the solution, a Donnan potential ($\Delta\Psi_i$) results. We denote the superscripts m for membrane phase and s for solution phase.

$$\int_s^m d \ln c_i = -z_i \int_s^m d\Psi \quad (1.13)$$

By integrating this equation, we get

$$\ln \frac{c_i^m}{c_i^s} = -z_i (\Psi^m - \Psi^s) = -z_i \Delta\Psi \quad (1.14)$$

$$c_i^m = c_i^s \exp(-z_i \Delta\Psi) \quad (1.15)$$

The bulk aqueous electrolyte solutions as well as the membrane phase are electrically neutral. For a 1:1 salt, there are positive and negative species in the solution having concentrations c_+ and c_- respectively. Inside the membrane, there are three species of charge: positive and negative ions provided by the solution which we denote as $\bar{c}_+$ and $\bar{c}_-$ respectively, and the intrinsic fixed ion concentration of the membrane, $\bar{c}_R$. Applying electroneutrality condition in the

membrane phase, the following equation is achieved.

$$z_+ \bar{c}_+ + z_- \bar{c}_- + z_m \bar{c}_R = 0 \quad (1.16)$$

For, 1:1 salt, z_+ is +1, z_- is -1. The z_m is negative for a cation exchange membranes and positive for an anion exchange membrane. For a cation exchange membrane and a 1:1 salt the following equation is achieved.

$$\bar{c}_+ - \bar{c}_- + \bar{c}_R = 0 \quad (1.17)$$

Using Equation 1.15 and 1.17 for the c_1 side of the membrane we get,

$$c_1 \exp(-\Delta\Psi_1) - c_1 \exp(\Delta\Psi_1) - \bar{c}_R = 0 \quad (1.18)$$

This equation can be arranged as,

$$c_1 - c_1 \exp(2\Delta\Psi_1) - \bar{c}_R \exp(\Delta\Psi_1) = 0 \quad (1.19)$$

The solution of Equation 1.19 is,

$$\exp(\Delta\Psi_1) = \frac{\bar{c}_R + \sqrt{\bar{c}_R^2 + 4c_1^2}}{2c_1} \quad (1.20)$$

$$\Delta\Psi_1 = \ln \frac{\bar{c}_R + \sqrt{\bar{c}_R^2 + 4c_1^2}}{2c_1} \quad (1.21)$$

Similarly, for the c_2 side of the membrane

$$\Delta\Psi_2 = \ln \frac{\bar{c}_R + \sqrt{\bar{c}_R^2 + 4c_2^2}}{2c_2} \quad (1.22)$$

The total Donnan potential ($\Delta\Psi_D$) is the sum of the potential generated on both sides of the membrane, i.e. $\Delta\Psi_1$ and $\Delta\Psi_2$.

$$\Delta\Psi_D = -\Delta\Psi_1 + \Delta\Psi_2 \quad (1.23)$$

$$\Delta\Psi_D = -\ln \frac{c_2}{c_1} \frac{\sqrt{\bar{c}_R^2 + 4c_1^2} + \bar{c}_R}{\sqrt{\bar{c}_R^2 + 4c_2^2} + \bar{c}_R} \quad (1.24)$$

Another contribution of potential which is due to the ions diffusing through the membrane from the high concentration side to the low concentration side when the membrane is not selective. This is generated due to difference in the diffusivity of ions inside the membrane which is called the diffusion potential.

Maintaining the zero current condition, the co-ion and counter-ion flux is zero and it is given by the following equation. From equation 1.11

$$-\bar{D}_+ \left(\frac{\partial \bar{c}_+}{\partial x} + \bar{c}_+ \frac{\partial \Psi}{\partial x} \right) + \bar{D}_- \left(\frac{\partial \bar{c}_-}{\partial x} - \bar{c}_- \frac{\partial \Psi}{\partial x} \right) \quad (1.25)$$

Where, $\bar{D}_+$ and $\bar{D}_-$ are diffusion coefficient of counter-ions and co-ions inside a cation selective membrane.

Combining equations 1.17 and 1.25,

$$-\left(\frac{d\bar{c}_+}{dx} + \bar{c}_+ \frac{d\Psi}{dx} \right) + \frac{\bar{D}_-}{\bar{D}_+} \left(\frac{d(\bar{c}_+ - \bar{c}_R)}{dx} - (\bar{c}_+ - \bar{c}_R) \frac{d\Psi}{dx} \right) = 0 \quad (1.26)$$

Taking the differentiation of the quantities and considering $\bar{c}_R$ is constant across the membrane thickness.

$$\frac{d\Psi}{dx} = \frac{(\frac{\bar{D}_-}{\bar{D}_+} - 1)}{-\frac{\bar{D}_-}{\bar{D}_+} \bar{c}_R + (\frac{\bar{D}_-}{\bar{D}_+} + 1) \bar{c}_+} \frac{d\bar{c}_+}{dx} \quad (1.27)$$

From Donnan equilibrium condition the relation between ion concentrations in the membrane phase and bulk can be related as,

$$\bar{c}_{1,2} = \frac{1}{2} \sqrt{\bar{c}_R^2 + (2c_{1,2})^2} + \frac{1}{2} \bar{c}_R \quad (1.28)$$

Using equation 1.28 and integrating this equation across the width of the

membrane, the diffusion potential is obtained.

$$\Delta\Psi_{diff} = -\bar{u} \ln \frac{\sqrt{\bar{c}_R^2 + 4c_2^2} + \bar{u}\bar{c}_R}{\sqrt{\bar{c}_R^2 + 4c_1^2} + \bar{u}\bar{c}_R} \quad (1.29)$$

where,

$$\bar{u} = \frac{\bar{D}_+ - \bar{D}_-}{\bar{D}_+ + \bar{D}_-} \quad (1.30)$$

Sum of $\Delta\Psi_D$ and $\Delta\Psi_{diff}$ gives the total membrane potential.

$$\phi = -\frac{RT}{F} \ln \frac{c_2}{c_1} \frac{\sqrt{\bar{c}_R^2 + 4c_1^2} + \bar{c}_R}{\sqrt{\bar{c}_R^2 + 4c_2^2} + \bar{c}_R} - \frac{RT}{F} \bar{u} \ln \frac{\sqrt{\bar{c}_R^2 + 4c_2^2} + \bar{u}\bar{c}_R}{\sqrt{\bar{c}_R^2 + 4c_1^2} + \bar{u}\bar{c}_R} \quad (1.31)$$

1.4 New generation 2D membranes

Ion transport through ion exchange membranes and resins are well studied for several years and the transport mechanism is quite well understood. These membranes are used for several purposes commercially. However, there is a constant quest for developing novel membrane materials which can be used for other applications in smaller devices mostly focusing on biosensing. In the past few years, there has been an increase in interest regarding membranes which have infinitesimally small thickness leading to as minimum resistance as possible to the incoming fluid, resulting in a very high permeation [30, 31].

1.4.1 Carbon nanotubes

The first evidence of fast water transport through thin nanochannels was described for carbon nanotubes (CNT). CNTs are nanomaterials as two of its spatial dimensions are in nanoscale range (below 100 nm) [32, 33]. The sub nanometer diameter of CNTs results in a fast permeation of water while rejecting salt ions. The fast water permeation is attributed to the atomic smoothness of the CNT walls and a molecular ordering phenomena due to nanometric (1-2 nm) confinement. Corry, in a molecular dynamics simulation, has shown that ions are impeded

by CNT cylinders due to a large energy barrier compared to water molecules [33, 34]. The reason of this large energy barrier is due to the nanometric entrance of the CNTs which doesn't allow hydrated ions to enter. In addition, the energy barrier is high for an ion to move from the bulk into a nanotube with a lower dielectric constant. Water creates a stable hydrogen bond with the walls of carbon nanotubes resulting in fast permeation.

1.4.2 Graphene oxide (2D)

The use of graphene oxide as membrane material has been first developed by Nair et al. (See Figure 1.2). They have experimentally shown that water molecules can pass 10^{10} times faster compared to the smallest atom Helium, through the interlayer spacing of graphene oxide layers [35]. Since that study, there has been several other attempts to use graphene and its derivatives as membranes [36–38]. Han et al. have used base refluxed reduced graphene oxide membranes supported on polyvinylidene fluoride (PVDF) or mixed cellulose ester membranes which shows very high rejection ($> 99\%$) for organic dyes (methyl blue and direct red 81) compared to salt ions (20-60%) [37]. They have experimentally proven that the rejection mechanism in this case is not only due to size exclusion, as electrostatic interaction also play a major role in the rejection. The presence of carboxylic group on graphene oxide (GO) surface makes it negatively charged upon deprotonation which results in a high retention of negatively charged dye compared to the electroneutral rhodamine B (78%). Further studies have been conducted for a detailed understanding of the ion transport through the interlayer spacing between graphene oxide layers. Sun et al. have shown that heavy metal ions are infiltrated slowly compared to sodium salts [39]. In continuation of this work they further investigated the ion recognition mechanism of graphene via experiments and density functional theory (DFT). The difference in transport of alkali and alkaline earth cations was attributed to differences in cation - π interactions with the sp^2 clusters within the GO interlayer spacing along with dehydration effect [40]. These studies show that GO membranes can be a promising material for water transport with high ion rejection. At the same time, ion transport can be

Figure 1.2 — Schematic diagram of fluid permeation through the interlayer spacing of GO flakes. (Adapted with permission from Copyright © 2012, American Association for the Advancement of Science) [35].

influenced by introducing surface charge groups.

1.4.3 Nanoporous graphene (2D)

Along with the study of ion transport through the interlayer spacing of GO, scientists were also interested to study the transport through nanopores in a single layer of graphene. Nanoporous graphene is a promising material for diverse applications [41–46]. Konatham et. al. have performed molecular dynamics (MD) simulations to study water and ion transport through nanopores with 7.5 - 14.5 Å diameter pores in a monolayer graphene [31]. Their study shows that ion exclusion can be achieved up to a 7.5 Å pore diameter of non functionalized (uncharged) pores. Pores larger than that can not block the ions. It should be noted that dielectric exclusion will also be an important mechanism of exclusion for such a pore size close to 7.5 Å, which was not mentioned in the article. When the pores are functionalized, they influence the ion rejection mechanism. For example, carboxylic acid functionalized groups shows improved ion rejection because of a higher free energy barrier experienced by water and ions. Due to the ion screening effect, this free energy barrier decreases with increasing salt concentrations in the bulk. Cohen-Tanugi et. al. have also used MD simulation to show that multilayer graphene membranes can desalinate water more effectively than monolayer graphene. They have studied the salt rejection mechanism as a function of pore diameter, layer spacing and applied pressure. The smaller nanopores (3 Å) exhibit full salt rejection compared to larger pores (4.5 Å) and fully aligned pores with multiple layers combine high salt rejection with high

water flux [30].

The nanopores in graphene can be present as intrinsic defects or can be artificially created [47–49]. Different techniques are used to create these nanopores artificially including ion beam bombardment, oxygen plasma etching, high electric pulses, and focused ion beams [48, 50, 51]. O’Hern et. al. have reported size selective transport of molecules through the intrinsic defects (1–15 nm pores) in chemical vapour deposited (CVD) graphene supported on porous polycarbonate track etched (PCTE) substrates [47]. Similarly, Jain et al. has demonstrated that intrinsic sub-2 nanometer graphene pores show diverse ion transport behaviour depending on electrostatic interaction and ion dehydration [49]. Another work by the O’Hern group demonstrated the charge selective transport through graphene nanopores which are artificially created by ion beam bombardment [48].

Figure 1.3 — Schematic diagram of pore creation in graphene by ion beam bombardment followed by oxidative etching. (Adapted with permission from Copyright © 2014, American Chemical Society) [48].

In the study by O’Hern et.al., the graphene pores were supported on track

etched PCTE membranes and pores were enlarged by oxidative etching in acidic potassium permanganate solution. The number of pores were 10^{12} per cm^2 and the pore sizes were in the sub nanometer (0.40 ± 0.24 nm) range. For short oxidative etching times, the resulting membrane showed cation selective behavior because of steric exclusion as well as the presence of negatively charged surface groups at the pores. A membrane potential around 4 mV was observed for 0.5 M KCl/0.1667 M KCl which is lower compared to the theoretical Nernst potential for this salt concentration ratio (28.1 mV). This indicates that the pore sizes may be larger than 0.4 nm as the selectivity is expected to be higher at 0.5 M KCl due to dielectric exclusion. The membrane potential decreased with increase in pore size obtained after longer oxidative etching times.

Another fabrication method to create graphene nanopores concerns oxygen (O_2) plasma etching. The group of Surwade et. al. have used CVD graphene transferred onto a SiN substrate with a $5\ \mu\text{m}$ hole subjected to O_2 plasma etching. This creates nanometer sized holes in the graphene which was confirmed by Raman spectroscopy. Nanopores created by this method have shown very high salt retention at lower etching time due to the small pore size [51].

Figure 1.4 — Schematic diagram of pore creation in graphene supported on $5\ \mu\text{m}$ SiN hole by oxygen plasma etching . (Adapted with permission from Copyright © 2015, American Chemical Society) [51].

The transport properties of ions through these nanoporous interfaces are stud-

ied both without or with externally applied electric fields [52–58]. All studies show a cation selective nature in the case of nanoporous graphene [59, 60]. For many studies it has been observed that the current-voltage relationships show a non-linear trend for these systems [49]. A diode rectification effect has widely been observed in case of solid state conical nanopores [52, 54]. For graphene nanopores and other 2D materials (MoS_2 , hBN) the rectification effects has been observed for both intrinsic and purposely created pores [59, 61–65]. Nanoporous graphene supported on PET shows an ion rectification effect due to the presence of conical nanopores in the PET as a result of asymmetric etching [61, 64, 65]. The ion selectivity can be tuned by gating the graphene with an external potential [66].

So far, most studies were limited to sub-nanometer sized pores in graphene where the ion rejection was mainly dominated by steric exclusion. Rollings et. al. fabricated a single nanopore supported on SiN_x by an electrical pulse method [50]. The pore in graphene showed a selectivity of K^+ over Cl^- even up to a diameter of 20 nm. The selectivity calculated by the GHK model was around 100, a value much higher than the selectivity (1.3) observed by O’Hern et. al. for pore sizes of sub-nm level (0.4 nm). The selectivity was furthermore dependent on the pH. With decrease in pH, the cation to anion selectivity decreases which they attributed to the protonation of surface charged groups e.g. carboxyl at the graphene edge. Additionally, the membrane could differentiate between monovalent and divalent cations by conducting monovalent cations 5 times faster than divalent cations. This work was the first experimental evidence for ion selective transport through nanoporous graphene with pore sizes larger than a nanometer [50, 67].

1.5 Motivation and outline of this thesis

Transport phenomena through ion exchange membranes have been studied for decades. In 1926, L. Michaelis first observed the effect of membrane charge on the ion transport through them [17, 68]. Since these initial studies, there have been

a number of research in this field and the transport phenomena is well understood in case of the conventional dense ion exchange membranes. In the current era of miniaturisation, devices are getting smaller and therefore ion transport through solid state nanopores is gaining attention from the scientific community [69–73]. The future of miniaturisation lies in 2D materials for their promising applications in nanofluidic device, biosensing, and DNA translocation [41–44]. There are limitations for these materials due to the presence of intrinsic defects and low surface charge density. Membranes with multiple pores have a pore size distribution which may compromise its ion selectivity. These membranes present low surface charge which limits rejection of ions. To minimise such bottle necks, a novel fabrication technique with a good understanding of transport phenomena through these 2D interface is required. Transport under nano-confinement in 2D is expected to be different compared to strongly charged ion exchange membranes. This thesis provides a meaningful investigation of ion transport through graphene nanopores created by heavy ion beam bombardment.

Chapter 2 describes a novel fabrication route for nanoporous graphene supported on a polymer PET foil. The composite membrane is irradiated with swift heavy ions which create pores in graphene and tracks in the polymer substrate. Subsequent etching results in a nanoporous graphene layer on top of track etched PET. These pores are characterised by SEM and TEM. In **Chapter 3**, the ion transport through these nanopores is investigated experimentally. Membrane potential measurements are carried out which demonstrate the cation selective nature for these membranes, where selectivity is varying with concentration. At low concentrations high selectivity is observed due to Donnan exclusion of ions and at high concentration the selectivity disappears. Distinct Donnan and diffusion plateaus are observed as is commonly observed in dense ion exchange membranes. We have described our experimental results by a modified version of the TMS theory. **Chapter 4** depicts the ion selectivity nature of the graphene membrane for bivalent cations. Bivalent cations show reduced selectivity compared to monovalent cations. Evidence of reversible adsorption of bivalent ions

on graphene is presented. The observation of cation specific Donnan plateaus observed in Chapter 4 is explained by conducting bi-ionic potential measurements. **Chapter 5** describes ion transport through nanoporous graphene for varying pH. With a decrease in pH, the membrane potential reduces and eventually reverses sign at pH 3. The streaming current measurement results are consistent with these membrane potential measurements. The zeta potential is derived from the streaming current data and fitted with the 1-pK_a model. In **Chapter 6**, the selectivity behavior of nanoporous graphene membranes is investigated by fitting the experimental data with different surface potentials and pore sizes using COMSOL simulation. The result indicates that for a membrane being only a single atom thin, the surface charge is very low and not sufficient to reject most counter ions. **Chapter 7** provides a discussion of the implications of this work for the field of membrane science and provides an outlook on interesting questions for future research directions.

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CHAPTER 2

Fabrication of Graphene Membrane by Ion Beam Bombardment

Abstract — Nanoporous graphene has been fabricated using a process combining swift heavy ion bombardment with chemical etching. As graphene is only a single atomic layer thin (0.34 nm), a stable support layer is needed for handling a larger area. For this reason we use a PET support layer which provides robustness to this nanoporous material. The ion beam irradiation creates holes in graphene and tracks in the PET layer. This process is followed by a chemical etching process which leads to the pore creation in the support layer. By optimizing the etching process, the pore size in the track layer can be controlled. To protect the graphene layer from delamination during the etching process, a poly methyl methacrylate (PMMA) layer is applied on top of the graphene. This method leads to a high coverage area of nanoporous graphene layer suspended on a polymer support film. We have examined the morphology of this composite membrane using scanning and transmission electron microscopy.

This chapter is an adaptation of parts of the previous publication Lukas Madauß, Jens Schumacher, Mandakranta Ghosh, Oliver Ochedowski, Jens Meyer, Henning Lebius, Brigitte Bandt, Maria Eugenia Toimil-Molares, Christina Trautmann, Rob G.H. Lammertink, Mathias Ulbricht and Marika Schleberger, *Fabrication of Nanoporous Graphene /Polymer Composite Membranes*, Nanoscale. (2017).

2.1 Introduction

Nano-porous materials are interesting for their potential applications in the field of nanofluidics, ion separation, DNA translocations or as sensors [1–9]. There has been several studies where nano-pores are prepared in polymers or silicon nitride films [10, 11]. Transport of ions through these nanopores has shown interesting behaviour including ion rectification and charge inversion due to size exclusion and electrostatic interactions [3, 12–15]. Graphene seems to be an ideal material to create nanopores because it is mechanically and chemically robust even when being atomically thin. A defect free graphene layer is completely impermeable [16, 17, 17]. For this reason, pore creation is necessary to investigate transport mechanisms through graphene nanopores [18–20]. Pore creation in this two dimensional material is challenging as it is difficult to handle this monolayer graphene without creating additional defects and cracks.

There has been a limited number of studies on transport properties through graphene nanopores. Some of the studies focus on the transport through intrinsic defects in the graphene layer [18]. Others investigate the ion transport through only a single pore [20]. Most of these studies are limited to a very small exposed area of graphene on the order of μm^2 . Nanopores were created by electrical pulse methods, oxygen plasma etching, and focused ion beam [20–22]. There have been several attempts to transfer large area graphene onto porous polymeric track-etched membranes followed by ion irradiation. Most of the times this resulted in low coverage of graphene and pore sizes that were difficult to control [19].

