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MOLECULAR DYNAMICS SIMULATION OF GRAPHENE-
BASED THIN FILMS FOR SEAWATER DESALINATION

MOLECULAR DYNAMICS SIMULATION OF GRAPHENE- BASED THIN FILMS FOR SEAWATER DESALINATION

MADHAVI DAHANAYAKA

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**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute
Environment Process Modelling Centre**

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2020

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Associate Professor Kun Zhou

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Authorship Attribution Statement

This thesis contains material from three papers published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 3 is published as M. Dahanayaka, B. Liu, Z. Hu, Z. Chen, A. W.-K. Law and K. Zhou (2017). "Corrugated graphene layers for seawater desalination using capacitive deionization." *Physical Chemistry Chemical Physics*, 19(12): 8552-8562.

The contributions of the co-authors are as follows:

- Associate Professor Zhou proposed the research idea, supervised the research and revised the manuscript.
- I performed the simulation work, analysed the simulation results and drafted the manuscript.
- Dr. Liu provided simulation support and revised the manuscript.
- Associate Professor Law, Professor Chen and Dr. Hu contributed to the revision of the manuscript.

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- Dr. Hu provided simulation support and revised the manuscript.
- Associate Professor Law, Professor Chen, Dr. Liu and Dr. Pei contributed to the revision of the manuscript.

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The contributions of the co-authors are as follows:

- Associate Professor Zhou proposed the research idea, supervised the research and revised the manuscript.
- I performed the simulation work, analysed the simulation results and drafted the manuscript.
- Dr. Babicheva performed the density functional theory calculation, provided simulation support and revised the manuscript.
- Associate Professor Wu, Associate Professor Law and Professor Chen contributed to the revision of the manuscript.

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Abstract

Since 71% of the earth's surface is covered by the sea, seawater desalination plays a pivotal role in addressing the water crisis. Membrane separation technologies, including reverse osmosis, electrodialysis, forward osmosis, pervaporation and membrane capacitive deionization, have been the recent focus for many research studies because of their simplicity and relatively low energy cost in comparison to the thermal driven distillation processes. Nanotechnology has opened a window for researching new nanomaterials which enhance desalination performance in an economical and sustainable manner. Experimental synthesis of nanomaterials with optimized desalination performance is a trial and error process, requiring considerable resources and time. Molecular dynamics (MD) simulation is an efficient method in investigating the transport behaviours at the nanoscale and thus provides a powerful tool for the design and performance analysis of graphene (GE)-based thin films. This Ph.D. thesis research aims to investigate the seawater desalination performance in capacitive deionization, FO, electronanofiltration and PV systems by adopting four GE-based nanostructures, namely, corrugated GE layers, stacked GE sheets, ionized graphene oxide (GO) layers and GO/metal organic framework (MOF) nanocomposite, via MD simulation.

The surface corrugation of GE can modify its electronic, optical, mechanical and chemical properties. The seawater desalination performance through the corrugated GE nanochannel via capacitive deionization process is studied. The simulation results reveal that the corrugation of GE sheets greatly enhances the ion adsorption capacity, while adversely affecting the water flow rate in a capacitive deionization system. The strong anchoring effect existing in the regions which are bounded by crests and troughs of the upper and lower GE layers, respectively is identified to be responsible for the enhanced

ion removal capacity. Moreover, desalination performance of such a system depends on the entrance configuration with its entrance effect becoming more significant at a higher electric field intensity.

The stacked GE membrane performance greatly depends on the membrane structural parameters such as pore size (i.e., nanoslit width), pore offset, interlayer distance and number of GE layers. The complete rejection of ions is observed in the bilayer GE laminates, as a forward osmosis membrane, for the nanoslit widths less than 9 Å. The bilayer GE membrane can accomplish a complete ion rejection and maintain a higher water flux even at a nanoslit width larger than 9 Å, when an optimum interlayer distance of 8 Å and a completely misaligned pore configurations are adopted. Overall, the GE membranes in a forward osmosis system yield a low water flux but an enhanced ion retention capability in comparison to the GE membranes in a reverse osmosis system.

Ionization of the functional groups such as the carboxylic acid of a GO sheet introduces a negative charge on the membrane surface and the desalination performance through such a membrane is investigated. The ionized GO membrane is selective for both Na^+ and Cl^- ions for nanocapillaries much larger (10 Å) than the maximum pore size of 7 Å, which allows 100% solute rejection in the reverse osmosis system. These ionized GO sheets can be effectively used for seawater desalination under the effect of an external electric field applied in the direction opposite to the water flow.

GO as a pervaporation desalination membrane demonstrates a low water permeability. To enhance their water permeability, GO sheets can be combined with the hydrophilic HKUST-1 MOF structure. Meanwhile, HKUST-1 has a low structural stability in water which can be improved through the combination with GO. The desalination performance of the GO/HKUST-1 nanocomposite is explored. The nanocomposite membranes demonstrate excellent water flux higher than that of ZIF-8

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The findings in this Ph.D. research advance the understanding of ion separation mechanisms through GE-based nanostructures and provide guidance on the experimental synthesis of GE-based thin films for seawater desalination.

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Chapter 1. Introduction

Seawater desalination is one of the leading solutions for the scarcity of fresh water. Semi-permeable membranes which are capable of removing solute ions from water have been the center of many desalination technologies. Separation performance of those membranes which are usually made of polymers is suffered from the trade-off between the membrane flux and ion separation, high swelling, and low mechanical stability. Recently, graphene (GE), because of its excellent mechanical and chemical properties, has been extensively studied as a desalination membrane. This has raised the importance of understanding the water and ions transport mechanisms through the GE-based thin films as the fluid confined in nanochannels undergoes a dramatic change due to the close contact with the channel walls. This chapter introduces the background of seawater desalination and GE-based separation membranes. Furthermore, the motivations and objectives of this dissertation are presented along with its outline.

1.1 Background

Water is the most abundant substance and one of the essential elements for all living beings on the earth where a little amount is available for human consumption. Presently, three billion people around the world have no access to clean drinking water [1]. Water requirements are mainly fulfilled through the surface water (resources such as rivers and lakes) and groundwater, are distributed heterogeneously across the world. Most of these water sources are either polluted or are facing the challenge of getting contaminated with effluents from industries, sewage treatment facilities, and pollutants from anthropogenic activities and natural origin [2, 3]. Moreover, the hydrological cycle is affected by climate change which exacerbates the water scarcity. As a result, a balance between the

burgeoning demand and the finite resources needs to be restored to face the alarming global water crisis. Since 71% of the earth's surface is covered by the sea, seawater desalination plays a major role in addressing the water crisis.

According to the World Health Organization, the permissible salinity level of water is 500 ppm [4]. Seawater salinity level falls in the range of 35000–45000 ppm in the form of total dissolved salts [4] and thus desalination process requires a significant amount of energy to remove salts and minerals from water. Theoretically, a minimum energy of 0.7 kWh/m³ [5] is required to obtain pure water from seawater, whereas energy in the range of 2–5 kWh/m³ is used in existing desalination facilities [6]. There are three types of technologies, namely, (1) thermal driven (2) membrane separation and (3) chemical separation available for seawater desalination [7, 8]. Energy consumption, feed quality, environmental and technological compatibility, and economic feasibility are key factors that determine the viability of a desalination method.

Thermal desalination methods, such as multi-stage flash distillation (MSFD), multi-effect distillation (MED), membrane distillation and thermal vapor pressure compression (TVC), are generally energy intensive because they are based on the water evaporation and subsequently the condensation of water vapor [9-11]. Membrane separation is a filtration process in which feed water is forced through a membrane by applying a driving force in terms of pressure or concentration to overcome the osmotic pressure in seawater. Reverse osmosis (RO) electrodialysis (ED), membrane capacitive deionization (MCDI), pervaporation (PV) and forward osmosis (FO) are few examples for membrane separation. Ion exchange and liquid-liquid extraction are commonly adopted in chemical separation techniques. Besides, hybrid processes, involving phase change and separation techniques, such as membrane distillation, FO-membrane distillation and RO-MSFD, are

claimed to be energy efficient, quality relevant and waste valorizing tool in the context of sustainability in seawater desalination [8, 12-14].