In our work, we are creating multiple pores in a relatively large graphene area (1 cm^2) by heavy ion beam irradiation. To avoid defects and improve handling, a PET polymer support is used. The dense PET support also covers the intrinsic defects. A monolayer of graphene is sandwiched between the PET film and a sacrificial PMMA layer and subjected to irradiation with swift heavy ions (SHI). Each individual ion traverses the stack and creates a nano-meter sized pore in the graphene and a nanometer sized ion track inside the polymer substrate. The irradiated sample is then immersed in a sodium hydroxide (NaOH) etching

solution. In the etching step the ion tracks in the PET film are converted into open channels. The pore diameters in the PET support can be adjusted between a few tens up to several hundred nanometers, depending on the etching conditions. The porous graphene remains largely unaffected by the etchant during etching and is protected by PMMA layer which effectively suppresses the delamination of graphene from the PET substrate. After the selective removal of the PMMA layer, the graphene/PET composite membrane remains. This fabrication method results in generation of multiple pores in a comparatively large area of graphene. In this work we show that we are able to manufacture tightly sealed graphene/PET composite membranes with a high graphene coverage (99%). By varying the irradiation fluence (number of ions irradiated per cm^2 area of graphene), the number of pores per unit area of graphene can be controlled as each ion produces an individual track.

2.2 Membrane fabrication and characterization

2.2.1 Ion beam irradiation

Commercially available graphene (obtained from Graphenea, Spain), grown by chemical vapour deposition (CVD) on a copper foil are used in this approach. First a 200 nm thin layer of PMMA is spin coated on the graphene surface ($1 \times 1 \text{ cm}^2$). Then the sample is transferred onto a PET film (3 cm in diameter, 13 μm thin) by first chemically etching the Cu substrate and recovering the floating graphene with the PET substrate (see Figure 2.1(a)). Subsequently, the heavy ion beam irradiation is done at the facility of GANIL (Caen, France). Two types of beamlines which we used are SME (medium energy) and IRRSUD (low energy) beamlines. Depending on the availability, different ions (Au/Xe/U) are used for irradiation. The fluence (number of ions irradiated per unit area) can be varied to control the number of pores in the graphene layer. The beam incidence was normal to the samples surface, the applied fluences are between 1×10^5 and 1×10^8 ions per cm^2 (see Figure 2.1(b)). The energy deposition in the materials occurs via

Figure 2.1 — Fabrication of graphene membrane in three steps.

electronic excitations and ionizations and is usually expressed in energy deposited per track length, the so-called energy loss. Only a minor fraction of energy is deposited via nuclear collisions, usually given in terms of nuclear energy loss. According to the SRIM2013, the penetration depth of the ions in PET is around $70\text{ }\mu\text{m}$, thus sufficient for the ions to traverse the complete PMMA/graphene/PET multilayer film with an almost constant energy loss.

2.2.2 Chemical etching and pore creation in PET

The ion beam irradiation creates nanometer sized holes in the graphene layer and ion track in the PET support layer. The composite membrane is etched in 1.5 M NaOH solution at 80°C or alternatively in a 3.0 M NaOH solution at 50°C (see Figure 2.1(b)). This etching process converts the ion tracks into open channels in the PET layer. The etching process is stopped by immersing the sample into deionized water. During the etching process, the PMMA layer protects the graphene layer from the etching solution. Finally, the PMMA layer is removed by immersing it in acetone (see Figure 2.1(c)).

2.2.3 SEM and TEM

The scanning electron microscope (SEM) images are taken at the high resolution SEM (Zeiss MERLIN HR-SEM) facility at the NanoLab of University of Twente with acceleration voltage of 20 - 30 kV. The samples did not require any conductive surface coating and were mounted on a stage which can be freely rotated. For cross-sectional imaging, the sample was dipped in a liquid nitrogen bath and

Figure 2.2 — Aluminium holder to irradiate only graphene covered portion of PET substrate.

subsequently broken for an edge-on view.

For transmission electron microscope (TEM) images, the FEI Analytical TEM facility at NanoLab of University of Twente has been used. The sample was mounted on a TEM grid after adjusting the size.

2.3 Results and discussion

2.3.1 Optimizing the fabrication method

We have used aluminium holders as shown in Figure 2.2. In this way we have limited the irradiation area to the graphene covered portion of the PET support. Figure 2.3(a) shows the PMMA covered graphene supported on PET. After irradiation, chemical etching and removing the PMMA, a white circular region appears at the irradiated composite structure as shown in Figure 2.3(b). The turbid region is caused by the track etched pores in the PET support.

Samples irradiated with 1.5 GeV uranium ions by the Sortie Moyenne Energie (SME) facility at GANIL did not show any selectivity for any type of ions in these composite membranes. SEM (Figure 2.4) and permoporometry measurements show that pore sizes generated by this method are around 20 nm. The membranes

Figure 2.3 — (a) PMMA/Graphene/PET structure before ion beam irradiation. The graphene surface is $1 \times 1 \text{ cm}^2$ in size, placed at the center of a 3 cm diameter PET substrate. (b) Graphene/PET structure after irradiation and etching. The circular white region at the center of the membrane is the irradiated area. The aluminium holder ensures that only the graphene covered portion is irradiated.

irradiated with 1.1 GeV Au ions by the Universal linear accelerator (UNILAC) of GSI (Darmstadt, Germany) showed some cation selectivity (around 43% for a 0.01/0.05 mM KCl dialysis experiment). The best cation selectivity for membranes were observed when they were fabricated with 0.71 MeV/u Xe irradiation by the low energy IRRSUD facility of GANIL. For the rest of the ion transport measurements we have used the membranes irradiated with this low energy IRRSUD facility of GANIL.

2.3.2 SEM images of the composite membrane

A SEM image of the graphene/PET composite membrane is shown in Figure 2.5. The image shows the PET side of the composite membrane. The pores in the PET layer are approximately 250 nm in diameter. The graphene side of this composite membrane is shown in Figure 2.6. Ripples on the monolayer graphene are clearly observed here. The vaguely visible holes again are the pores in PET support layer below the graphene which are approximately 100 nm in diameter. The pores in the PET in contact with graphene layer are smaller in size than the backside of the PET which confirms their conical shape. This is also observed in

Figure 2.4 — SEM image of a single graphene pore generated by uranium ion irradiation.

Figure 2.5 — SEM image of the composite membrane, PET side. The pores in the SEM image is the pore in PET.

the cross sectional view of the composite membrane (Figure 2.7).

2.3.3 TEM images of the graphene pores

The tapered pores in PET layer were being successfully imaged by normal and high resolution SEM. The next challenge was to take the image of graphene pores which were expected to be between 1-10 nm diameter. These small pore sizes were not visible even with high resolution SEM. The sample was damaged by electrons during the imaging. TEM images were taken through the holes of the PET support layer. Figure 2.8 shows a pore in graphene of size around 8 nm.

Figure 2.6 — SEM image of the composite membrane, graphene side. The pores in the SEM image are the pore in the PET support below the graphene.

Figure 2.7 — SEM image of the cross section of the composite membrane. The PET pores are slightly tapered towards the top side.

Figure 2.8 — Pore size of graphene in TEM image.

2.4 Conclusion

We developed a novel technique to fabricate single-layer nanoporous graphene sheets supported on a PET polymer sheet by swift heavy ion irradiation. Track-etching creates a cylindrical tapered hole in the the PET layer underneath each graphene pore. A PMMA protective layer protects graphene layer from the etching solution and confirms complete coverage of the polymer support by the graphene layer without delamination. This fabrication method for graphene suspended on larger support pores presents a key step towards the utilization of porous graphene for filtering, sensor applications and fundamental studies on ion transport through nanoporous graphene. Our membrane fabrication method provides improved coverage of graphene compared to transferred graphene on already track-etched polymer. Graphene pores are directly aligned with the underneath PET pores which is crucial for our ion transport experiments.

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CHAPTER 3

Membrane potential measurement of perforated graphene for monovalent cations

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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 K₂SO₄. 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 non-idealities and surface charge regulation effects.

3.1 Introduction

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 [7, 8]. However, when nano-pores 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 size of the graphene pores were tuned 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 ultra-short 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 mM to 100 mM max). They explored the

selectivity of a single pore, whereas for practical application multiple pores are required.

However, 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 in detail to date. In this work, we perform a detailed experimental investigation of membrane potential of 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 percent of the theoretical Nernst potential which either results from some non-idealities 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].

3.2 Teorell Mayer and Sievers Theory

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:

$$\Delta\psi = -\frac{RT}{F} \ln \frac{C_2}{C_1} \frac{\sqrt{\bar{C}_R^2 + 4C_1^2} + \bar{C}_R}{\sqrt{\bar{C}_R^2 + 4C_2^2} + \bar{C}_R} - \frac{RT}{F} \bar{u} \ln \frac{\sqrt{\bar{C}_R^2 + 4C_2^2} + \bar{u}\bar{C}_R}{\sqrt{\bar{C}_R^2 + 4C_1^2} + \bar{u}\bar{C}_R} \quad (3.1)$$

Figure 3.1 — Membrane Potential vs. C_2 for different $\bar{C}_R$ values and constant $\bar{u}$. $C_1/C_2 = 5$.

where R is the universal gas constant, T is the temperature, F is the Faraday constant, $\bar{C}_R$ is the fixed ion concentration in the membrane, C_1 is the high concentration and C_2 is the low concentration solution. $\bar{u}$ is a term representing the different diffusion rates of cation ($\bar{u}_+$) compared to anion ($\bar{u}_-$) in the membrane, given by:

$$\bar{u} = \frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-} \quad (3.2)$$

The first term in equation 4.1 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 4.1 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 supplementary information (SI) [25].

Figure 3.2 — Membrane Potential vs. C_2 for different $\bar{u}$ values and constant $\bar{C}_R$. $C_1/C_2 = 5$.

At low concentration (when C_1 and $C_2 \ll \bar{C}_R$), the Donnan potential is high and reaches the plateau of the Donnan dominated regime. On the other hand, with increasing concentration (when C_1 and $C_2 \geq \bar{C}_R$) and finite $\bar{u}$, the diffusion potential starts dominating.

The variation of potential with C_2 for different membranes (different value of $\bar{C}_R$) and for the same salt (constant value of $\bar{u}$) is shown in Figure 3.1. We note that the Donnan dominated plateau and diffusion dominated plateau reach the same value for different $\bar{C}_R$ but the transition point from the Donnan plateau to the mixed potential (Donnan + diffusion) occurs at different concentrations. With a higher value of $\bar{C}_R$ the membrane reaches the Donnan plateau at a higher concentration. On the other hand, the potential curve for the same membrane (fixed $\bar{C}_R$) but for different salts (different values of $\bar{u}$) is shown in Figure 3.2. In this case the curves reach the same Donnan plateau but different diffusion plateaus, as expected.

Figure 3.3 — PMMA/Graphene/PET

Figure 3.4 — Ion bombardment on the composite structure

Figure 3.5 — After etching and PMMA removal

Figure 3.6 — Schematic diagram of the experimental concept. Left reservoir contains low concentration solution. Right reservoir contains high concentration solution. Graphene membrane is placed between the two reservoirs. Circles denote anions and cations in the solution. The inset shows the membrane potential curve with varying salt concentrations.

3.3 Experimental Procedure

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, 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 5×10^8 ions/cm², which implies that 5×10^8 holes are created in 1 cm² [26]. The membrane fabrication process is done in three main steps, which are illustrated in Figure 3.3, 3.4, 3.5. We use commercially available graphene (Graphenea, Spain) grown by chemical vapour deposition (CVD) on a copper substrate. First, PMMA coated graphene is wet transferred to a clear, biaxially oriented, 13 μ m thick PET support (Goodfellow, England). PET provides robustness to the membrane and covers intrinsic defects present in graphene. PMMA protects the graphene layer during the wet transfer on to the PET support layer. In the next step, the sample is irradiated with 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 μ m², while the diameters of the holes varies between 1-10 nm [27]. Finally, to create holes in PET at the track etched area, the membrane is immersed in an etching solution (3M 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 minutes and a Graphene/PET composite membrane is obtained. More details about the fabrication process can be found in the supplementary 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 3.6. During the measurement, equal volume of solution is 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, UK) are used to sense the potential, correcting for the offset voltage between the two electrodes. During the experiment with the graphene membrane, we vary concentration in each reservoir keeping C_1/C_2 at a constant value of 5 (unless otherwise stated). The concentration for each solution is varied from 0.3 mM 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 sulphate (K_2SO_4 , 1:2).

3.4 Results and discussion

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 ($\Delta\psi_N$). The Nernst potential is the theoretical potential when a membrane is 100% selective to a particular ion ($\Delta\psi_N = (RT/F) \ln(C_1/C_2)$).

In Figure 3.7, the membrane potential scaled to the Nernst potential is plotted against the lower concentration (C_2) for KCl, LiCl and K_2SO_4 salts. The figure shows a similar trend as predicted by the TMS theory i.e., a plateau of high potential at very low concentration (Donnan dominated) and a plateau of low potential at very high concentration (diffusion dominated). 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 percent of the theoretical Nernst potential). This is similar to the ratio found by Rollings et al. for a single nanopore in a

Figure 3.7 — Membrane potential ($\Delta\psi$) scaled to the Nernst potential ($\Delta\psi_N$) plotted against different concentrations. Solid squares are the values for KCl, the open circles are the values for K_2SO_4 and the open triangle denotes the values of LiCl. The relative standard deviation of measurements is approximately 1%.

graphene membrane when using 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 [20]. When the concentration of the solution increases, the difference between $\bar{C}_R$ 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 counter-ions through the membrane.

We have also performed our experiment with PET foils irradiated with the same fluence (5×10^8 ions /cm²), same SHI setting and etched in similar condition (3 M NaOH, 50 °C, half an hour) as 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 nano-porous 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 α to the Donnan potential term in the TMS theory.

$$\Delta\psi = \alpha\Delta\psi_{\text{Donnan}} + \Delta\psi_{\text{Diffusion}} \quad (3.3)$$

We fit the experimental data shown in Figure 3.7 with the modified TMS model (Equation 3.3) with the fitting parameters, $\bar{C}_R$, α 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 3.7 represent the curves fitted to 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 error are on average approximately 1%. The curves show a very similar pattern. At low concentration, all of them reach a plateau at similar potential, whereas the membrane potential at very high concentration is 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 Donnan to diffusion potential dominated regime is evident. For KCl both K^+ and Cl^- ions have similar diffusivities in the bulk which results in 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 behaviour. Unlike KCl and LiCl we could not measure the potential at very high concentration for K_2SO_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 [32].

For KCl and LiCl we use the equation for a 1:1 salt whereas for K_2SO_4 we use the TMS model for a 1:2 salt [25]. 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 5.1. We obtain similar $\bar{C}_R$ values for KCl and LiCl whereas the $\bar{C}_R$ value for K_2SO_4 is much lower. The lower value of $\bar{C}_R$ for K_2SO_4 is possibly due to charge regulation effects or to insufficient data points at high concentration. As mentioned, the low solubility of K_2SO_4 in water limited the experimental range for this salt.

Salt	C_R (mM)	α	$\bar{u}_-/\bar{u}_+$	Bulk($\bar{u}_-/\bar{u}_+$)
KCl	79.1 ± 13.3	0.69 ± 0.02	0.99 ± 0.05	1.04
LiCl	86.9 ± 10.7	0.58 ± 0.01	1.64 ± 0.08	1.97
K_2SO_4	42.2 ± 5.8	0.76 ± 0.01	0.43 ± 0.03	0.54

Table 3.1 — Fitting parameters for the three salts with a C_1/C_2 ratio of 5 and their 95% confidence intervals

The value of correction factor (α) varies from 0.58 to 0.76 for the three salts. The bulk value of u_-/u_+ for KCl, LiCl and K_2SO_4 are 1.04, 1.97 and 0.54 respectively [32]. The table shows that the fitted values of u_-/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 diffusivity ratio 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 Nafion-117 the diffusion coefficient of K^+ is around half of its bulk value [33].

The variation of potential with concentration can be physically understood from the concept of electric double layer for charged membranes [34]. 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 [19].

Figure 3.8 — Membrane Potential vs. Concentration at different C_1/C_2 ratios.

Figure 3.8 shows the variation of membrane potential scaled to the Nernst potential with varying concentration for two different KCl salt concentration ratios. For both the 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 Donnan dominated regime to diffusion dominated regime happens at lower concentration (C_2) as shown in Figure 3.8. This implies that it is the high concentration side of the solution which determines the transition from Donnan dominated regime to the diffusion dominated regime in the membrane potential versus concentration plot.

To check the reproducibility of the membrane behaviour, 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 Figure 3.9. The standard deviation for measurement represents the sample to sample variation.

Figure 3.9 — Membrane Potential ($\Delta\psi$) with KCl concentration averaged for three different graphene membranes prepared by the same fabrication method. The standard deviation as shown here denotes 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 5.2. We note that the values of $\bar{C}_R$ 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 preparation. We compare the measured potential vs. concentration and TMS fits results for 3 individual membranes, along with the fit for the average

of the data in Table 5.2.

	C_R (mM)	α	$\bar{u}_-/\bar{u}_+$
Sample 1	79.1 ± 13.3	0.69 ± 0.02	0.99 ± 0.05
Sample 2	19.5 ± 1.7	0.63 ± 0.01	0.97 ± 0.02
Sample 3	31.1 ± 3.0	0.70 ± 0.01	1.01 ± 0.03
Average	32.2 ± 9.1	0.67 ± 0.04	0.96 ± 0.07

Table 3.2 — TMS Fit Values for 3 Different Membrane Samples

From Table 5.2, we observe that the α , $\bar{u}_-/\bar{u}_+$ values are approximately similar for the three membranes and only $\bar{C}_R$ values are different. This indicates that the effective fixed charge is varying between the samples. This can be due to the distribution in the pore-sizes in the sample and differences in the charged functional groups in the nanopores.

3.5 Conclusion

We have investigated ion transport through nanopores in graphene membranes in detail by measuring the induced potential arising across different concentration reservoirs. The membranes show a variation in cation selectivity when we vary the concentrations of the ionic solution on the two sides of the membrane. For low concentrations, the membrane potential is higher than for high concentrations which implies a higher selectivity. With increasing concentration, the membrane potential decreases and becomes dominated by the diffusion potential. This observation can be matched to the TMS theory which describes the membrane potential for charged membranes. Although the theory slightly overpredicts the potential obtained in the dilute regime, it is remarkable that the theory seems suitable to be applied to a 2D membrane.

The rejection of co-ions and the permeation of counter-ions in the membrane can be related to the Debye layer overlap. Increase in concentration leads to a decrease in the Debye length which reduces the selectivity. We observe that the high concentration side of the membrane governs the transition from Donnan

to diffusion dominated regime. This is consistent with both a reduction of the Debye length, as well as any possible surface charge regulation. The different $\bar{C}_R$ values indicate there is a wide variability in the effective 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 membrane with concentration motivates further studies of ion transport through nanoporous graphene membranes..

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Supplementary Information

S1.Experimental set up

In this section we have described our experimental set up for the membrane potential measurements. As the composite membrane is smaller in size compared to the setup, we needed a holder to mount the membrane between the reservoirs. Figure 3.10 shows the holders used to place the membrane. Figure 3.11 shows the graphene membrane between the chambers.

Figure 3.10 — Holders that graphene is placed between.

Figure 3.12 shows the front view of the experimental set up. This contains two chambers and graphene is placed between the chambers with help of the holders. The side view of the experimental set up is shown in Figure 3.13. The calomel reference electrodes shown in the picture are used to measure the membrane potential. Also, the pipes are used to continuously circulate the fluid for better mixing.

S2.Experimental result for only PET membranes

We have measured the potential of a PET membrane irradiated with the same fluence and etched in the same condition as that of the graphene membrane mentioned in the paper. The result is shown in Figure 3.14. We have done our measurement with three different salts (KCl, LiCl, K_2SO_4) we have used

Figure 3.11 — Graphene is placed between the holders and sealed with O rings.

for the experiment with the composite Graphene/PET membrane. We have observed that for KCl the membrane potential is around zero which implies that the PET membrane is not selective for K^+ ions. The positive value of membrane potential for K_2SO_4 is due the diffusion potential generated for fast moving K^+ ions than SO_4^{2-} ions and the negative value of membrane potential for LiCl is due to diffusion potential generated due to the fast-moving Cl^- ions than the Li^+ ions. The potential remains steady with time. This result confirms that the selectivity we have observed in our membrane is appearing only do to the graphene membrane and PET pores have no influence on ion transport through the graphene nanopores.