RO has been the leading technology in the market for water desalination because of its simplicity and relatively low energy cost in comparison to the thermally driven distillation processes. Generally, a high pressure of 8 MPa is essential in RO to overcome the osmotic pressure of seawater (i.e., about 2.5 MPa) [6]. In RO, separation relies on a semi-permeable membrane that allows transport of water molecules through it while restricting permeation of ions. Mathematically, water flux through a membrane is inversely proportional to the membrane thickness. Hence, the performance of the membrane depends on its thickness and energy consumption can be lowered by reducing the membrane thickness.

Existing desalination membranes have a thickness of about 100–200 μm . Polymers are extensively used in membrane fabrication as they are competitive in terms of performance and economics. However, manufacturing a thin polymer membrane, which can withstand high pressure applied in RO, is extremely challenging. On the other hand, these membranes degrade easily in the presence of chlorine. Hence, polymer membranes are susceptible to fouling as disinfection becomes difficult that impinges the water flow rate under constant pressure or increases the driving force. Furthermore, polymer membranes suffer from the trade-off between the membrane flux and separation, high swelling and low mechanical stability.

In a conventional semi-permeable membrane, ions and water transport through a randomly structured polymer matrix by the solution-diffusion mechanism. Multi-dimensional curvilinear molecular paths within a polymer matrix make water transport across this membrane relatively inefficient and thus require more energy than membranes with porous structures. Consequently, porous materials, which facilitate the water flow,

are of potential interest because of their unique pore structure [15]. As a result, inorganic materials, such as zeolite, titania and silica, are adopted in the separation membrane fabrication [16-19]. Those membranes offer good permeability and long-term stability, but at the same time require careful handling due to brittleness, yield low selectivity because of cracks and pin holes, and are generally expensive. Despite the progress being made in addressing the above issues, challenges, in terms of energy reduction and recovery rate optimization, remain to be overcome for developing a sustainable desalination solution.

Nanotechnology has opened a window for researching new materials which enhance desalination performance in an economical and sustainable manner. Recently, due to excellent chemical and mechanical properties and successful isolation of GE layers from graphite in the research by Geim and Novoselov [20], GE has become the subject of intense research on membrane design and fabrication [21-30]. GE is a two-dimensional (2D) material, in which a single layer of sp^2 hybridized carbon atoms are arranged in a hexagonal lattice structure [31]. Planar orbitals in GE make stable and localized σ -bonds with three neighboring carbon atoms in the honeycomb lattice and these bonds are responsible for the binding energy and elastic properties [32] while remaining delocalized electrons in π -orbital occupy voids in the aromatic ring making GE impermeable to many materials [33] except protons [34]. It is a material harder than diamond, stronger than steel with the Young's modulus of approximately 1100 GPa [35] and the fracture strength of 125 GPa [35]. Also, this ultra-light weight (0.77 mg/m^2) [36] material with one atomic thickness has a high thermal conductivity of up to $5300 \pm 0.48 \text{ W/m/K}$ [37], an electrical conductivity of 200 S/m [38], and a specific surface area of theoretically $2630 \text{ m}^2/\text{g}$ [39] and is chemically inert.