S3.TMS equation for 1:2 salt

The dimensionless membrane potential is expressed as,

$$\Delta\bar{\psi}_{TMS} = \frac{1}{z_2} \ln \frac{k_2^P}{k_2^f} + \frac{\bar{u}_+ - \bar{u}_-}{z_2\bar{u}_- - z_1\bar{u}_+} \ln\left(\frac{T_r k_2^P + t_1 \zeta_f}{k_2^f + t_1 \zeta_f}\right) \quad (3.4)$$

Where, $\Delta\bar{\psi} = \frac{F\Delta\psi}{RT}$, $t_1 = \frac{|z_1|\bar{u}_+}{|z_1|\bar{u}_+ + |z_2|\bar{u}_-}$, $\zeta_f = \frac{\bar{c}_R}{|z_1|v_1 c_f}$, $T_r = \frac{c_p}{c_f}$

Figure 3.12 — Front view of the experimental setup. Graphene is placed between the reservoirs using the holders.

z_i is the electrochemical valence, $\bar{u}_+$ is the diffusion coefficient of cations and $\bar{u}_-$ is the diffusion coefficient of anions and k_i is the partition coefficient of ion i . T_r is the transmission, which denotes the ability of solute to pass through the membrane. v_i is the stoichiometric coefficient of electrolyte, 1 represents counter ions. $\zeta_{p(f)}$ is the ratio of the volume charge density to equivalent salt concentration in the feed side or in the permeate side of membrane. F is the Faraday constant, R is the gas constant and T is the temperature. $\Delta\psi$ is the membrane potential. $\Delta\bar{\psi}$ is the dimensionless form of the membrane potential. $\bar{c}_R$ is the constant volume charge density of charged membrane (mole/l of pore volume). c_f is the high concentration and c_p is the low concentration.

For, 1:2 asymmetric salt, the partition coefficient of co-ions can be expressed as,

$$k_2^{p(f)} = [\Gamma_{1:2,p(f)}]^{-2} \quad (3.5)$$

Figure 3.13 — Side view of the setup. Two inlets and outlets are used to circulate water inside the reservoirs. Electrodes are placed on both sides of the membrane at an equal distance

$$\Gamma_{1:2,p(f)} = \left[\frac{\Lambda(1, 1, \zeta_{p(f)})^{1/3}}{6} - \frac{2\zeta_{p(f)}}{\Lambda(1, 1, \zeta_{p(f)})^{1/3}} \right]^{-1} \quad (3.6)$$

$$\Lambda(1, 1, \zeta_{p(f)}) = 108 + 12\sqrt{3}\sqrt{(27 + 4\zeta_{p(f)}^3)} \quad (3.7)$$

Figure 3.14 — Membrane potential for PET is measured with respect to time for KCl, LiCl and K₂SO₄.

CHAPTER 4

Understanding graphene with Bi-ionic potential measurements

Abstract — Nanoporous graphene displays salt dependent ion-permeation. In this work, we investigate the differences in Donnan potentials arising between reservoirs, separated by a perforated graphene membrane, containing different cations. We compare the case of monovalent cations interacting with nanoporous graphene with the case of bivalent cations. This is accomplished through both measurements of membrane potential arising between two salt reservoirs at different concentrations involving a single cation (ionic potential) and between two reservoirs containing different cations at the same concentration (bi-ionic potential). In our present study, Donnan dialysis experiments involve bivalent MgCl_2 , CaCl_2 and CuCl_2 as well as monovalent KCl and NH_4Cl salts. For all salts except CuCl_2 , a clear Donnan and diffusion potential plateau was observed at respectively low and high salt concentrations. Our observations show that the membrane potential scaled to the Nernst potential for bivalent cations has a lower value ($\approx 50\%$) than for monovalent cations ($\approx 72\%$) in the Donnan exclusion regime. This is likely due to the adsorption of these bivalent cations on monolayer graphene. For bivalent cations, the diffusion regime is reached at a lower ionic strength compared to the monovalent cations. For Mg^{2+} and Ca^{2+} , the membrane potential does not seem to depend on the type of ions in the entire ionic strength range. A similar behaviour is observed for the KCl and NH_4Cl membrane potential curves. For CuCl_2 , the membrane potential curve is shifted towards lower ionic strength compared to the other two bivalent salts and the Donnan plateau

is not observed at the lowest ionic strength. Bi-ionic potential measurements give further insight into the strength of specific interactions, allowing to estimate the relative ionic selectivities of different cations based on comparing their bi-ionic potentials. This effect of possible ion adsorption on graphene can be removed through ion exchange with monovalent salts.

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4.1 Introduction

Ion transport through charge selective interfaces has been studied extensively in the scientific community due to their relevance in applications such as filtration, desalination, and sensors [1–3]. Most of the studies to date have focused on dense ion exchange membranes or porous networks [1, 2, 4–6]. Graphene as a membrane material has sparked studies to develop a fundamental understanding of ion transport through this material [7–14]. Graphene has a thickness of only 0.34 nm (single layer), suggesting that ion transport through nanoporous graphene is quite different versus 3D nanoporous materials. As a pore will be atomically-thin, transport through it will be dominated by entrance/exit effects. Our main motivation in this study is to provide further understanding of the interaction of different cations with graphene surfaces and its influence on the ion transport through atomically thin membranes.

In our previous work, we experimentally investigated the interaction of monovalent cations with monolayer perforated graphene membrane supported on a polyethylene terephthalate (PET) foil [15, 16]. Our findings showed that the total electrical potential across a single-layer graphene membrane separating different ion concentration reservoirs could be described as a cation-selective layer using a modified version of the Teorell-Meyer-Sievers (TMS) theory, which is a continuum theory designed for thicker membranes [17, 18]. At low electrolyte concentrations, the potential enters into a Donnan-like regime where the potential vs. concentration at a fixed concentration ratio between compartments shows a plateau. At high salt concentrations, a diffusion potential based on the ionic mobility contrast of cation and anion was retrieved. For single-layer graphene, the ratio of diffusion coefficients of anion and cation in the membrane was consistent with the ratio of values in bulk solution, which in general is not observed in typical ion-exchange membranes [19]. Our previous study with monovalent cations involved three salts (K_2SO_4 , KCl , LiCl), resulting in three distinct Donnan plateaus. The reason for these three distinct Donnan plateaus is interesting to investigate as it provides further knowledge of ion interaction with the graphene surface.

There are some studies to understand the interaction of any particular ion with graphene oxide surface [20, 21]. Studies that compare the behaviour of different cations with graphene surfaces are limited, although such studies are abundant for conventional nanofiltration membranes. In a recent work, Khannanov et al.(2019) have experimentally shown the differences in concentration profile for ions having different valencies [22]. Rosenberg et al.(1957) have shown that cation selectivity for multivalent ions are lower than that for monovalent ions [23]. Caglar et al. (2020) showed that for a tetravalent cationic salt (HfCl_4), graphene with intrinsic defects shows a transition from cation selective to anion selective behaviour. This transition happened even at constant concentrations of HfCl_4 on either side of two reservoirs containing different concentrations of KCl , which is a strong indication that adsorption of the HfCl_4 led to charge inversion due to adsorption of the high valence cation on an initially negatively charged surface [24]. There are a number of MD simulation studies to understand the interaction of ions and the salt rejection mechanism of nano-porous graphene [25–30]. These studies reveal that the salt rejection depends highly on the pore diameter, the type of ions passing through the pores and the chemical functionality of the pore. Jiang et al. (2016) have studied the double layer structure at the graphene electrode/electrolyte interface for different monovalent electrolytes. Their study shows that each ion has its distinct electrical double layer (EDL) at the graphene electrode surface and the potential distribution in the EDL is determined by the ion type [27]. The MD simulation study of Cohen-Tanugi et al. (2012) indicated that functional groups at the pores determine the salt rejection [25]. Hydrogenated pores have higher salt rejection than hydroxylated pores as hydroxyl groups substitute the water molecules from the ions hydration shell. We need to stress here, that in these MD simulations, ion dissociation of the graphenes hydroxyl groups was not taken into account. He et al. (2013) have shown that nano pores with four carboxylate groups have a preferential transport of K^+ ions over Na^+ which is explained by crystal field theory [28]. The work of Ruan et al. (2016) shows that Mg^{2+} ions are transported more easily than Li^+ ions [30]. All these studies indicate that the functional groups at graphene nano-pores have specific ion interactions that are

crucial in the transmembrane transport of ions.

The ion interaction can be understood by membrane potential experiments [31]. In our current study, we have conducted bi-ionic potential measurements which allows us to study the interaction between graphene membranes and different counter ions [18, 32–35]. To further investigate the impact of cations on charge-transport in nanoporous single layer graphene, we include bivalent cations in our present study. Multivalent ions have a higher ability to screen surface charge than monovalent counter ions. This can lead to inversion of surface charge [36–40]. This behaviour is often observed in ion exchange membranes and resins, due to the adsorption of multivalent cations on the fixed negative charges [23, 41]. The nature of the surface charge on the graphene pore surface has been debated, in literature, with the presence of surface functional groups or hydroxide adsorption being its origin [12, 24]. In either case, the pH of the solution reservoirs can have a strong influence on the resulting ion-selectivity. In this work, we work at a fixed pH. Our ongoing work does indicate that the cation or anion selectivity of nanoporous graphene is pH dependent, which will be reported in a future paper. Galizia et al. (2017) have shown that even at low salt concentrations, the salt sorption coefficient is higher for multivalent counter ions than monovalent counter ions as is expected due to the weaker Donnan exclusion for multivalent salts and consistent with the charge inversion observed by Caglar et al. (2020) [24, 41]. In this work, we have expanded the ion transport study for bivalent cations (Mg^{2+} , Ca^{2+} , Cu^{2+}) through perforated graphene and have compared the results with the monovalent case (KCl , NH_4Cl). We have conducted bi-ionic potential measurements to understand the differences in Donnan plateaus for different salts. This measurement quantifies the differences in the affinity of graphene towards different cations, providing a useful tool for assessing the effect of different ions on the charge-selectivity of graphene or other nanoporous materials. We also examined how the surface adsorption of bivalent cations affects the membrane potential characteristics and systematically investigated the membrane recovery process.

4.2 Theoretical Background

In our previous paper we have described the potential difference between two reservoirs at different ion concentrations separated by a perforated graphene membrane using a modified version of the Teorell, Meyer and Sievers (TMS) theory [15]. The TMS theory was derived to describe the potential difference across dense continuous ion exchange membranes [17]. The theory describes the membrane potential as a sum of Donnan and diffusion potential. The Donnan potential is generated due to the well known Donnan exclusion of co-ions by the membrane and the diffusion potential is generated due to corresponding mobility contrast of co-ions and counter-ions inside the membrane. At very low ionic concentration of the electrolyte, the fixed ion concentration of the membrane is typically much higher than the electrolyte concentration. In this regime the Donnan potential of the membrane dominates and the membrane potential is only dependent on the electrolyte concentration ratio. With an increase in electrolyte concentration (or ionic strength) the membrane potential decreases towards the diffusion potential. At a very high concentration, when the electrolyte concentration is comparable or larger than the fixed ion concentration of the membrane, the diffusion potential starts to dominate and the membrane potential again reaches a plateau. By adjusting the Donnan potential term to take into account the non-idealities of the graphene membrane, we were able to describe our experimental data. The modified TMS model is given in the following equation.

$$\Delta\psi = -\alpha \left(\frac{RT}{F} \ln \frac{C_2}{C_1} \frac{\sqrt{\bar{C}_R^2 + 4C_1^2} + \bar{C}_R}{\sqrt{\bar{C}_R^2 + 4C_2^2} + \bar{C}_R} \right) - \frac{RT}{F} \bar{u} \ln \frac{\sqrt{\bar{C}_R^2 + 4C_2^2} + \bar{u}\bar{C}_R}{\sqrt{\bar{C}_R^2 + 4C_1^2} + \bar{u}\bar{C}_R} \quad (4.1)$$

where R is the universal gas constant, T is the temperature, F is the Faraday constant, $\bar{C}_R$ is the fixed ion concentration in the membrane, C_1 is the high concentration and C_2 is the low concentration solution and α is the non-ideality factor. $\bar{u}$ is a term representing the different diffusion rates of cation ($\bar{u}_+$) compared

to anion ($\bar{u}_-$) in the membrane, given by:

$$\bar{u} = \frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-} \quad (4.2)$$

By fitting our experimental data with the modified TMS model we obtain the non-ideality factor α , fixed ion concentration of the membrane $\bar{C}_R$ and the ratio of diffusivities of anion to cation $\bar{u}_-/\bar{u}_+$.

Figure 4.1 — Membrane Potential vs. Concentration (C_2) predicted by the TMS theory for KCl, MgCl_2 , CaCl_2 and CuCl_2 . C_1/C_2 is 5 for all cases.

Figure 4.1 shows the membrane potential for monovalent KCl and bivalent MgCl_2 , CaCl_2 and CuCl_2 as predicted by the TMS theory. According to the theory, for KCl the Donnan plateau is expected at 41.3 mV (for a 5/1 concentration ratio) and a diffusion plateau at around 0 mV (due to the similar diffusivities for K^+ and Cl^- , assuming bulk diffusivity values). The membrane potential for bivalent salts are predicted from the TMS theory for 2:1 salts [42]. For bivalent salts, the predicted Donnan plateau is 20.6 mV which is generated due to the Donnan exclusion of the Mg^{2+} , Ca^{2+} and Cu^{2+} ions at low electrolyte concentrations while the diffusion plateau is at around -15 mV for MgCl_2 , around -14 mV

for CaCl_2 and around -16 mV for and CuCl_2 which is generated because Cl^- ions have a higher diffusivity than Mg^{2+} , Ca^{2+} and Cu^{2+} ions [43].

To understand the differences in the Donnan plateau for different cations and to further quantify the degree of specific ion interactions, bi-ionic potential measurements are conducted. A bi-ionic potential develops when a cation exchange membrane separates two different electrolyte solutions with different counter ions but the same co-ions. If the concentration of both the reservoirs are the same, the affinity is quantified by a selectivity factor K_A^B . This selectivity factor is 1 when the ions have similar affinities and the factor is not equal to 1 when the membrane has differences in affinities between two cations. For two cations A and B the bi-ionic potential E_{Bi} is given by the formula,

$$E_{Bi} = -\frac{RT}{zF} \ln \left(\frac{\bar{u}_B}{\bar{u}_A} K_A^B \right) \quad (4.3)$$

Where, R is the molar gas constant, T is the temperature of the solution, z is the valance and F is Faraday constant. $\bar{u}_B$, $\bar{u}_A$ are the diffusion coefficient of the cations inside the membrane.

In this work we will show that the factor K_A^B can be related to the non-ideality factor α that we previously introduced. In this way, we can quantify the differences in affinity of graphene towards different cations.

4.3 Experimental method

The experimental method is similar to that described in our previously published paper [15]. We have used commercially available chemical vapor deposition (CVD) grown monolayer graphene. The PMMA coated graphene is transferred to a $13\text{ }\mu\text{m}$ thin PET support which provides robustness to the membrane and ease of handling. Swift heavy ion irradiation (SHI) is used to create holes in the monolayer graphene at the IRRSUD beamline facility at GANIL, France [16]. The energy of the irradiation is 0.56 MeV/u (Pb) and the fluence is 5×10^7 ions/ cm^2 .

During the irradiation, pores are created in graphene and tracks in the PET support. Assuming each ion creates a single pore, we expect 5×10^7 pores to be created in the graphene per cm^2 area [44]. Pore diameters are expected to be on the order of 1-10 nm [45]. To create holes along the ion tracks in the PET support we etch the composite membrane in 3 M sodium hydroxide solution at 50°C for 34 minutes. During etching, the PMMA layer protects the graphene layer from the etching solution. The etching process creates somewhat truncated holes in PET. Nevertheless, the PET pores are much larger than the graphene pores and do not influence the ion transport through the graphene pores. The experimental results for PET support without any graphene layer is shown in the supplementary information. After the etching process the PMMA layer is removed by immersing it in acetone and the graphene/PET composite membrane is obtained. We measured the membrane potential across the composite membrane by placing it between two reservoirs containing salt solution with high (C_1) and low (C_2) ionic strength at a constant ratio of 5. The potential is measured with the help of two calomel reference electrodes and a potentiostat. We vary the ionic strength of both reservoirs while keeping a constant ionic strength ratio ($C_1/C_2=5$). We have used MgCl_2 , CaCl_2 and CuCl_2 as bivalent salts and KCl and NH_4Cl as monovalent salt for comparison. The solution is continuously circulated by a pump to minimise concentration gradients near the membrane. The temperature is regulated at 25°C with a temperature bath. For the bi-ionic potential measurements, we have kept the same experimental setup but maintained the same ionic strength of the different cations on both sides of the membrane and measured the potential.

4.4 Results and discussion

In Figure 4.2, the experimentally measured membrane potential is shown as a function of the ionic strength of the low concentration reservoir along with the fit using the modified TMS model. Based on the observed positive membrane potential we can conclude that our membrane is cation selective. Our goal is to

understand the interaction of the graphene membrane with bivalent cations as compared to the monovalent cations. Later bi-ionic potential measurements are conducted to confirm the differences in the interaction of cations. In Figure 4.2, the ionic strength is plotted instead of absolute concentration. The ionic strength of the used bivalent salts are three times higher than the monovalent salts for a given ionic concentration. For KCl, the Donnan plateau is observed at around 30 mV which is 72% of the theoretical Nernst potential ($(RT/zF) \ln 5 = 41.3$ mV). For both the bivalent salts, CaCl_2 and MgCl_2 , a lower Donnan potential is obtained compared to the monovalent salts within the same ionic strength range (between 0.3 mM-1.5 mM). The Donnan plateau is approximately 10 mV which is only about 50% of the theoretical Nernst potential (20.6 mV). In case of CuCl_2 , the membrane potential did not reach the Donnan plateau at the lowest ionic strength experimentally accessible. At concentrations lower than 0.1 mM the membrane potential is very noisy and not reliable anymore. For the entire range of the ionic strength the membrane potential remained positive for monovalent KCl implying a cation selective nature of the membrane. With an increase in ionic strength the membrane becomes non-selective and the diffusion potential appears. At very high concentrations, the potential due to diffusion is expected to approach zero as K^+ and Cl^- ions have similar diffusion coefficients as already reported in our previously published paper [15]. For bivalent cations (Mg^{2+} , Ca^{2+}), the potential reaches a plateau around -14 mV for MgCl_2 and around -12 mV for CaCl_2 . These values correspond well to the diffusion potential of the respective ion pairs. The Donnan plateaus for both CaCl_2 and MgCl_2 are similar and their transition from the Donnan to the diffusion regime occurs at the same ionic strength. In contrast to CaCl_2 and MgCl_2 salts, CuCl_2 reaches its diffusion potential regime at lower ionic strength suggesting a lower effective fixed charge on the membrane. The value of the diffusion potential (around -16 mV) again corresponds to the potential generated due to the faster moving Cu^{2+} ions than the Cl^- ions.

For the modified TMS theory, it was not possible to fit the CuCl_2 data as experiments did not reveal a clear Donnan plateau at the lowest ionic strength

Figure 4.2 — Membrane Potential (experimental and fitted with modified TMS model) vs. ionic strength for KCl, MgCl₂, CaCl₂ and CuCl₂. C_1/C_2 kept at 5.

experimentally accessible in our work. The fitted values for other salts are shown in Table 1 where, $\bar{C}_R$ represents the effective fixed ion concentration in the membrane, α is the factor taking care of non-idealities presents in the membrane and $\bar{u}_-/\bar{u}_+$ represents the ratio of anion to cation diffusivity inside the membrane.

Salt	$\bar{C}_R$ (mM)	α	$\bar{u}_-/\bar{u}_+$	Bulk(u_-/u_+)
KCl	21.3 ± 3.8	0.72 ± 0.02	0.81 ± 0.04	1.04
MgCl ₂	10.3 ± 2.2	0.53 ± 0.07	2.85 ± 0.16	2.87
CaCl ₂	11.6 ± 2.5	0.52 ± 0.06	2.61 ± 0.015	2.56

Table 4.1 — Fitting parameters for the three salts with a C_1/C_2 ratio of 5 and their 95% confidence intervals.

The Fitted value of $\bar{C}_R$ for KCl (21.3 mM) is approximately twice the value for MgCl₂ and CaCl₂ (10.3 mM, 11.6 mM respectively). The non-ideality factor α is 0.72 for KCl and around 0.5 for the bivalent salts, which indicates that the membrane is more selective for potassium cations than for bivalent cations. The fact that the $\bar{C}_R$ values for the bivalent salts are the same explains the similar transition regime of both of the salts. The ratio of diffusivities ($\bar{u}_-/\bar{u}_+$) of ions

for MgCl_2 and CaCl_2 matches well with the bulk diffusivity ratios (u_-/u_+) for these salts. This is unlike the case for their diffusivity ratios in ion exchange membranes [19]. Graphene is atomically-thin which may explain the little changes in the diffusivities of ions inside the membrane. In order to properly describe the diffusion regime we have incorporated the activity coefficients of the ions to compute the activity of the ionic solution. At the higher ionic strengths the ratio of activity coefficients may not necessarily be constant. The details of the calculation of the activity coefficients are provided in the supplementary information. As discussed, the membrane potential values for CuCl_2 could not be fit with the modified TMS model due to the absence of a Donnan potential plateau. However, the overall curve seems to be shifted to the lower ionic strength and this indicates that for CuCl_2 , the effective $\bar{C}_R$ is even lower than the other two bivalent salts.

Our results clearly show that the same membrane is less selective for salts with bivalent counter ions in the Donnan plateau regime. A plausible explanation for the reduced cation selective behaviour of the membrane can be the over compensation of surface charge at the graphene pore by the bivalent cations compared to the monovalent cations. At higher ionic strength the membrane potential becomes negative for MgCl_2 , CaCl_2 and CuCl_2 , as expected from their corresponding ionic mobilities (Figure 4.1). The expected membrane potential for the bivalent salts from the TMS model shows that the diffusion potential for MgCl_2 is around -15 mV, for CaCl_2 is around -14 mV and for CuCl_2 is around -16 mV which is similar to our experimentally observed values. Our results suggest that the bivalent cations adsorb on the surface of the membrane, screen the surface charge of the pore which reduces the membrane selectivity. However, CuCl_2 behaves quite differently from the other two bivalent salts. We theoretically expect it to behave like the other bivalent salts as shown in Figure 4.1. The experimentally observed difference is possibly due to the stronger adsorption of Cu^{++} ions on graphene than the other two cations. Usually, the adsorption affinity depends on the size of the ion, but all three bivalent ions have similar hydrated radii [46]. The reason for higher Cu^{2+} adsorption may be caused by the

different electronic structure of Cu^{2+} ions compared to Mg^{2+} and Ca^{2+} ions.

To further investigate these differences in interaction experimentally, we have conducted bi-ionic potential measurements [18, 34, 35]. In this method, we have first selected one pair of salts which have different cations but similar anions. We have kept the same cationic strength on both sides of the membrane and have conducted our experiments in two regimes. One is in the Donnan dominated regime and the other is outside the Donnan dominated regime. In the Donnan dominated regime, the membrane remains cation selective and the membrane potential measured in this regime is due to the transport of the cations and a separation factor (K_A^B) due to the differences in affinities of the ions towards the membrane. This implies that if the membrane has higher affinity towards one type of ions (A or B), it will facilitate its transport. Outside the Donnan dominated regime the membrane loses its selectivity.

In our measurements, we have taken the following pair of salts: LiCl/KCl , $\text{NH}_4\text{Cl}/\text{KCl}$, $\text{K}_2\text{SO}_4/\text{KCl}$. For bivalent cation salts, we selected $\text{MgCl}_2/\text{CaCl}_2$ and $\text{MgCl}_2/\text{CuCl}_2$. We have measured the bi-ionic potential experimentally for each pair of salts. Now, theoretically we have determined the expected potential by taking the self diffusion coefficient of the ions in the bulk and the separation factor to be 1 and we call it the ideal bi-ionic potential. In the ideal bi-ionic potential calculation, we have also taken in to account the activity coefficient. In our earlier work, we have already observed that the ion diffusion coefficient ratio for graphene nanopores is similar to the bulk diffusion coefficient ratio [15]. The separation factor (K_A^B) is evaluated from equation 4.3 by inserting the experimental bi-ionic potential, diffusion coefficients and activity coefficients of the ions under investigation. Table 5.2 shows the experimental and the ideal value of bi-ionic potential in the low concentration Donnan dominated regime. For KCl/LiCl pair the experimental value is different than the ideal value. The calculated selectivity factor is 0.86 which is close to the ratio of the α values of LiCl and KCl salts (0.84) in our previously published paper [15]. This indicates that the graphene membrane has difference in affinity of for Li^+ and K^+ ions which leads to two distinct Donnan plateaus for these two salts. The results for

the KCl/NH₄Cl salt pair is shown in Figure 4.3. We observe that for these two salts, the membrane potential vs. ionic strength plots almost completely overlap. This behaviour is also evident in our bi-ionic membrane potential measurements. As NH₄⁺ and K⁺ ions have similar diffusivities, the expected theoretical potential is around 0 mV. Our experimentally observed membrane potential is also around 0 mV which indicates that the membrane has similar affinities for both the ions. The calculated K_A^B for KCl/NH₄Cl salt pair is 1.01 which is again similar to the ratio of alpha values for these two salts, i.e. 1.04. For the K₂SO₄/KCl pair, ideally the measured potential should be zero. We have observed a finite potential value for this case which matches our experimental observation of different Donnan plateaus for K₂SO₄/KCl. In our previous work we found that the ratio of α for K₂SO₄/KCl salt pair is higher than 1 (1.10) which is consistent with the bi-ionic potential measurement. For the bivalent ion pairs MgCl₂/CaCl₂ the measured and ideal value of bi-ionic potential are almost similar which is also reflected in Figure 4.2 where the plots for these two salts almost overlap. The calculated value of K_A^B for this case is 1.00 which again matches quite well with the ratio of α values (1.02) for these two salts. This indicates that the membrane has similar affinity for transport of Mg⁺² and Ca⁺² ions. Our membrane potential vs. ionic strength data for Cu⁺² ions show a completely different behaviour in comparison to other bivalent ions. Mg⁺² and Cu⁺² ions having similar bulk diffusivities, should result in an ideal bi-ionic potential that is almost zero (0.14 mV) while our experimental result shows a value of -2 mV in the Donnan dominated regime which implies a different interaction of Cu⁺² and Mg⁺² ions with the graphene membrane. The evaluated K_A^B for this salt pair is 1.18 which confirms the difference in the interactions. We could not compare this value for α ratio in this case as we have not reached the Donnan plateau for CuCl₂ salt.

For the experiments outside the Donnan dominated regime, the membrane loses cation selectivity because of increased screening of charges at higher concentration. At this point, for all the salt pairs the measured value of bi-ionic potential approaches the ideal value, except for the KCl/K₂SO₄ pair (Table 4.3).

K_A^B depends on the concentrations of the electrolyte solution and thereby

Salt pair	Concentration (mM)	Measured bi-ionic potential (mV)	Ideal bi-ionic potential (mV)
KCl/LiCl	0.3	-12.46	-16.41
KCl/NH ₄ Cl	0.3	0	0
KCl/K ₂ SO ₄	0.6/0.3	-3.15	0
MgCl ₂ /CaCl ₂	0.3	1.53	1.47
MgCl ₂ /CuCl ₂	0.3	-1.99	0.14

Table 4.2 — Experimental and Ideal bi-ionic potential for salt pairs in the Donnan dominated regime.

Figure 4.3 — Membrane potential vs. Ionic strength including NH₄Cl salt.

depends on the activity coefficients of the salts. At higher concentrations the activity coefficient of the ions (and ratio of these) deviates from 1 which is incorporated in the given bi-ionic potential equation. The reason of non zero value of bi-ionic potential for KCl/K₂SO₄ is possibly due to the fact that the counter ions having two different valencies of anions have a net transport through the membrane. As the membrane is not perfectly selective even in the Donnan dominated regime as shown in our previous study, there will be some counter-ions moving through the membrane. We have done measurements for more than one salt concentrations which is shown in the supplementary information. This

confirms that our measurement is consistent at other salt concentrations as well.

Salt pair	Concentration (mM)	Measured bi-ionic potential (mV)	Ideal bi-ionic potential (mV)
KCl/LiCl	10	-15.57	-16.31
KCl/NH ₄ Cl	10	0	0
KCl/K ₂ SO ₄	10	-1	0
MgCl ₂ /CaCl ₂	10	1.37	1.26
MgCl ₂ /CuCl ₂	10	0.62	-0.12

Table 4.3 — Experimental and ideal bi-ionic potential for salt pairs outside the Donnan dominated regime.

MD simulation studies support our observation that differences in the Donnan plateaus and Donnan regimes with different ions can be due to differences in the interactions of ions with the graphene nano-pores based on their chemical termination [25–28, 28–31].

Figure 4.4 — Membrane potential vs. ionic strength after bivalent ion treatment and after recovery of the membrane. C_1/C_2 kept at 5.

The membrane potential measurements for bivalent cations suggest that the bivalent ions adsorb on the graphene surface. To investigate the reversibility of the surface adsorption, we conducted the following experiment. After our study with MgCl₂ and CaCl₂, we used the same membrane to perform the experiment

once again with monovalent KCl with the same salt concentration ratio of 5. We now observed a lower value for the membrane potential for the same ionic strength, as if the membrane was less selective. Figure 4.4 shows the membrane potential for KCl, after being exposed to bivalent salts and after the membrane is recovered by treating it with monovalent KCl. After the membrane was contacted with bivalent salts, the membrane potential for KCl is around 4-6 mV lower than the value we obtained previously. The difference in the membrane potential is larger at the low ionic strengths compared to the higher ionic strength. The reduced Donnan potential for KCl after exposure to MgCl_2 can be understood from the adsorption of bivalent cations to the membrane surface. This adsorption lowers the membrane charge and thus selectivity giving lower Donnan potential values. As we see in Figure 4.4, at a very high concentration both of the curves tend to converge at a value around 0 mV as both K^+ and Cl^- ions have similar diffusivities in the membrane. After subsequent exposure to 1 M KCl we found that the initial membrane performance was recovered. The same recovery was observed when the membrane was immersed in HCl (pH 1.89) overnight. The high concentration of monovalent cations results in a complete exchange of the adsorbed bivalent cations.

4.5 Conclusion

In our work, we have investigated the interaction of mono and bivalent cations with perforated graphene membranes. When the ionic strengths of salts on both sides of the membrane are varied keeping a constant ratio, the membrane potentials for MgCl_2 and CaCl_2 follow a similar trend as predicted by a modified TMS theory for dense ion exchange membranes. A Donnan potential plateau is observed at the low ionic strengths and a diffusion potential plateau at higher ionic strengths. The Donnan potential observed for both MgCl_2 and CaCl_2 is much lower than the theoretical Nernst potential (50%) and the one observed for monovalent KCl (72% of its corresponding Nernst potential). MgCl_2 and CaCl_2

reach the diffusion potential limit already at an ionic strength where KCl has still not reached its diffusion dominated regime. For CuCl_2 , the Donnan dominated regime is not reached, while the diffusion dominated regime is reached at a lower ionic strength compared to the other salts. Although a complete fit with the TMS model could not be made, the location of the transition between Donnan and diffusion dominated regimes suggests that the fixed ion charge on the membrane is lowest for the experiments with CuCl_2 . A possible explanation for these effects is that the bivalent cations adsorb on the single layer graphene thereby reducing its effective surface charge. Hence, the observed Donnan potential is much lower than the theoretical Nernst potential. Among the bivalent cations, Cu^{2+} seems to adsorb the most strongly.

Further experiments have validated our hypothesis on bivalent cation adsorption. Membranes previously exposed to MgCl_2 , CaCl_2 show a reduced potential value for KCl at low ionic strength. This indicates that the adsorbed ions are strongly attached to the surface and are not easily removed. Nevertheless, recovery of the membrane selectivity is possible by immersing the membrane in 1 M KCl or HCl (pH 1.89).

We have found that the membrane behaves as a weakly charged nano-filtration membrane having differences in affinities for different cations ions in the Donnan dominated regime. This leads to different Donnan plateaus for different salts. The experimental bi-ionic potential for LiCl/KCl is found to be different from the ideal theoretical bi-ionic potential. This implies that the membrane has separate affinity towards these ions ($\text{K}^+ > \text{Li}^+$) resulting in different Donnan plateaus for these two salts. For $\text{KCl/K}_2\text{SO}_4$, the ideal bi-ionic potential should be zero. We found a non zero value of for the bi-ionic potential for this case which is due to possible transport of co-ions through the non ideal graphene. Ions which have similar affinities towards the membrane ($\text{Mg}^{+2}/\text{Ca}^{+2}$, NH_4^+/K^+) have a similar value for the membrane potential in the Donnan dominated regime. For the $\text{Mg}^{+2}/\text{Cu}^{+2}$ pair, the bi-ionic potential should ideally be zero but we measured a non-zero value for this salt pair. This implies that the membrane has differences in affinities towards these two ions. It is difficult to comment on which ion as

higher affinity for transport in this case as we haven't reached the Donnan plateau for CuCl_2 and other phenomena like adsorption on graphene surface is expected in case of Cu^{+2} ions. We quantified the selectivity and showed that the values are in good match with the ratio of α values for the corresponding salts. Our work provides a clear indication of different interactions of bivalent cations with a two dimensional porous graphene membrane. Their relation to selective ion transport through these graphene based membranes in comparison to monovalent cations opens up new avenues on further investigation of ion transport phenomena with 2D materials in this field.

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Supplementary Information

S1.TMS Equation for 1:2 salts

For the 2:1 salts (MgCl_2 , CaCl_2), the dimensionless membrane potential is expressed as,

$$\Delta\bar{\psi}_{\text{TMS}} = \frac{1}{z_2} \ln \frac{k_2^P}{k_2^f} + \frac{\bar{u}_+ - \bar{u}_-}{z_2\bar{u}_- - z_1\bar{u}_+} \ln \left(\frac{T_r k_2^P + t_1 \zeta_f}{k_2^f + t_1 \zeta_f} \right) \quad (4.4)$$

Where, $\Delta\bar{\psi} = \frac{F\Delta\psi}{RT}$, $t_1 = \frac{|z_1|\bar{u}_+}{|z_1|\bar{u}_+ + |z_2|\bar{u}_-}$, $\zeta_f = \frac{\bar{c}_R}{|z_1|v_1 c_f}$, $T_r = \frac{c_p}{c_f}$

z_i is the electrochemical valence, $\bar{u}_+$ is the diffusion coefficient of cations and $\bar{u}_-$ is the diffusion coefficient of anions and k_i is the partition coefficient of ion i. T_r is the transmission, which denotes the ability of solute to pass through the membrane. v_i is the stoichiometric coefficient of electrolyte, 1 represents counter ions. $\zeta_{p(f)}$ is the ratio of the volume charge density to equivalent salt concentration in the feed side or in the permeate side of membrane. F is the Faraday constant, R is the gas constant and T is the temperature. $\Delta\psi$ is the membrane potential. $\Delta\bar{\psi}$ is the dimensionless form of the membrane potential. $\bar{c}_R$ is the constant volume charge density of charged membrane (mole/l of pore volume). c_f is the high concentration and c_p is the low concentration.

The partition coefficient of co-ions of 2:1 asymmetric is,

$$k_2^{p(f)} = [\Gamma_{2:1,p(f)}^-]^{-1} \quad (4.5)$$

$$\Gamma_{2:1,p(f)}^- = 2\sqrt{\frac{\zeta_{p(f)}}{3}} \cos \frac{\theta}{3} \quad (4.6)$$

$$\theta = \arccos \left(\frac{1}{2} \left(\frac{\zeta_{p(f)}}{3} \right)^{-1.5} \right) \quad (4.7)$$

S2. Membrane potential for bare PET

To clearly show that the PET pores have no influence on the ion selectivity of the monolayer graphene, we have measured the membrane potential for the bare PET sample (i.e. no graphene on PET) prepared in the same way we prepared the graphene samples (See Figure 4.5). For KCl, the time averaged membrane potential is around 0 mV which implies that the bare PET sample does not show any selectivity. Both K^+ and Cl^- ions have similar diffusion coefficients which results in zero membrane potential. For $MgCl_2$, $CaCl_2$ and $CuCl_2$ salts, we see a time averaged membrane potential of -13.3 mV, -14.9 mV and -15.1 mV respectively. This again implies that the bare PET membrane doesn't have any selectivity for Mg^{++} , Ca^{++} , Cu^{++} ions and the negative potential appears because Cl^- ions have higher diffusion coefficients than the Mg^{++} , Ca^{++} and Cu^{++} ions.

Figure 4.5 — Membrane potential vs. time for PET membrane without any graphene on top

S3. Activity Coefficient

The activity coefficients for the individual salt ions (K^+ , Li^+ , Mg^{++} , Ca^{++} ,

Cu^{++}) are calculated from the extended Debye-Hückel formula represented by the following equation. The values calculated from the formula are incorporated in modified TMS model to fit the experimental data.

$$\log(\gamma_i) = -Az_i^2 \left(\frac{\sqrt{I}}{1 + Ba_i\sqrt{I}} \right) \quad (4.8)$$

γ_i represents the activity coefficient of salt i, I is the ionic strength, a_i is the effective size of the corresponding ion.

For water at 25 °C, $A=0.5085\text{M}^{-\frac{1}{2}}$, $B=3.281\text{ M}^{-\frac{1}{2}}\text{ nm}^{-1}$

S4: Bi-ionic Potential Measurement

We have measured the bi-ionic potential for different salt pairs at different concentrations. Values of potential at different concentration is provided in the following tables.

KCl/LiCl		
Concentration (mM)	Bi-ionic potential (mV)	Ideal bi-ionic potential(mV)
0.3	-12.46	-16.41
0.6	-10.97	-16.41
1.25	-11.99	-16.40
2.5	-12.60	-16.39
4.375	-14.29	-16.36
5	-14.86	-16.36
7.5	-13.69	-16.34
10	-15.57	-16.31

Table 4.4 — Experimental and Ideal Bi-ionic potential for KCl and LiCl salt pair.

KCl/NH ₄ Cl		
Concentration (mM)	Bi-ionic potential (mV)	Ideal bi-ionic potential(mV)
0.3	0	0
0.5	0	0
0.6	0	0
1	0	0
2.5	0	0
5	0	0
7.5	0	0
10	0	0
10.75	0	0

Table 4.5 — Experimental and Ideal Bi-ionic potential for KCl and NH₄Cl salt pair.

KCl/K ₂ SO ₄		
Concentration (mM)	Bi-ionic potential (mV)	Ideal bi-ionic potential(mV)
0.6	-3.15	0
1	-3.30	0
1.25	-2.40	0
2.5	-2.68	0
5	-2.12	0
7.5	-1.5	0
10	-1	0
10.75	1.46	0

Table 4.6 — Experimental and Ideal Bi-ionic potential for KCl and K₂SO₄ salt pair.

MgCl ₂ /CaCl ₂		
Concentration (mM)	Bi-ionic potential (mV)	Ideal bi-ionic potential(mV)
0.3	1.53	1.47
0.6	1.57	1.44
1	1.72	1.43
1.25	1.70	1.42
2.5	2.52	1.38
5	2.16	1.31
7.5	2.19	1.26
10	1.37	1.21
10.75	1.77	1.09

Table 4.7 — Experimental and Ideal Bi-ionic potential for MgCl₂ and CaCl₂ salt pair.

MgCl ₂ /CuCl ₂		
Concentration (mM)	Bi-ionic potential (mV)	Ideal bi-ionic potential(mV)
0.3	-1.99	0.14
0.6	-2.72	0.12
1	-3.04	0.10
1.25	2.40	0.10
2.5	0.91	0.06
5	0.24	0.01
7.5	0.74	-0.07
10	0.62	0.12

Table 4.8 — Experimental and Ideal Bi-ionic potential for MgCl₂ and CuCl₂ salt pair.

CHAPTER 5

Charge Regulation in Nanoporous Graphene

Abstract — In this work, we have studied the pH dependent surface charge nature of nanoporous graphene. This has been investigated by membrane potential and by streaming current measurements, both with varying pH. We observed a lowering of the membrane potential with decreasing pH for a fixed concentration gradient of potassium chloride (KCl) in the Donnan dominated regime. Interestingly, the potential reverses its sign at pH 3. The fitted value of effective fixed ion concentration ($\bar{C}_R$) in the membrane also follows the same trend. The streaming current measurements show a similar trend with sign reversal at around pH 4.2. The zeta potential data from the streaming current measurement is further analyzed using a 1-pK model. The model is used to determine a representative pK (acid-base equilibrium constant) of 4.2 for the surface of these perforated graphene membranes.

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5.1 Introduction

Perforated monolayer graphene is a two dimensional material in which pores have been created in a controlled manner by e.g. heavy ion beam bombardment, focused ion beams, electrical pulse method, and oxygen plasma etching [1–7]. Nano-porous graphene membranes have potential applications in the fields of separation, filtration and biomolecular translocation [8–11]. As ions can diffuse through these pores in graphene, it can be used as electrodes for lithium ion batteries, spacers as well as supercapacitors [12, 13]. To achieve all these potential applications in practice it is important to study the transport characteristics through these two dimensional nanoporous materials. In our previous work, we have investigated the ion transport properties of perforated graphene by varying the concentration of monovalent and bivalent cations to understand how the single layer membranes behave [14]. For all the salts under investigation (KCl, LiCl, K₂SO₄, MgCl₂, CaCl₂, NH₄Cl), we observed clear Donnan and diffusion dominated regimes due to Donnan exclusion of ions and differences in the self diffusion coefficients of ions, respectively. These membranes further show strong adsorption phenomena for bivalent cations. A further measurement of the bi-ionic potential confirms that there are differences in the interaction of ions with the graphene surface which lead to the differences in the Donnan dominated plateaus. We could also quantify the extent of differences in the selectivities of different ions and relate it to the ratio of their non-ideality factors. All these experiments conducted so far, are done at pH neutral condition, where the membrane is found to be cation selective. The cation selective nature implies a presence of fixed negative charges at the surface. These charges are possibly introduced during the fabrication process (e.g. deprotonation of surface hydroxyl or carboxyl) or by adsorption of anions on the membrane surface. This motivates us to further investigate the nature of surface charge present at these nanoporous graphene membranes and its effect on ion transport. The charge of these surface groups is expected to be subjected to acid-base equilibrium. The influence of pH can be related to the surface pK which represents the surface acid dissociation constant.

So far, there are very few studies on the surface charge groups present on the nanoporous monolayer graphene as the conventional experimental techniques, including titration or FTIR techniques, are not suitable for single layer graphene. Most of the studies available concern graphene oxide (GO), reduced graphene oxide (rGO) or are purely based on MD simulations [15–17]. Konkena et al. (2012) have shown that GO sheets contain acidic groups with pK of 4.3 and groups with pK of 6.6 and 9.0 by conducting zeta potential measurements, pH titration and infrared spectroscopy [15]. Shih et al. (2012) have investigated the surface activity with varying pH through MD simulations. Their result shows that at low pH the carboxyl groups become less hydrophilic and form aggregates [16]. Orth et al. determined the pK of graphene like materials via titration and the obtained pK values match with carboxylic acid groups, less acidic carboxylic groups and alcohol groups [17].

It is well known for pristine graphene to be highly hydrophobic due to the absence of functional groups, making processing in water difficult. Therefore graphene is typically functionalized using covalently bound groups (e.g. graphene oxide) or non-covalently bound groups (e.g. surfactants) to enable dispersion stability in water [18–20]. Bepete et al. (2017) were able to produce stable dispersion of single-layer graphene in water without any functionalization via electrostatic stabilization [21]. Here, the surface charging mechanism was proposed to be from hydroxide ion adsorption. Charge reversal was observed around pH 4, which is typical for inert hydrophobic surfaces in an aqueous environment, caused by competitive adsorption of hydroxide and hydronium ions [22]. Rollings et. al. have shown that for a 3 nm pore in graphene fabricated by electrical pulse method, the K^+/Cl^- selectivity has a sharp decrease from pH 6 to pH 4 and is negligible at pH 2 [3]. They have attributed this effect due to protonation of surface charge group (e.g. carboxyl) present at the graphene edge.

Here, we present measurements of membrane potential induced by salt (KCl) concentration gradients across perforated graphene membranes at different pH. These measurements provide direct insight in the surface charge state of the graphene membrane. We have corroborated our experimental results with stream-

ing current measurements at a fixed salt concentration and varying pH. The extracted zeta potentials show a similar influence of pH compared to the membrane potential. From the zeta potential data, a surface pK value was fitted for our graphene surface [23–25].

5.2 Theory

Two frequently used charge regulation models for surfaces in contact with electrolyte solutions are the 1-pK and 2-pK models [25]. The major difference between these models is the considered changes in the protonation states of a representative functional group. As implied by the name, the 1-pK model considers one protonation step, with the charge varying between $-1/2e$ and $+1/2e$. The 2-pK model accordingly accounts for two protonation steps, with the charge varying between $-1e$, 0 and $+1e$. Hence, at the cost of one additional fitting parameter the 2-pK model, at least in theory, allows for a more accurate representation of the experimental data. However, it was shown by Piasecki and Rudzinski [25] that even under consideration of various experimental methods both models can work equally well, although resulting in somewhat different physical parameters. Therefore the physical correctness of the model and the resulting parameters should be taken with care. In light of the limited characterization methods conducted in this work, it is reasonable to limit the number of fitting parameters to ensure a unique solution. Thus, the 1-pK model is used in combination with the Basic Stern model (BSM), which describes the electric double layer forming at the graphene/electrolyte interface. Neglecting other ion adsorption, this results in the following set of equations [25]:

$${}^1K_H^{int} = \frac{[SOH^{(1/2)-}] \cdot a_H}{[SOH_2^{(1/2)+}]} \cdot \exp\left(\frac{-e\Phi_0}{k_B T}\right) \quad (5.1)$$

$$\Phi_0 - \Phi_d = \frac{\sigma_0}{C_1} \quad (5.2)$$

$$\Phi_d = \frac{2k_B T}{|z|e} \cdot \ln \left(\frac{-\sigma_d}{\sqrt{8\epsilon_0\epsilon_r k_B T I}} + \sqrt{\frac{\sigma_d^2}{8\epsilon_0\epsilon_r k_B T I} + 1} \right) \quad (5.3)$$

$$\sigma_0 = \frac{1}{2}(e \cdot [SOH_2^{(1/2)+}] - e \cdot [SOH^{(1/2)-}]) \quad (5.4)$$

$$\sigma_d = -\sigma_0 \quad (5.5)$$

$$N_s = [SOH_2^{(1/2)+}] + [SOH^{(1/2)-}] \quad (5.6)$$

Here ${}^1K_H^{int}$ is the equilibrium constant of protonation which is determined by the point of zero charge (PZC), $[SOH^{(1/2)-}]$ and $[SOH_2^{(1/2)+}]$ are the number of negative and positive functional groups on the surface (m^{-2}), a_H is the proton activity in the bulk solution (mol/dm^3), Φ_0 and Φ_d are the electrical potentials at the surface and outer Helmholtz plane, σ_0 and σ_d are the charge densities (C/m^2) at the surface and inside the diffusive boundary layer. The two fitting parameters are the Helmholtz capacity C_1 and the total density of functional groups N_s . All other physical constants have their typical denotation with ϵ_r being 78.25 (relative permittivity of water at 25 °C) and I the ionic strength of the solution ($ions/m^3$). Assuming $\zeta \approx \Phi_d$, the system of equations is iteratively solved and fitted to the experimental zeta potential data via a least-square approach using a gradient-free search algorithm.

5.3 Experimental Procedure

For our study, we have used single layer graphene supported on PET substrate. These membranes were irradiated with 5×10^8 ions/cm² using ${}^{129}Xe^{23+}$ ions having specific energy of 0.71 MeV/u. This irradiation creates pores in the nanometer range in the graphene. After etching, the PET pores are around 20 to 40 times larger than the graphene pores, therefore presenting insignificant influence on the

ion transport through graphene. For further details of the fabrication process, please look at our previously published papers [2, 14].

5.3.1 Membrane Potential with Varying pH

The membrane is placed between two reservoirs containing electrolyte solutions of different concentrations. The high and low KCl concentration solutions are circulated in each compartment and through a 25 °C temperature bath. The high and low electrolyte concentration compartments are kept at a ratio of 5 to 1. Calomel reference electrodes are used to measure the potential across the membrane using a potentiostat (Autolab PGSTAT302N). The pH is adjusted using HCl and NaOH solutions. The pH and conductivity of the solutions are measured before and after the membrane potential measurements to make sure that these two remain constant throughout the measurement.

5.3.2 Zeta Potential with Varying pH

Streaming current measurements are carried out by SurPASS electrokinetic analyser (Anton Paar) [26, 27]. The setup contained an adaptable gap cell with two sample holders where two graphene membranes are placed facing each other. In our calculations we have considered the streaming current value. The flow of electrolyte solution is adjusted over the cell by two syringe pumps. In order to measure the streaming current with varying pH, HCl and NaOH solution are added to the KCl solution automated by the device software. The device software calculates the zeta potential of the surface from the streaming current values based on the Helmholtz-Smoluchowski equation (Equation 5.7) [28].

$$\zeta = \frac{dI}{d\Delta p} \times \frac{\eta}{\epsilon \times \epsilon_0} \times \frac{L}{A} \quad (5.7)$$

Where, $\frac{dI}{d\Delta p}$ is the slope of streaming current vs. differential pressure, η is electrolyte viscosity, ϵ is the dielectric coefficient of electrolyte, ϵ_0 is permittivity, L is the length of the streaming channel and A is the cross sectional area.

5.4 Results and discussion

Figure 5.1 shows the variation of the normalized membrane potential ($\Delta\Psi/\Delta\Psi_{Nernst}$) with pH at different electrolyte concentrations (at a fixed ratio of 5). Additional HCl and NaOH concentrations in both reservoirs are taken into account to calculate the Nernst potential ($\Delta\Psi_{Nernst}$). As the concentrations of protons and hydroxide are equal for both reservoirs there is no concentration gradient for these ions.

Figure 5.1 — Scaled Membrane Potential with Nernst Potential with varied pH at different KCl electrolyte concentrations at the constant ratio of 5. The concentrations in the legend are concentrations of the low concentration side of the reservoirs.

Figure 5.1 shows that the scaled membrane potential is almost constant in the pH 5 - 10 range for low KCl concentration range (0.6 mM, 1.25 mM, 6 mM at the low concentration side). It shows a steep decrease in the pH range 5 to 3 and around pH 3 it reverses its sign. Scaled membrane potential at a high concentration (200 mM) shows a more or less constant trend in the entire pH range. The lowering of the membrane potential for lower pH indicates a reduction in membrane selectivity towards cations. Here, a membrane potential of 0 means non-selective ion passage. This can be explained by a reduction of surface charge at the membrane pores. At higher pH range (5-10) potential surface charge groups

are more dissociated or more hydroxide is adsorbed. At this point, the surface charge density remains constant with increasing pH. With a decrease in pH the surface charge reduces via protonation, as the hydroxide concentration is negligible. This neutralizes the effective surface charge and ultimately introduces a positive surface charge, confirmed by the sign change of the membrane potential. The variation of surface charge with pH will be discussed in detail later on. At high KCl concentration, the surface charge of the graphene surface is more screened by the counterions. At this point, the potential generated is partly due to the difference in diffusivities of cations and anions inside the membrane. For KCl, this so-called diffusion potential is close to zero. For this reason, the potential at higher concentration is close to zero and is independent of pH.

Figure 5.2 — Scaled Membrane Potential with Nernst Potential vs. low concentration at pH 3, pH 4 and pH neutral.

Figure 5.2 shows the variation of the membrane potential with KCl concentration for different pH values (pH 3, pH 4 and neutral). For the three pH values, the potential displays a plateau for low KCl concentrations (0.6-8 mM). At high concentration this value is close to zero. This trend in membrane potential resembles the sigmoid curve observed for dense ion exchange membranes. For pH neutral and 4, a positive Donnan plateau is observed, confirming a cation selective

behavior. For pH 3, the Donnan plateau is negative, as expected for an anion selective membrane. The membrane potential at high KCl concentrations is close to zero for all three pH values. In this concentration range, we expect the diffusion potential to dominate. The membrane potential vs. concentration data is fitted with a modified version of Teorell Meyer Sievers (TMS) model as described in our previous paper [14, 29–32]. The best-fit value for fixed ion concentration ($\bar{C}_R$), the non-ideality factor (α) and the diffusivity ratio for anion to cation ($\frac{\bar{u}_-}{\bar{u}_+}$) are given in Table 5.1. With higher $\bar{C}_R$ the membrane is expected to have higher rejection of co-ions. At pH neutral value, the $\bar{C}_R$ value is around 78 mM which is quite high compared to the other two pH values. At pH 3 the surface charge changes its sign. For pH 4, the membrane potential is close to zero and the Donnan plateau is very low compared to the Nernst potential. This indicates a transition region, and gives a $\bar{C}_R$ value with a high error range indicating a surface charge close to zero. This result is highly consistent with our streaming current data which will be explained later.

pH	$\bar{C}_R$ (mM)	α	$\bar{u}_-/\bar{u}_+$
3	-14 ± 4	0.46 ± 0.04	1.07 ± 0.03
4	71 ± 89	0.20 ± 0.04	1.00 ± 0.1
Neutral	78 ± 28	0.70 ± 0.04	0.96 ± 0.1

Table 5.1 — Best-fit parameters of the modified TMS model for the three values of pH and their 95% confidence intervals

To support the variation of surface charge with pH, streaming current measurements have been carried out. As mentioned in the theory, the zeta potential is calculated from the streaming current value by the Helmholtz-Smoluchowski equation. Figure 5.3 shows the variation of the zeta potential with varying pH (11 to 3) at 15 mM KCl concentration. At higher pH values (11 to 7), the zeta potential values remain negative at an almost constant value. With decrease in pH (7 to 3), the zeta potential becomes less negative and at low pH values becomes positive. These results are consistent with the membrane potential experiments and can be explained by proton dissociation processes.

Using the 1-pK BSM model, the zeta potential of the membrane surface can

Figure 5.3 — Experimental zeta potential data fitted with 1-pK model. The surface charge density estimated from the zeta potential data also follows the same trend and is plotted in the right Y axis. This shows that zeta potential corresponds to a surface charge density in a direct manner.

be used to estimate the membrane surface charge density. The estimated surface charge density is also plotted in Figure 5.3. This follows the same trend as the zeta potential. This result has a good correlation with the fitted $\bar{C}_R$. $\bar{C}_R$, multiplied with the sign of the surface charge (-ve in our case) and the Faraday constant (F), is converted to the charge in Coulomb/cm³ as shown in Table 5.2. The table shows that the $-F*\bar{C}_R$ values exhibits similar variation with pH.

pH	$-F*\bar{C}_R$ (C/cm ³)
3	1.32
4	-6.82
Neutral	-7.48

Table 5.2 — Variation of $-F*\bar{C}_R$ with the pH. This shows similar trend in the surface charge vs. pH

This supports the assumption that the average surface charge of graphene is representative for the local charge at pores. It is important to note that the streaming current measurement takes the average over the whole graphene surface and therefore does not account for potential charge heterogeneities. The transport

of ions, however, is determined by the local surface charges at the nanopores with a diameter of 1-10 nm and density of $5 \mu\text{m}^{-2}$ [14]. Independent of the mechanism of charge regulation, it is assumed that the estimated zeta potential gives a reasonable indication of the local potential at the pores relevant for ion transport through the pore. Disregarding additional ion adsorption, the zeta potential as a function of pH can be described quite well by the model as shown in Figure 5.3. The resulting fitting parameters for a pK value of 4.2 are a Helmholtz capacity C_1 of $14.4 \mu\text{F}/\text{cm}^2$ and a surface site density N_s of 0.0914 nm^{-2} . The average specific integral capacitance of the electric double layer is determined as $C_{EDL} = \sigma_0/\Psi_0 = 9.6 \mu\text{F}/\text{cm}^2$ [33], which is in the order of magnitude previously observed for graphene [34] ($2.5 \mu\text{F}/\text{cm}^2$) and reduced graphene oxide [35] ($6.5 \mu\text{F}/\text{cm}^2$). Hydroxide adsorption was proposed by Bepete et al. [21] for single-layer graphene sheets dispersed in water, which resulted in similar zeta potential and point of zero charge as observed in this work. Charge reversal to positive surface charge could be caused by adsorption of protons. For graphene oxide, it is known that carboxylic acid groups are located at the edges [1, 36, 37]. This was also observed for reduced graphene oxide. If the nano-pores are oxidized during the fabrication process, carboxylic acid groups could likely form. The determined pK value for these groups present in reduced graphene oxide is around 8 [15]. Carboxylic acid as the sole charge regulation mechanism, however, would not explain the relatively high positive zeta potential observed below pH 4.

5.5 Conclusion

In summary, we have observed the variation of membrane potential of graphene with pH. The membrane potential decreases with decrease in pH. At high pH the surface charge groups remains negative resulting in cation selectivity of the membrane, mostly independent of the hydroxyl bulk concentration. With a decrease in pH, the membrane surface charge group become more protonated.

This is confirmed by both the surface streaming potential measurements as well as the membrane potential measurements during Donnan dialysis. At high salt concentrations little change in membrane potential with pH is observed because of the screening of the surface charge groups. By fitting our data with the 1-pK BSM model, the surface pK is determined around 4, which is quite different from the expected pK for surface carboxylic acid groups. Both measurements (Donnan dialysis and streaming potential) indicate the same trends regarding surface charge regulation by bulk pH.

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CHAPTER 6

Investigating charge-selectivity in 2D nanoporous graphene using the Poisson-Nernst-Planck Model

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Abstract — 2D nanoporous membranes are of interest in recent years due to the possible lower transport resistance compared to dense membranes. In this work we investigate the phenomena regarding ion-selectivity in 2D nanoporous graphene membranes by numerical simulations using the Poisson-Nernst-Planck equations and compared with our experimental observations. The membrane surface potential depends on the ionic concentration, which is included by accounting for the potential drop over the Stern layer. Using the Gouy-Chapman-Stern theory, we obtain reasonable agreement with our previous experimental work where a difference between the Nernst potential and measured potential was observed for low salt concentrations. This discrepancy can be understood to result from an insufficient surface charge in order to achieve full exclusion for the range of experimentally accessible salt concentrations. The agreement for all salts used (KCl, LiCl and K₂SO₄) was quite reasonable, in particular considering the relatively simple description of the Stern layer effect. The sensitivity of the module to parameters such as pore radius, surface potential and Stern layer thickness, as well as the possible influence of thermodynamic non-ideality (activity coefficients) was also investigated.

The manuscript based on this chapter is ready for submission

Jurgen B. Roman, Mandakranta Ghosh, Rob G.H. Lammertink, Jeffery A. Wood, *Charge-Selectivity in 2D Nanoporous Graphene Membranes*

6.1 Introduction

Charge selective interfaces are interesting to study because of their wide range of applications in ion separation [1–4]. Often the materials used for these are dense ion exchange membranes or hydrogels. The ion rejection mechanism through these materials are quite well understood [1, 3]. Porous polymer structures made of hydrogels, conducting polymer or anodic alumina present 3D ion channels [5, 6]. 2D nanoporous materials are structurally different than 3D charged porous structures as they have infinitesimally small thickness and thereby no cylindrical channel exists similar to 3D pores. In the past few years, 2D nanoporous materials are gaining attention to be used as charge selective interfaces, with potential applications in separation processes and most notably bio-sensing [7–14]. The actual charge transport phenomena occurring near these thin interfaces needs a more thorough understanding to keep developing this new technology. In most studies, nanoporous graphene membranes have been found to be cation selective [15–17]. The behaviour of the surface charge and thereby the selectivity of these materials depends on the adsorption of ions on the surface, as well as pH. The origin of the negative surface charge has been investigated by different groups. Walker et al. (2017) proposed that the negative charges in graphene arise likely due to the adsorption of OH^- in aqueous environments [18]. Secchi et al. (2016) proposed a similar phenomenon inside carbon nanotubes (CNT) [19]. Their study shows that at low salt concentrations, the surface conductance in CNT shows a power law behaviour instead of a constant surface conductance. They could explain this behaviour with a model considering hydroxide adsorption at the carbon surface [19]. Bepete et al. (2017) also suggested hydroxide ion adsorption as a primary charging mechanism for graphene oxide [20]. For a pore radius around 3 nm in graphene, the cation selectivity is shown to decrease with decrease in pH by Rollings et al. (2016) [16]. They attributed this to the presence of carboxyl groups present on the surface.

The selectivity of these membranes is estimated by conducting membrane potential experiments. O'Hern et al. (2014) observed very low cation selectivity

of graphene as the potential observed was very low compared to the theoretical Nernst potential at the working concentration ratio [15]. They attributed this to intrinsic defects in the graphene sample. We also observed similar result in our study. We investigated the membrane potential vs. concentration for nanoporous graphene, for different salts (KCl, LiCl and K_2SO_4) [21]. The transport was induced by maintaining a concentration difference across the membrane. The potential vs. concentration trend showed a diffusion plateau at high concentration and a Donnan dominated plateau at low concentration. Ideally, for a 100% selective membrane, the Donnan potential should reach the theoretical Nernst potential. The Donnan potential in case of our membranes always showed a lower potential compared to the Nernst potential for the working concentration ratio of 5. Initially, we postulated that this was caused due to some non-idealities present in the membrane such as bigger defects, pore size distribution or low surface charge density of graphene. However, the actual reason behind this membrane not achieving full selectivity even at low electrolyte concentrations (1 mM), was still unclear as full Debye layer overlap should be achieved for expected pore-sizes. For the pore-size range in our work (6-8 nm) the ion-selectivity mechanism is expected to be charge-based (Donnan exclusion). This is in contrast to the case of sub-nm pores, where other exclusion mechanisms (size and dielectric exclusion) play a more prominent role. In our current work, the main motivation is to understand the discrepancy between ideal Nernst behaviour and experimental measurements for our graphene membranes at low salt concentrations. In order to do this, we perform 2D numerical simulations based on the Poisson-Nernst-Planck (PNP) equations in order to understand the origin of the the deviation between the TMS model and the experimental results. In our model, we have investigated different surface potentials and pore radii and tried to relate these to the membrane potential and thereby cation selectivity of nanoporous graphene. We have also included the effect of Stern layer in our simulations, which allows for an effective concentration-dependent zeta potential [22, 23]. By comparing various theoretical descriptions for the charge behaviour of the pores, we could test for consistency with experimental observations. We also compare the Gouy-Chapman-

Stern (charge-regulation case) with simple boundary conditions (constant surface potential or surface charge). Through the use of parametric sensitivity analysis and least-squares fitting of these models, we can understand the origin of the non-ideality factor observed throughout our previous experimental studies.

6.2 Theory and Model Details

The Poisson-Nernst-Planck (PNP) equations allow for the description of ionic species transport under dilute conditions. This provides the potential distribution between two constant (but different with respect to each other) concentration reservoirs separated by a thin nanopore.

The fact that it is a 2D membrane means that everything is governed by the pore entrance/exit and the electrical double layer. In this case, we neglect the influence of the effectively uncharged support substrate as per our previous experimental findings which showed that the PET support layer is not selective towards ions [21]. This can be understood due to the one order magnitude large pore radius in the PET support compared to the graphene pore.

Defining D_i as the diffusion coefficient, c_i as the concentration, z_i as the charge number of the ion, F as Faraday's constant, R as the universal gas constant, T as the temperature, ϕ as the potential, γ as the activity coefficient and $\varepsilon_r\varepsilon_0$ as the water permittivity, the PNP equations can be written as follows for the case where activity coefficients of each individual ionic species are included (see supplementary information (SI) for the derivation):

$$J_i = -D_i \left(\nabla c_i + \frac{z_i F c_i}{RT} \nabla \left(\phi + \frac{RT}{z_i F} \log \gamma \right) \right) \quad (6.1)$$

$$\nabla^2 \phi = -\frac{F}{\varepsilon_r \varepsilon_0} \sum_i^n z_i c_i \quad (6.2)$$

Using the PNP equations the concentrations of individual species as well as the potential can be computed. While the concentration of each species in the

reservoirs are approximately constant in the bulk, this is not the case near the charged pore wall. This could make inclusion of activity coefficients relevant, as there can be locally large gradients in the concentrations of individual species. The average activity coefficients of a salt pair cannot be used since, due to the charged nature of the pore, there is a Donnan exclusion effect and therefore locally the concentration of anions and cations will be unequal at the graphene pore. To calculate the activity coefficients of individual ionic species the Wateq form of the extended Debye-Hückel equations were used with the ion dependent parameters (a and b) determined by Parkhurst et al. [24] (tabulated in [25]) (equation 6.3). The values of individual diffusion coefficients (taken from [26]) and activity coefficient parameters (taken from [25]) can be found in the Table 6.3.

$$\log_{10}(\gamma) = \left(\frac{-Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} \right) + b_i I \quad (6.3)$$

In eq. 6.3, A and B are temperature dependent constants ($A = 0.51$ and $B = 0.33$ at 25°C when a and b are in $\text{\AA}$). I is the ionic strength in mol/kg (molality). For simplicity, we assume a constant density of water and use the molarity (mol/m^3) as an approximation for molality.

In order to model this system some simplifications were made. The pores are assumed to be perfect cylinders with 0 length. This allows for an axisymmetric formulation of the problem (r - z). As discussed earlier, the effect of the uncharged PET support layer is neglected in these simulations.

A graphical representation of the system can be seen in Figure 6.1 and the imposed conditions in Table 6.2. The line AB has a set concentration (the bulk concentration of the species). The line EF also has a set concentration, which is different from the concentration at line AB. The line EF is treated as a floating potential boundary condition. This floating potential is the membrane potential, which we will compare to the experimental values. The other reservoir wall (AB) is taken as a reference ground (0V). Diffusion coefficients for each species are used and assumed to be constant. A more detailed graphical representation, which also displays the boundary conditions, is available in the supplementary

material. The model equations were solved using the finite element method in COMSOL Multiphysics. In COMSOL, the second order Lagrange elements were used to simulate the potential profile and the first order for both the cation and anion concentration profiles. The numerical independence of the solution was determined through successive refinement of the mesh, resulting in approximately 73000 elements.

In order to incorporate the effect of the Stern layer into the model we first state that, using the Gouy-Chapman-Stern model, we can write the surface potential of the pore wall ϕ_s as a function of the zeta-potential ζ and the Stern layer potential drop: [22, 23]

$$\phi_s = \Delta\phi_{Stern} + \zeta \quad (6.4)$$

$$\zeta = \phi_s / (1 + \frac{\lambda_s}{\lambda_D}) \quad (6.5)$$

$$\lambda_s = \frac{\epsilon_s}{C_s} \quad (6.6)$$

where λ_s is the effective Stern layer thickness and λ_D is the Debye screening length. The Debye screening length is a function of the concentration, which in this case is taken relative to the high concentration reservoir. The influence of this assumption will be discussed in the results and discussion. By using this model for surface potential, at low ionic concentrations the system will behave as having a constant potential equal to the surface potential and at higher ion concentrations (when λ_D becomes smaller) a lower zeta-potential will be observed. Note that this is an order of magnitude approximation of the Stern layer potential drop based on the predicted slope ($\nabla\phi$) at the outer Helmholtz plane by the Gouy-Chapman theory [22, 23].

This was incorporated by taking a constant value for the surface potential and then calculating the value of the zeta-potential using equation 6.4. This zeta potential was set as a potential of the membrane surface, line CD in Figure 6.1. By using this Gouy-Chapman-Stern approach we account for the Stern layer effect

Figure 6.1 — Model schematic referencing boundary conditions. Boundary conditions are mentioned in Table 6.2.

through a Robin-type boundary condition setting a concentration-dependent zeta potential.

To avoid additional fitting parameters, Stern layer thickness values for various salts were used from literature [27]. In this case, chlorine was the anion for all salts. Here, we assume that the cation is dominant in the determination of the effective Stern layer thickness. The following Stern layer thicknesses were therefore used for the different compounds:

Compound	λ_s (Å)
KCl	6
LiCl	8
K ₂ SO ₄	6

Table 6.1 — λ_s values for different compounds [27]

Line	Imposed condition
AE	Symmetry axis
BF	No flux
CD	Imposed zeta potential and impermeable
AB	Low concentration and 0V
EF	High concentration and floating potential

Table 6.2 — Boundary conditions corresponding to Figure 6.1.

Ion	D_i (10^{-9} m ² /s)	a_i (Å)	b_i (Å)
K ⁺	1.96	3.71	0.01
Li ⁺	1.03	4.76	0.20
Cl ⁻	2.03	3.71	0.01
SO ₄ ²⁻	1.07	5.31	-0.07

Table 6.3 — Physical Properties of Ions.

6.3 Results and discussion

6.3.1 Comparison of model with experimental results

Our first approach was to set a surface charge density or constant zeta-potential at the membrane (see the SI for detail). In this approach, it was found that the model results were very different from what was observed in the experiments. Using a surface charge density which is dependent on the ion concentration in the reservoirs led to better agreement, but a theoretical justification was unclear.

Figure 6.2 shows the numerical result for KCl by setting a varying zeta-potential (ζ) according to the Gouy-Chapman-Stern theory. The constant value of the surface potential (ϕ_s) used is -60 mV, from which the zeta-potential was calculated using equation 6.4. On the y-axis the calculated/experimentally observed potential divided by the ideal Nernst-potential is shown. The x-axis shows the concentrations in the lower concentration reservoir on a log scale. The reservoirs were kept fixed at a concentration ratio of 5.

Decreasing the value of the pore radius shifts the curve to the right, effectively shifting the transition from the Donnan dominated regime towards the diffusion dominated regime to a higher concentration. Since the Debye screening length

Figure 6.2 — Model results when accounting for a potential drop over the Stern layer and activity of ions

becomes smaller at higher concentrations, the potential in the middle of the pore will be smaller. However, the potential of the pore wall can still be high, leading to a higher selectivity (higher dimensionless potential). When increasing the surface potential the curve is shifted to the right as well.

As stated before, the ion concentration near charged walls can be different than in the bulk and there can be significant gradients in concentrations near the membrane pore. Therefore activity coefficients of each ionic species were included using equation 6.3. The inclusion of activity coefficients turned out to have a limited effect on the results of the model for the conditions studied. The likely reason for this is that at low salt concentrations, the effect of activity coefficients/activity coefficient gradients are negligible (near-ideal solution behaviour). At high salt concentrations, the activity coefficient effect is more substantial but in this case the membrane selectivity is lost and this dramatically reduces the influence of activity coefficient gradients.

The agreement using the Gouy-Chapman-Stern model is improved a lot compared to setting a constant zeta-potential or surface charge density. These effects

could also be the reason for the discrepancy with the TMS model in our previous work [21]. The best agreement is observed when the model contains pore sizes of 2 nm. Meaning that the actual pore radius would be 2.6 nm, when accounting for the Stern layer. In our previously published work, we have experimentally observed that the membrane potential reached the Donnan exclusion regime at a value of 12.5 mM concentration for the high concentration side of the membrane at a concentration ratio of 5 [21]. For this concentration (12.5 mM), the Debye layer value is approximately 2.7 nm which is very close to the pore radius predicted from the model. TEM images showed pore sizes on an average around 7 nm diameter which is reasonably close to the pore diameter obtained from the simulation (5.2 nm). The TEM images were taken with a different sample than the one which is used for our membrane potential measurements, but both of them are fabricated in identical conditions. The difference of pore size observed in the TEM image can be due to sample to sample variation which we also observed in our previous experimental results [21]. In addition, the TEM images may not always give the most accurate pore size as direct the visualisation of pore was challenging. Still, our model predicted values are in agreement with the experimentally observed pore sizes.

Figure 6.3 shows that the effect of the value of the Stern layer thickness is very minor for the resulting membrane potential. A larger Stern layer thickness (for example for Li^+ compared to Na^+) will shift the curve downwards. The Stern layer being larger means that a larger potential drop across the Stern layer will have to be accounted for, meaning the zeta-potential will be lower for the same surface potential compared to a surface with a smaller Stern layer thickness. This again means a lower potential in the center of the pore, leading to a lower selectivity of the membrane. This result would change slightly depending on the reference concentration for the Debye length used to compute the effective zeta potential but this would simply shift the curve. Including the Stern layer did yield an improvement in the ability to describe the experimental results.

Experimental data was finally fit to the simplified Gouy-Chapman-Stern model in a least-squares sense. The value of the effective Stern layer thickness of

Figure 6.3 — The effect of the Stern layer thickness on the resulting membrane potential according to the model.

potassium was found to be slightly lower (0.5 nm) than the value that was found by Brown et. al. (0.6 nm) but is quite consistent with the expected thickness of a Stern layer [27]. In Table 6.4, the fitted values of the surface potential, Stern layer thickness and pore radius are given (along with the effective pore radius, which is the fitted pore radius + Stern layer thickness). All values are physically consistent with plausible surfaces and given the fabrication procedure for the membranes used. However, given the simplicity of the model, parameters should not be interpreted as the precise physical conditions of our membranes.

Parameter	fitted value (95% confidence)
ϕ_s (mV)	-56 (-53.9 : -58.1)
λ_s (nm)	0.5 (0.45 : 0.56)
r_{pore} (nm)	2.1 (1.92 : 2.3)
$r_{pore,total}$ (nm)	2.6 (2.37 : 2.86)

Table 6.4 — fitted parameters

The agreement for the other salts was also good, as can be seen from Figure 6.4. All generated curves represent 2 nm pore radius with a surface potential of -60

Figure 6.4 — Model results compared to experimental results for 3 different salts. Markers show the experimental results and lines show our model results.

mV and a Stern layer thicknesses as given in Table 6.1. The parametric sensitivity analysis for the pore radius as done for KCl (Figure 6.2), can be found in the SI, Figure 6.14 and 6.15 for LiCl and K_2SO_4 respectively. This highlights that the parameter set determined is not specific to one salt but broadly applicable to the specific membranes used.

6.3.2 Selectivity of the membrane

We see that the membrane never reaches the ideal Nernst potential (see Figure 6.4), just as in our experimental investigations. This means that the system considered is not 100% selective towards cations. The main cause for this can be attributed to the insufficient surface potential of graphene to achieve the full Nernst potential, even for a 2 nm (2.6 nm including Stern layer) sized pore. The likely existence of a pore-size distribution or defects in graphene result in additional loss of selectivity due to reduced Debye layer overlap at higher concentrations. This can help to explain the (small) offset at higher concentrations.

In order to improve the selectivity of these membranes also at higher bulk

Figure 6.5 — Model results for high surface potentials.

concentration, the surface potential would need to be significantly higher. This could be achieved by gating the membrane, for which graphene could be very suitable as it is electrically conducting. There are some recent studies where the ion rejection has been tuned by applying an external bias on conducting membranes [28–34]. In a recent article, Wyss et. al (2019) have shown that the salt rejection factor is increased when the graphene membrane is externally biased [28]. Nishiwa et. al (1995) and Maartin et. al. (2001) have experimentally observed that gold coated track etched polycarbonate membranes can be made selective towards anions or cations depending on the externally applied electric field [33, 34]. In Figure 6.5, results from the model can be seen where higher surface potential were applied, excluding any Faradaic reactions. It can clearly be seen that the selectivity is increased and retained up to higher bulk concentrations. The effect of activity coefficients now becomes very relevant at these higher concentrations, so these were incorporated as well.

6.4 Conclusion

In this work, we present the results of numerical simulations regarding charge-selectivity in 2D nanoporous graphene membranes. A concentration dependent zeta-potential is needed in order to aptly describe the experimental data. A relatively simple description of the potential drop across the Stern layer describes the experimental data quite well. A sensitivity analysis was done to evaluate the effect of a constant surface potential, pore radius and Stern layer thickness. It was observed that a higher surface/zeta potential increases the selectivity, and a smaller pore radius retained this selectivity to a higher ion concentration. Cations with a larger Stern layer thickness will cause a larger potential drop over the Stern layer, which decreases the selectivity. Atomistic thin membranes, like nanoporous graphene, are unable to provide high selectivity when possessing realistic surface potentials in the pore size range studied here (> 1 nm). Our simulations indicate that one of the more promising methods for increasing the selectivity would be by increasing the potential of the membrane through biasing, for which graphene is a good candidate because of its high electron conductivity. For sub-nm pores, dielectric and size exclusion will become relevant as in the case of reverse osmosis membranes [35–37]. At higher surface potentials, such as those employed when gating a graphene membrane, the influence of activity coefficients should be accounted for. Our results shows that the previous discrepancy between the theoretical Nernst potential and our experimental measurements can be explained by this numerical framework, based only on nanometer pore sizes with realistic surface potentials.

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Supplementary Information

S1: Accounting for Activity coefficients in PNP

The PNP equation is derived from the fact that the flux is caused by a change in chemical potential of the species:

$$\mu = RT \log(c) + \frac{zF}{RT} \varphi \quad (6.7)$$

When accounting for the activities of ions the chemical potential becomes:

$$\mu = RT \log(c) + RT \log(\gamma) + \frac{zF}{RT} \varphi \quad (6.8)$$

$$\mu = RT \log(\gamma c) + \frac{zF}{RT} \varphi \quad (6.9)$$

The PNP equation describes a diffusive flux of species, which by definition is due to a difference in chemical potential. The system will want to go to an equilibrium state, where chemical potentials are equal (so the flux will become 0). This makes the standard PNP equation take the following form:

$$J_i = -c_i D_i \nabla \log(\gamma_i c_i) - \frac{z_i F}{RT} c_i D_i \nabla \varphi \quad (6.10)$$

$$J_i = -c_i D_i \nabla \log(c_i) - c_i D_i \nabla \log(\gamma_i) - \frac{z_i F}{RT} c_i D_i \nabla \varphi \quad (6.11)$$

$$J_i = -D_i \nabla c_i - c_i D_i \nabla \log(\gamma_i) - \frac{z_i F}{RT} c_i D_i \nabla \varphi \quad (6.12)$$

$$J_i = -D_i \nabla c_i - c_i D_i \nabla \log(\gamma_i) - \frac{z_i F}{RT} c_i D_i \nabla \varphi \quad (6.13)$$

$$J_i = -D_i \nabla c_i - c_i D_i \frac{z_i F}{RT} \nabla \left(\varphi + \frac{RT}{z_i F} \log(\gamma_i) \right) \quad (6.14)$$

S2: Boundary conditions schematic

Figure 6.6 — Schematic of the boundary conditions.

S3: Surface charge density and constant zeta potential models

In this section a short overview of different methods found in literature for describing surface charge and in particular concentration-dependent surface charge as well as constant surface charge are discussed. The surface charge density is correlated with an amount of charged groups on the surface. The results are shown in Figure 6.7 for fitting the data to a constant surface charge model. It is good to note that for these results the activity coefficients of individual ions

were not taken into account, however this effect is negligible at both low and high concentrations based on the results discussed in the main text.

In order to compare the model results to the experimental results least square fitting was done [21]. Different fitting parameters were chosen. First a constant surface charge density of the membrane at a fixed pore radius was tried, the result of which can be seen in Figure 6.7. The potentials plotted were made dimensionless by dividing by the ideal Nernst potential.

Figure 6.7 — Constant Surface Charge Fit of Membrane Potential for KCl.

In Figure 6.8, we fit the pore radius and a surface charge density (σ_s) simultaneously. From Figure 6.8, it is observed that the same results can be obtained from changing the pore radius and then fitting a different surface charge density. Pore radius and pore surface charge density are correlated in terms of their impact on the resulting membrane potential. This is also observed when using a concentration dependent surface charge. This fits the data better. It should be noted that there are some physical limits to membrane potential as well as the pore radius. From Figure 6.7, it can be seen that in order to get to a similar potential in the Donnan dominated regime a lower surface charge density is needed, since it overpredicts the potential. This however will lead to the whole curve shifting

down, greatly underpredicting the potentials in the intermediate concentration region (the diffusion dominated regime is neatly predicted most of the time). This could be caused by the fact that the surface charge density (or its apparent value) is not constant, for example due to adsorption of species. This highlights that a constant surface charge model is insufficient to describe the experimental system.

Figure 6.8 — Fit of model results to experimental data

Secchi et. al. proposed a relation of the surface charge density and the ion concentration in carbon nanotubes, which can be thought of as rolled-up graphene sheets [19]:

$$\sigma \propto c^{\frac{1}{3}} \quad (6.15)$$

$$\sigma = \sigma_1 \left(\frac{c_{low}}{c_0} \right)^{\frac{1}{3}} \quad (6.16)$$

This gave a fit which can be seen in Figure 6.9.

This scaling however was proposed to be due to adsorption of OH^- at the surface of the carbon nanotubes. However, the agreement of this model to our experimental data is also not as good as the Gouy-Chapman-Stern approach.

Figure 6.9 — Fit of model results to experimental data using hydroxyl adsorption power law scaling of the surface charge density

Another proposed scaling behaviour is discussed by Brown et. al. [38], which is not specific to graphene/carbon. They describe changes in surface charge density could be explained by changes in the thickness of the Stern layer with ion concentration due to an osmotic pressure difference. This could lead to a relation between the surface charge density and the concentration like:

$$\sigma = \sigma_0 + A \log(c) \quad (6.17)$$

Now we will have 2 unknown parameters: σ_0 and A . σ_0 is the surface charge density at a concentration of $c = 1$ and A is a scaling factor. This led to a fit which can be seen in Figure 6.10.

S3.1: Constant zeta potential

Figure 6.10 — Concentration-Dependent surface charge model[38].

Figure 6.11 — Using a constant zeta potential for different values of this imposed zeta potential.

Figure 6.12 — Using a constant zeta potential for different values of the pore radius.

From Figure 6.11 and Figure 6.12, it can be easily seen that even though the agreement of an imposed constant potential is better than an imposed constant surface charge density, it still does not describe the experimental result particularly well and the improvement observed previously for concentration-dependent surface charge indicates that a concentration-dependent zeta potential would likely lead to an improvement in the predictive power of the model.

Based on these model approaches, the advantages of the Gouy-Chapman-Stern order of magnitude estimation model are clear (minimal fitting parameters, simple implementation and connection to physical reality). For other membrane potentials measured with other salts, the parameters determined based on KCl data are used for prediction with other salts and very good agreement with experimental membrane potentials is achieved. The results for assuming 2 nm pore radii (without including a Stern layer) for different salts are shown in Figures 6.13 to 6.15. This again highlights that the parameter set determined is not specific to one salt but broadly applicable to the specific membranes used. As discussed in the main text, directly relating pore size and surface potential from

the model to the experimental system should be done with caution due to the simplicity of assuming a uniform pore-size distribution and the simplicity of the model geometry.

S4: Results of the model with Stern layer potential drop for all 3 salts

Figure 6.13 — Results for KCl.

Figure 6.14 — Results for LiCl.

Figure 6.15 — Results for K₂SO₄.

CHAPTER 7

Summary and Discussion

This thesis described research on a novel fabrication technique of nanoporous graphene on polymer support and ion transport through these two dimensional charge selective interfaces. Both experimental and theoretical studies of charge transport were conducted. Factors including electrolyte concentration, electrolyte species and pH have been investigated to understand their influence on the membrane potential and surface charge properties. The experimental and numerical results presented in this thesis have implications for research in the field of nanofluidics and ion transport processes as found in fuel cells and desalination. Our research provides insight in the ion transport characteristics through these ultra-thin materials [1].

7.1 Novel fabrication technique

We describe a new method of nanoporous graphene fabrication using swift heavy ion (SHI) beam irradiation [2]. A strong and flexible polymer support layer is used for robustness and better handling. In this way, the intrinsic defects are mostly covered by the underneath PET and thus do not take part in the transport. Only the purposely created nanopores by the ion beam are activated when the PET channels are created. In previously reported fabrication methods, the graphene is transferred on already track etched polymer membranes followed by ion beam irradiation [3–5]. In that case, there is a higher chance that intrinsic defects in the graphene are exposed compromising its function. Our fabrication method provides

pores aligned with underlying channels in the polymer support. This method provides flexibility of achieving the desired polymer channel width by optimising the etching time of the irradiated composite membrane without changing the size of the pores created in the graphene. Another advantage of this method concerns the PMMA layer covering the graphene protecting it from delamination. This fabrication method presents a key step towards large area graphene based membrane fabrication.

Further optimisation of the fabrication method is needed to improve control over the pore sizes and pore size distribution in these membranes. Despite the protecting PMMA layer, the etching solution can still reach the graphene through the etched PET pores. Controlling these methods can lead to a better coverage of graphene.

7.2 Transport of ions and membrane potential measurement

We investigate ion transport across a single-atom thin charge-selective interface. The ion selectivity of these 2D membranes are studied with respect to both monovalent and multivalent cations, by measuring the resulting potential between two different concentration electrolyte compartments separated by the nanoporous graphene. Our experimental findings remarkably showed that the total electrical potential across a single-layer graphene membrane can be described as a cation-selective layer using a modified version of the Teorell-Meyer-Sievers (TMS) relationship [6–9]. At low electrolyte concentrations, the potential enters into a Donnan regime where the potential shows a plateau vs. concentration at a fixed concentration ratio between compartments and this occurs due to Donnan exclusion of ions. The observed Donnan potential is lower than the theoretical Nernst potential. This is later explained by the low surface charge of the membrane which is not sufficient to provide full selectivity even at very low salt concentrations (Chapter 6). At high salt concentrations, the potential results due to the induced diffusion potential based on different ionic mobilities

of cation and anion. For single-layer graphene the diffusion coefficient ratios are consistent with the values in bulk solution which is not necessarily the case for conventional ion-exchange membranes. We found that the same regions of the TMS theory were observed for our single-atom thin membranes. We did find a significant sample to sample variation in our measurements which indicates that the membrane fabrication reproducibility is an issue possibly because of the pore size distribution and defects [1].

7.3 Understanding interaction of ions with graphene with bi-ionic potential measurements

Membrane potential measurements reveal distinct Donnan plateaus for different cations which can be explained by specific interaction of ions with the graphene surface. This is further investigated by conducting bi-ionic potential measurements which confirm and quantify the differences in the affinities of ions towards graphene. A bi-ionic potential arises when the membrane separates two electrolyte reservoirs at equal concentrations having identical co-ions but different counter ions [10, 11]. For salt pairs for which the experimental bi-ionic potential is the same as the theoretical value, the Donnan plateaus are found to be overlapping with each other. This implies that both the counter ions have similar affinity towards graphene. On the other hand, for the salt pairs which have different experimental and theoretical bi-ionic potentials, the Donnan plateaus are distinct. This indicates that those salts pairs interact differently with graphene.

Bivalent cations show around a 20% lower value of scaled Nernst potential compared to monovalent cations in the Donnan dominated regime. This is likely due to the ion adsorption on the graphene surface. These adsorbed ions decrease the membrane's surface charge and result in a lowering of the membrane potential for monovalent cations. The performance is restored by immersing the membrane in high concentration KCl solution. This is further confirmed by fitting the experimental data with the modified TMS model. The fitted value for the fixed

charge concentration is lower for bivalent cations compared to monovalent cations indicating a lower value of surface charge due to ion adsorption. Among bivalent cations, CuCl_2 shows a different trend in membrane potential experiment, as the entire curve seems to be shifted to a lower concentration likely due to higher adsorption of Cu^{2+} ions. The exact reason for this is still unclear and further investigation is needed in this field for better understanding of interaction of transitional metal ions with graphene surfaces.

7.4 Nature of surface charge with varying pH

In order to further study the nature of the surface charge groups, membrane potential during Donnan dialysis is measured at different pH values. The membrane potential decreases with decreasing pH and at pH 3 it changes its sign. This indicates that at high pH, the surface is negatively charged and with increase in pH protonation reduces the net negative surface charge rendering the membrane ultimately positively charged below pH 3. This change in membrane potential occurs only at low salt concentration measurements i.e. in the Donnan dominated regime. At high salt concentration, the potential is close to zero and independent of pH due to the screening of surface charge groups. Zeta potential values derived from streaming current measurements also show a similar trend with pH. The streaming potential data was fitted with the 1-pK model, resulting in a pK value of 4.2. The possible surface charge groups include carboxylic acid groups or adsorbed hydroxyl group. A validation of the surface charge groups needs further measurements, such as FTIR or titration measurements which is quite challenging for our existing samples as graphene is just single atomic layer supported by a thick PET substrate.

7.5 Reason behind low Donnan potential for graphene

In our measurements, we have observed that the Donnan potential never reaches the theoretical Nernst potential. We tried to explain this by using an additional term called non-ideality factor (α) in the TMS model. But it has to be noted that Graphene is a 2D material while the TMS model has been derived based on dense ion exchange membranes with much larger width. Another possible reason for the non-ideality is that graphene may not have sufficient charge to resist all the incoming co-ions and thereby resulting in lower membrane potential. Our simulation results, based on Nernst Planck and Poisson equations, suggest that the low selectivity of graphene is due to its low surface potential. For higher surface potentials, the membrane potential reached the ideal Nernst potential and α value close to 1 indicating 100% selectivity.

7.6 Future perspective

To elucidate the exact graphene morphology, including pore geometry and defects, direct imaging methods would be preferred. In our current system, the imaging was very difficult because of the thick background PET layer. The electrically insulating character of PET makes the TEM imaging difficult. One possible solution could be that before transferring the graphene on to PET support, the graphene can be transferred to a TEM grid followed by ion beam irradiation. This will certainly improve the direct imaging of graphene pores. We tried to image the graphene pores using atomic force microscopy (AFM) as well. We were able to identify the PET pores but could not detect the graphene pores separately. The type of irradiating ion and its energy strongly affects the pore geometry and should be studied further. Raman spectra analysis is a useful technique in estimating defect density in the graphene layer. However, the PET provided an intense background signal and the peaks partly overlap with those of graphene. Graphene, supported on substrates that do not have the peak at the same location as graphene (e.g. silicon) may be used for Raman spectroscopy measurement for

defect mapping. These measurements will provide a direct estimate of the pore sizes in graphene and their correlation with irradiating ion and energy.

The membrane potential measurements indicated a somewhat limited cation selectivity of the graphene membranes. The possible reasons include the low surface charge of graphene and larger defects in the graphene layer. Another aspect which was not further investigated in this thesis concerns the possible concentration polarization inside PET pores. An ion concentration gradient inside the pore in PET will lead to a lower concentration ratio of electrolyte across the graphene membranes. As the measurement electrodes are placed outside of this concentration polarization region, we believe that the membrane potential is correctly obtained. We ensured good mixing of electrolyte in each reservoir by continuously flowing the liquid with pump. A gradient in the pore of the support, however, will affect the near graphene ion concentration which can alter the graphene surface charge. In our measurements, we have also flipped the graphene membrane and measured the membrane potential and the value remained unaltered.

We have investigated the graphene surface charge by measuring the membrane potential at different pH. More direct and quantitative methods like pH titration and FTIR were not possible due to the atomistically thinness of the membrane. To identify these surface charge groups, MD simulations can be done. In these simulations surface charge species can be implemented and their interactions with the electrolyte can be investigated. Usually, for long range intermolecular interaction, LennardJones (LJ) potential is used and for short range interaction coulomb potential is implemented. For low concentration ionic systems, a non-polarizable potential energy function is used. Electrostatic charge interactions along with the non polar interactions can be included to describe the ionic interaction at the molecular level. Once the surface charge groups are identified, the changes in the structure and dynamics of the groups can be studied for varying pH [12–15].

In order to enhance the limited surface charge of these graphene membranes, their surface was functionalized with a positively charged polyelectrolyte (PDADMAC)

[16–18]. The graphene membrane was immersed in a solution of 1 g PDADMAC in 50 mM NaCl overnight. The membrane potential measured prior to this PDADMAC coating was 19 mV, which reversed to a value of -15 mV after PDADMAC coating. This result indicated that the surface charge of graphene can be adjusted by poly-electrolyte (PDADMAC) adsorption. To further explore in this area, it would be a very interesting to study the membrane potential vs. pH as well as the poly-electrolyte desorption process.

7.7 Results beyond explanation

7.7.1 Transport behaviour with an applied electric field

All the transport properties we have discussed so far, are due to the diffusion of ion in a concentration gradient. We also have, studied the transport of ions driven by an electric field [19–22]. We used a six compartment cell as shown in the Figure 7.1 [23, 24]. The outer chambers are separated by commercial cation exchange membranes (CMX, 99% permselective) and the middle one is separated by the graphene membrane. All inner 4 compartments have equal electrolyte concentrations. In this way electrode reactions are isolated from the measurement compartments. The electric field is applied through the working electrodes inside the outermost compartments, while salt bridge reference electrodes are used to measure the potential across the membrane. The outer electrode compartments (1,6) are filled with K_2SO_4 solutions. The two shielding compartments (2,5) use the same type of salt solution as the test solution in compartment 3 and 4 (KCl). All the compartments contain the same concentration of salt solution to eliminate any diffusive transport. We investigated the transport through graphene membrane samples irradiated with different fluences. For a fixed fluence (2×10^9 ions/cm²), we found that the ion transport resistivity decreases with increasing ion concentration (Figure 7.2). This is expected due to higher number of ions at high concentration.

Then we investigated the voltage (V) vs. current (I) relationship for samples

Figure 7.1 — Six compartment electro dialysis cell

Figure 7.2 — Voltage vs. current plot at different KCl concentrations for a sample irradiated with 2×10^9 ions/cm².

Figure 7.3 — Voltage vs. current plot using a fixed KCl concentration for samples irradiated with different fluence.

irradiated with difference fluences (2×10^9 , 1×10^9 , 5×10^8 ions/cm², Figure 7.3). We expected that membranes irradiated with a low fluence will have higher resistance whereas, ion irradiated with high fluence will have low resistance. We did not see any obvious trend in the V-I curves for these membranes. At a higher concentration (5 mM, Figure 7.4), the V-I data for all the fluences overlap. All the measurements with blank PET did not show any resistance which confirms that the resistance is due to the nanoporous graphene layer. Based on the used KCl concentrations, we expect still some selectivity. The expected resistivity difference for different fluence was however not observed. We have also conducted impedance measurements to gain information about the capacitive double layer and resistivity of the membrane. Similar to the DC measurements, the results were inconclusive. The most important factor which we could not explain concerned the potential offset at zero current, sometimes up to tens of millivolts. All the compartments have equal concentration, so local concentration differences could be caused by salts from the salt bridge reference electrodes (containing 2 M KCl).

Figure 7.4 — Voltage vs. current plot at different KCl concentrations for a sample irradiated with 2×10^9 ions/cm².

Possibly, this type of six compartment set up with salt bridge electrodes was not suitable for measuring at such low concentrations.

For transport studies with an applied electric field, an alternative of salt bridge electrode is suggested. Maybe a platinum wire can be a better reference electrode for such low concentration measurements. Another possible reason is that the different fluences did not result in significantly different porosities.

7.7.2 Bi-layer, Tri-layer graphene

Would the ion transport be affected by the addition of more layers in the graphene/PET composite structure [25, 26]? We expected that with an increase in the graphene layers the membrane potential will reach a value closer to the Nernst potential. The samples we received were irradiated at the accelerator facility at Darmstadt, Germany. All samples were irradiated with 5×10^8 ions/cm² at 8.6 MeV/u Au ions. The samples showed faster etching of PET and very low

membrane potential (5% of the Nernst potential) for monolayer graphene. Bi and tri layer graphene samples showed somewhat higher potential than the monolayer but still only around 23% of the Nernst potential. Another batch of samples was irradiated at GANIL, France. Those samples suffered from the delamination of tri-layer graphene during the etching process. So further measurements could not be conducted.

7.7.3 Biasing graphene with an external potential

In our membrane potential measurements, one of the important observations is the low Donnan potential plateau compared to the theoretical Nernst potential. In Chapter 6, we have shown that this is due to the low surface potential of graphene which is a representative of the surface charge density of graphene. To attempt to increase the surface potential of graphene, we applied an external bias on graphene [27–30]. For this, we attached a copper electrode directly on the graphene and applied a positive or negative bias with respect to the low concentration reservoir that was grounded while measuring the membrane potential. We covered the top of the copper surface with a kapton tape which was in contact with the electrolyte solution in order to limit any electrode reactions.

When applying a negative bias, the membrane potential increased from its initial potential of ~ 25 mV (0 mV bias) to ~ 45 mV at -300 mV bias and around 0 mV at 300 mV bias (Figure 7.5). This showed that with increase in the external potential, the rejection mechanism can be improved. Though we are still not sure why the potential at -300 mV was more than the Nernst potential. Though we observed overall a similar trend in membrane potential vs. bias voltage data, the membrane potential results seems to differ a lot between membranes. It is important to note that we have not observed any change in the membrane potential for bare PET indicating the effect is only present for graphene.

This study is definitely a direct evidence that the membrane selectivity can be tuned with external bias. Though, we need more thorough measurements in this direction to understand what is exactly happening at the surface and why we see higher value of than the Nernst potential at the highest negative bias applied in

Figure 7.5 — Voltage vs. current plot at different KCl concentrations for a sample irradiated with 1×10^7 ions/cm².

our case.

7.8 Outlook

This thesis investigates ion transport through the nanopores of graphene with different external factors. The results have potential implications in biosensing application and DNA translocation [31–33]. So far, the DNA sequencing and translocation are dependent on biological and solid state nanopores [34–36]. The major drawback of biological nanopores is that these are mechanically unstable and are sensitive to ambient condition like pH, temperature and concentration. Depending on the variation of these external factors, the pores may open or close affecting the signal of ionic current. Chemical or geometrical modification of these materials is difficult, providing little control on these systems. In the case of solid state nanopores (e.g. Si_3N_4), a better control over the pore size and chemical

composition can be achieved. 2D nanoporous graphene can be advantageous because of its chemical and mechanical stability. Pore sizes from nm to sub-nm ranges can be created and chemically modified. We can vary the concentration and pH to tune its selectivity. A great advantage of this material is that it is electrically conducting. This provides the opportunity to externally bias the material and then tune the ion selectivity towards cations or anions [27–30, 37–39]. Nishiwa et. al (1995) and Maartin et. al. (2001) have experimentally showed similar effect in externally biased metal (polycarbonate nano channels coated with gold) [38, 39]. Also, the application of external bias on graphene, gives a control over the translocation of DNA as predicted by the MD simulation of Shankala et. al. They have shown that the transport of DNA molecules can be controlled by applying an external bias on graphene [30]. Their simulations showed that a positive surface charge on graphene can accelerate the DNA motion. Whereas a negative surface charge captures it. Our preliminary experiments show similar tunable selectivity of nanoporous graphene. There is an increasing demand of miniaturisation of devices in medical purposes. Sweat of human body contains different ions which can provide some early detection of diseases. A wearable sweat sensor made by graphene can be used because of its capability of being flexible, small and stable. Actual applications of these preliminary ideas evidently need further studies, for which this thesis serves as a good basis.

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Summary

Nanofluidics and controlled ion transport through two dimensional (2D) membranes is an emerging field as new technological opportunities such as ionic diode, nanopore base DNA squenching can be explored with these materials. Graphene is one of such 2D materials which has shown promising characteristics towards a possible technological breakthrough specially for smaller devices. Nanoporous graphene membranes have been fabricated using different methods by different groups and the ion transport properties through them has been investigated. Still there is a lack of understanding of interaction of ions with the nanopores and the control over the ion transport. We have tested the influence of external factors such as concentration, pH, ion type on the transport behaviour of ions through nanoporous graphene and explained our experimental observations using well established models with some modifications.

Chapter 1 describes the general ion transport mechanism through dense ion exchange membranes and the theory describing different exclusion mechanisms. We have mainly focused on the electrostatic exclusion phenomena of ion exchange membrane and have shown the origin and derivation of the mathematical formula explaining the ion transport phenomena. As our work focuses on two dimensional graphene, existing studies related to our investigation have been discussed in details in this chapter which also guides the reader to basic motivation behind our work.

In **Chapter 2**, we have discussed the fabrication method. We have created nanopores in graphene ($1 \times 1 \text{ cm}^2$ area) supported on a PET foil (3 cm diameter, 13 μm thickness) by heavy ion beam irradiation. This is done in the low energy irradiation facility at GANIL, France. Chemical etching is done to create cylindrical pores in PET tracks underneath graphene, created by ion beam irradiation.

The cylindrical pores are tapered towards the graphene covered area which is visualised by SEM. We also use TEM to visualize the graphene pore size which is around 7 nm. This graphene/PET composite membrane is used to study ion transport through the nanopores.

To study the ion transport, membrane potential experiments are carried out which is discussed in **Chapter 3**. Ion transport is initiated by creating a concentration difference of an electrolyte on both sides of the membrane. We have used three different salts with monovalent cations, KCl, K₂SO₄, LiCl. The membrane potential measurements indicate that the membrane is selective towards cations and the selectivity can be varied with the concentration of the electrolyte. We observe clear Donnan and diffusion plateaus at low and high concentrations, respectively which are explained by Teorell-Meyer-Sievers (TMS) theory. A factor α is multiplied with the Donnan potential term in the TMS theory to take in to account the non ideality of the membrane as the Donnan plateau does not reach the ideal Nernst potential. Three parameters fitted in our model are fixed ion concentration ($\bar{C}_R$), ratio of diffusivities of anion to cation ($\bar{u}_-/\bar{u}_+$) and the non ideality factor (α). The experimental data are in good agreement with the modified TMS model. Experimentally, we also find that the high concentration electrolyte side of the membrane determines the transition from Donnan to diffusion regime. The transition happens at lower concentration with higher concentration ratio. From our model, we have understood that there can be a sample to sample variation. The fitted model shows different value of $\bar{C}_R$ for different membranes fabricated in identical conditions. This implies that different amount of fixed charge groups are introduced to the membrane along with variation in pore size distributions.

In **Chapter 4** we extend our investigations to bivalent cations. For bivalent cations (Mg⁺⁺, Ca⁺⁺, Cu⁺⁺), the scaled membrane potential with respect to the Nernst potential is found to be even lower (50%) compared to the monovalent cation case (70%). This is experimentally verified to be due to the bivalent ion getting adsorbed on to the surface. For Mg⁺⁺, Ca⁺⁺ case, the fitted value of fixed ion concentration ($\bar{C}_R$) is found to be lower compared to the monovalent case indicating lower effective surface charge for bivalent case. For CuCl₂, the

$\bar{C}_R$ is expected to be even smaller as the entire potential curve is shifted to a lower concentration. The fitting can not be done in this case because of not having the Donnan potential plateau. In this chapter, we have also investigated the reason of distinct Donnan plateaus for some salts such as KCl, K_2SO_4 , LiCl. Bi-ionic potential measurement is conducted where two different salts having the same co-ions and the same concentration are placed on both sides of the membrane. Comparing the experimental bi-ionic potential to the theoretical potential selectivity factor is calculated which indicates the different or similar affinity of cations towards the membrane. For an example, for KCl/LiCl salt pair, the calculated selectivity factor is 0.86. The factor being different than 1 indicates different affinity of K^+ and Li^+ ions towards graphene resulting in two distinct Donnan plateaus. We also show that the calculated selectivity factor is close to the ratios of α values (0.84) obtained from Chapter 3. This observation is consistent with our other salt pairs. Those salt pairs for which the Donnan plateaus are overlapping (KCl/ NH_4Cl , $MgCl_2/CaCl_2$), the selectivity factor as well as the α ratios are found to be close to 1 indicating similar affinity towards graphene.

How the membrane potential is influenced by the pH of the solution is investigated in **Chapter 5**. This give us an indication of the nature of the surface charge groups in graphene and how they can be tuned with external pH. At high pH range (7-10), the membrane potential is high. With decrease in pH the membrane potential decreases and the membrane remain cation selective up to pH 4. At pH 3, the membrane potential reverses its sign indicating the inversion of the sign of the surface charge in graphene. This result is consistent with streaming potential measurements where the extracted surface charge remains constant and negative up to a value of pH 7. Below that pH, surface charge decreases and reverses its sign at low pH. The streaming potential data is fitted with 1-pK model resulting a pK value 4.2. Though this pK 4.2 corresponds to carboxylic acid group but do not explain the positive value of surface charge at lower pH. Another possibility is hydroxyl ion adsorption which is also established in other literature. These are discussed in chapter 5.

We have done numerical simulation to describe our experimental results obtained from membrane potential measurements. In chapter 1 we have observed that membrane potential never reaches the ideal Nernst potential even at the lowest concentration due to some nonidealities present in the membrane. **Chapter 6** provides an indication of what is possibly the reason of this non-ideality. The experimental data is well described by considering a concentration dependent zeta potential in our numerical simulations. We observe that a higher surface/zeta potential lead to a higher selectivity. A monolayer graphene does not have sufficient surface potential to resist all the co-ions and thereby can not reach ideal Nernst potential. The effect of pore radius and the stern layer is also studied. A pore size of around 5.2 nm describes the experimental data pretty well. The selectivity also depends on the stern layer thickness. A larger drop in stern layer results in lower selectivity of graphene.

The final chapter (**Chapter 7**) presents a reflection of the research that is presented in this thesis. In this chapter we have also described some ideas and experiments which did not work or could not be explained but have potential ability for further research in this field. In this chapter we have shown that by externally biasing graphene we can tune its selectivity which is predicted by our numerical simulations in chapter 6. This chapter also includes an outlook on the possible application with these materials which needs an in depth research in this field.

Samenvatting

Nanofluidica en gecontroleerd ionentransport door tweedimensionale (2D) membranen is een opkomend veld, aangezien nieuwe technologische mogelijkheden met deze materialen onderzocht worden, zoals ionische diode en DNA sequentie door nanoporiën. Grafeen is zo'n 2D-materiaal dat veelbelovende kenmerken heeft getoond voor een potentiële technologische doorbraak, vooral voor kleinere apparaten. Nanoporeuze grafeenmembranen zijn geproduceerd door verschillende groepen met behulp van verschillende methoden en de eigenschappen van het ionentransport er doorheen zijn onderzocht. Toch is er een gebrek aan begrip van de interactie van ionen met de nanoporiën en de controle over ionentransport. We testten de invloed van externe factoren op het transportgedrag van ionen door nanoporeus grafeen zoals concentratie, pH en ion-type en probeerden onze experimentele waarnemingen te verklaren.

Hoofdstuk 1 beschrijft het algemene ionentransportmechanisme door middel van dichte ionenuitwisselingsmembranen en de theorie die verschillende uitsluitingsmechanismen beschrijft. We hebben ons voornamelijk gericht op de elektrostatische uitsluitingsverschijnselen van een ionenuitwisselingsmembraan. De oorsprong en afleiding is beschreven van een wiskundige vergelijking die de ionentransportverschijnselen verklaart. Bestaande studies die verband houden met ons onderzoek worden in detail besproken, waaruit de basismotivatie voor ons werk leidt.

In **hoofdstuk 2** wordt de fabricagemethode besproken van het composietmembraan. Grafeen ($1 \times 1 \text{ cm}^2$ area) wordt ondersteund door een PET-folie (3 cm diameter, 13 μm dikte) en de nanoporiën in grafeen worden gecreëerd door bestraling met zware ionenbundels. De bestraling wordt gedaan in een energiezuinige installatie in GANIL, Frankrijk. De PET blijft ongedeerd tijdens de bestraling,

waardoor poriën in de PET chemisch geëtsd moeten worden. Het chemisch etsen creëert conische poriën die taps toelopen naar het grafeen bedekte gebied. SEM en TEM worden gebruikt voor visualisatie en om de poriegrootte te bepalen. De poriegrootte is rond de 7 nm. Dit composietmembraan van grafeen / PET wordt gebruikt om ionentransport door de nanoporiën te bestuderen.

Het ionentransport wordt experimenteel bestudeerd door het membraanpotentiaal te meten in **hoofdstuk 3**. Ionen transport wordt geïnitieerd door aan beide zijden van het membraan een concentratieverschil in een elektrolyt te creëren. We hebben drie verschillende zouten gebruikt met monovalente kationen, KCl, K₂SO₄, LiCl. De membraanpotentiaal metingen geven aan dat het membraan selectief is voor kationen en dat de selectiviteit kan worden gevarieerd met de concentratie van het elektrolyt. We zien duidelijke Donnan- en diffusieplateaus bij lage en hoge concentraties, die worden verklaard door de Teorell-Meyer-Sievers (TMS) theorie. De Donnan-potentiaal wordt vermenigvuldigd met een factor α in de TMS-theorie om rekening te houden met de non-idealiteit van het membraan, aangezien het Donnan-plateau niet het ideale Nernst-potentieel bereikt. Drie fit parameters worden gebruikt in ons model, de vaste ionenconcentratie ($\bar{C}_R$), verhouding in diffusiviteit van anion en kation ($\bar{u}_-/\bar{u}_+$) en de non-idealiteitsfactor (α). De experimentele gegevens stemmen goed overeen met het gemodificeerde TMS-model. Experimenteel vinden we ook dat de membraanzijde met hoge concentratie elektrolyt de overgang van Donnan naar diffusieregime bepaalt. Deze overgang vindt plaats bij een lagere concentratie met hogere concentratie ratio tussen de membraanzijdes. Uit ons model hebben we begrepen dat er een monster tot monster variatie is. Het gedetailleerde model toont verschillende waarden van $\bar{C}_R$ voor verschillende membranen die onder identieke omstandigheden zijn vervaardigd. Dit impliceert dat verschillende hoeveelheden vaste ladingsgroepen in het membraan worden geïntroduceerd samen met variatie in poriegrootteverdelingen.

In **hoofdstuk 4** breiden we ons onderzoek uit naar bivalente kationen. Voor bivalente kationen (Mg⁺⁺, Ca⁺⁺, Cu⁺⁺), blijkt het geschaalde membraanpotentiaal ten opzichte van het Nernst-potentieel nog lager te zijn (50%) vergeleken met het monovalente kationen (70%). Dit is experimenteel geverifieerd doordat

het bivalente ion geadsorbeerd wordt aan het oppervlak. De aangepaste waarde van de gefixeerde ionenconcentratie ($\bar{C}_R$) blijkt lager te zijn voor Mg^{++} en Ca^{++} in vergelijking met het monovalente ionen, wat wijst op een lagere effectieve oppervlaktelading voor bivalente ionen. Voor CuCl_2 wordt verwacht dat de CR nog kleiner zal zijn naarmate de gehele potentiële curve wordt verschoven naar een lagere concentratie. De modelfitting kan in dit geval niet worden gedaan omdat er geen Donnan-potentiaalplateau is. In dit hoofdstuk hebben we ook de reden onderzocht voor verschillende Donnan-plateaus van sommige zouten zoals KCl , K_2SO_4 , LiCl door middel van bi-ionische potentiaalmetingen. Bij bi-ionische potentiaalmeting worden twee verschillende zouten met dezelfde co-ionen en dezelfde concentratie aan beide zijden van het membraan worden geplaatst. De experimentele bi-ionische potentiaal wordt vergeleken met de theoretische potentiële selectiviteitsfactor, wat de verschillen of overeenkomsten in affiniteit van kationen voor het membraan aangeeft. Bijvoorbeeld, van een KCl/LiCl zoutpaar is de berekende selectiviteitsfactor 0.86. De factor die anders is dan 1 duidt op een verschillende affiniteit van K^+ en Li^+ -ionen voor grafeen, wat resulteert in twee verschillende Donnan-plateaus. We laten ook zien dat de berekende selectiviteitsfactor dicht bij de verhoudingen van α waarden (0.84) uit Hoofdstuk 3 ligt. Deze waarneming komt overeen met de andere zoutparen. De selectiviteitsfactor en de α verhoudingen liggen dicht bij 1 voor de zoutparen waarvoor de Donnan-plateaus elkaar overlappen ($\text{KCl}/\text{NH}_4\text{Cl}$, $\text{MgCl}_2/\text{CaCl}_2$), wat wijst op een vergelijkbare affiniteit voor grafeen.

De invloed van pH op het membraanpotentiaal is onderzocht in **hoofdstuk 5**. Dit geeft ons een indicatie van de invloed op de oppervlaktelading van de groepen op grafeen en hoe de oppervlaktelading afgestemd kan worden door een externe pH. Het membraanpotentiaal is hoog voor hoge pH (7-10) en neemt af vanaf pH 7. Het membraan blijft kation selectief tot pH 4, bij lagere pH verandert het symbool van de oppervlaktelading van grafeen. Dit resultaat is consistent met stromingspotentiaalmetingen, waarbij een constante negatieve oppervlaktelading is gemeten tot een pH van 7. Bij lagere pH neemt de oppervlaktelading af en wordt uiteindelijk positief. De stromingspotentiaal data is gefit met een 1-pK

model, resulterend in een pK waarde van 4.2. Een pK van 4.2 komt overeen met een carbonzuur groep, en verklaart niet de positieve oppervlaktelading bij lage pH. Literatuur noemt een geadsorbeerd hydroxyl-ion als mogelijke verklaring. Dit wordt besproken in hoofdstuk 5.

We hebben numerieke simulaties gedaan om onze membraanpotentiaal resultaten te beschrijven. In hoofdstuk 1 hebben we gezien dat membraanpotentiaal nooit het ideale Nernst-potentieel bereikt, vanwege enkele non-idealiteiten die in het membraan aanwezig zijn. **Hoofdstuk 6** geeft een indicatie van wat mogelijk de reden is van deze non-idealiteit. De experimentele gegevens zijn goed beschreven door een concentratie afhankelijke zeta-potentiaal te beschouwen in onze numerieke simulaties. We zien dat een hogere oppervlakte / zeta-potentiaal leidt tot een hogere selectiviteit. Een monolaag grafeen heeft niet voldoende oppervlaktepotentiaal om alle co-ionen te weerstaan en kan daardoor niet het ideale Nernst-potentieel bereiken. Het effect van de porie-radius en Stern-laag is tevens onderzocht. Een poriegrootte van ongeveer 5,2 nm beschrijft de experimentele gegevens redelijk goed. De selectiviteit hangt ook af van de dikte van de Stern-laag. Een grotere daling van de Stern-laag resulteert in een lagere selectiviteit van grafeen.

Het laatste hoofdstuk (**hoofdstuk 7**) geeft een overdenking van het onderzoek dat in dit proefschrift wordt gepresenteerd. In dit hoofdstuk hebben we ook enkele ideeën en experimenten beschreven die niet werkten of niet konden worden uitgelegd, maar die wel potentieel hebben voor verder onderzoek op dit gebied. In dit hoofdstuk hebben we laten zien dat we, door grafeen extern te beïnvloeden, de selectiviteit ervan kunnen afstemmen die wordt voorspeld door onze numerieke simulaties in hoofdstuk 6. Dit hoofdstuk bevat ook een blik op de mogelijke toepassing met deze materialen, die een diepgaand onderzoek op dit gebied vereist.

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About the author

Mandakranta Ghosh (Dona) was born on 11th August, 1985 in Malda district, West Bengal, India. She first did her Master's in physics (M.Sc) and then Master's in solid state technology (M.Tech) from Indian Institute of Technology, Madras (IITM). In between she also worked as a physics teacher in a higher secondary school. Her M.Tech thesis was on studying the optical property of confined water trapped between graphene oxide layers with spectroscopic ellipsometry. After her M.Tech she moved to Warsaw, Poland and worked as a researcher in Institute of Polish Academy of Science and worked on molecular beam epitaxy (MBE) growth of wide band gap semiconductors. In 2016 she was employed by NWO-I formerly known as FOM as a junior scientist and started her PhD at the University of Twente in Soft matter Fluidics and Interfaces group. Her PhD work was a part of NUTEGRAM project in which she collaborated with the project partners from Germany, France and Croatia. Her research interest was studying ion transport through nanoporous graphene membranes. Her work was supervised by Prof. Rob Lammertink and Dr. Jeffery Wood. She presented her work in a number of national and international conferences. She also acted as a secretary of Indian Students Association of University of Twente between 2017 and 2018.

Scientific output

List of publications

- **2020:** J.B.Roman, **M.Ghosh**, R.G.H Lammertink and J. A. Wood, Investigating Charge-Selectivity of 2D Nanoporous Graphene using the Poisson-Nernst-Planck Model. (Manuscript ready for submission)
- **2020:** **M.Ghosh**, M.A. Junker, R.T.M van Lent, L Madauß, M. Schleberger, H. Lebius, A. Benyagoub, J.A. Wood and R.G.H. Lammertink, Charge Regulation in Nanoporous 2D interface (submitted)
- **2020:** **M.Ghosh**, L. Madauß, M. Schleberger, H. Lebius, A. Benyagoub, J.A. Wood and R.G.H. Lammertink, Understanding Mono and Bivalent Ion Selectivity of Nanoporous Graphene using Ionic and Bi-Ionic Potential, *Langmuir* (2020), 36, 7400-7407
- **2018:** **M.Ghosh**, K.F.A. Jorissen, J.A. Wood and R.G.H. Lammertink, Ion transport through perforated graphene, *Journal of Physical Chemistry Letters* (2018), 9, 6339-6344
- **2017:** L. Madauß, J. Schumacher, **M. Ghosh**, O. Ochedowski, J. Meyer, H. Lebius, B. Ban-đ Etat, M. E. Toimil-Molares, C. Trautmann, R.G.H. Lammertink, M. Ulbricht and M. Schleberger, Fabrication of nanoporous graphene/polymer composite membranes, *Nanoscale*, 9, 10487-10493
- **2015:** **M.Ghosh**, L. Pradipkanti, V. Rai, D. K. Satapathy, P. Vayalamkuzhi and M. Jaiswal Confined water layers in graphene oxide probed with spectroscopic ellipsometry, *Applied physics letters*, 106, 241902

Conferences, Talks, Posters

2019

- **North American Membrane Society (NAMS), Pittsburgh, USA**
Oral presentation, *Ion Transport through Perforated Nanoporous Graphene*.
- **International Symposium on Electrokinetics (ELKIN), MIT, USA**
Pitch and Poster, *Study of Ion Transport through A Two-Dimensional Porous Charged Interface*
- **NUTEGRAM meeting, Dubrovnik, Croatia**
Oral presentation, *Ion Transport through a Perforated Graphene Membrane*
- **MESA+ day, University of Twente, Enschede, The Netherlands**
Poster, *Ion Transport through Nano-porous One-atom Thin Membrane*

2018

- **Euro membrane, Valencia, Spain**
Oral presentation, *Ion Transport through a One-Atom Thick Membrane*
- **NUTEGRAM meeting, UTwente, Enschede, The Netherlands**
Oral presentation, *Ion Transport through a Perforated Graphene Membrane*
- **Network Young Membrane (NYM), Valencia, Spain**
Oral presentation, *Study of Transport of Ions through A Nanoporous Graphene Membrane*
- **MESA+ day, University of Twente, Enschede, The Netherlands**
Poster, *Ion Transport through Nano-porous One-atom Thin Membrane*
- **Physics Veldhoven, The Netherlands**
Poster, *Ion Transport through Nano-porous One-atom Thick Membranes*

2017

- **Physics for impact, Wetsus, Leeuwarden, The Netherlands**
Invited talk, *Spectroscopic Ellipsometry Study of Graphene Oxide*
- **NUTEGRAM meeting, GANIL, Caen, France**
Oral presentation, *Ion Transport through a Perforated Graphene Membrane*
- **MESA+ day, University of Twente, Enschede, The Netherlands**

Poster, *Ion Transport through Nano-porous One-atom Thick Membranes*

- **Winter School (UTwente and RTWH Aachen University), Austria**

Pitch, *Graphene Membranes for Desalination*