Once perforated (engineered or intrinsic defects), monolayer GE allows ultra-fast transportation of selective molecules through the membrane via size selective sieving mechanism. These nanoporous GE (NPG) membranes can be applied in seawater desalination when the pore size is approximately around 7 Å [22, 40] and yield a high-water flux compared to TFC membranes with a water permeability approximately of $3.5 \times 10^{-12} \text{ m}^3/\text{m}^2/\text{Pa}/\text{s}$ [41]. Not only because of higher water flux and mechanical strength, but also due to their hydrophobic nature, GE membranes exhibit good antifouling properties compared to the commercial polytetrafluoroethylene membranes [42], where GE can alleviate the excessive chemical usage and maintenance cost associated with desalination plants. Both experimental and theoretical studies have demonstrated that GE-based membranes are more energy-efficient than conventional RO membranes [43]. However, the mass production of NPG membranes remains as a huge challenge for the industry. Recent studies on large-scale fabrication of GE-based thin films [44, 45] aspire the incorporation of GE into real-world applications. Therefore, understanding on the separation performance of those thin films is essential for the development of a sustainable seawater desalination system.

1.2 Motivations

In a typical seawater RO plant, the RO system contributes between 65 and 98% of total plant energy demand [15], which means there is a need to improve the energy efficiency of the RO system. As a result, the recent research focus has been on the development of an advanced desalination method requiring comparatively less energy than the RO system. FO, PV, ED and capacitive deionization (CDI) are few technologies with the potentials of lowering energy consumption and enhancing the performance of the desalination system.

The FO process associates with the transfer of water through a semi-permeable membrane from feed solution (FS) with high water chemical potential (low osmotic pressure) to draw solution (DS) with low water chemical potential (high osmotic pressure) [46]. The FO system exhibits advantages including lower energy consumption and more efficient water recovery compared to the RO process [47]. The main potential benefit of the development of a commercially viable FO system is the reduction of energy consumption by 20 to 35% times compared to the RO system that ultimately reduces the cost of water by 10 to 15% [15]. PV is used to separate liquid mixtures by partly vaporizing them through a permselective membrane. The advantages of the PV process include low energy consumption, low cost, high efficiency and most importantly, the potential to process feed solutions with high salinity which RO systems could not handle due to exceedingly high pressure requirements [48, 49]. Both FO and PV membranes have high selectivity towards water molecules.

In ED and CDI, an external electric field is used to remove salt ions from seawater as the electric field can force the ions to pass through ion exchange membranes and electrodes, respectively. Compared with ED, CDI is an eco-friendly and economically more flexible method. ED has limited application in low-salinity desalination since the selectivity of ion exchange membranes reduces when seawater is used as feed, and those membranes are more expensive than RO membranes [50]. Similarly, CDI is useful for desalination of brackish water as it becomes uneconomical at high salinity because the capacitance of the electrodes limits the ion adsorption [51]. However, the reduction of water production cost through an economically feasible ED and theoretically expected CDI systems are 5 to 15% and 30%, respectively [15]. Consequently, these advanced methods hold great potential in developing economical desalination process.

As expected, the desalination performance of those advanced methods could be further improved by incorporating GE-based nanomaterials into the fabrication of membranes and electrodes. Although many research works have investigated the underlying phenomena of NPG as RO membranes, few studies have focused on understanding the performance of advanced desalination systems by adopting GE-based thin films such as stacked GE laminates, which could be economically manufactured. Meanwhile, the surface corrugation and oxidation of GE can modify its electronic, optical, mechanical and chemical properties [52] that have a significant impact on the performance of GE, as a separation membrane or electrode, and thus a detailed exploration is needed. Moreover, it is indispensable to understand and predict the desalination performance of those GE-based nanostructures in order to provide guidance to experimental studies.

In addition, graphene oxide (GO) is considered a promising material for membrane fabrication due to its O-rich functional groups, large surface area, chemical stability and hydrophilicity [25, 29, 53, 54]. GO-based membranes have demonstrated high water flux [48, 55] and antifouling [56, 57] performances in water purification applications. Nevertheless, these membranes require further improvements since their narrowed interlayer spaces with strong interaction among sheets hinder the water permeation paths, though achieving high solute rejection at the same time. Indeed, in long-term usage, GO may swell in water and increase its interlayer distance, thus reducing its effectiveness as a molecular sieving membrane. Meanwhile, it has been reported that metal organic frameworks (MOFs) can be used as modifiers to improve the performance of GO membranes in water purification [58-60]. Therefore, this study focuses on designing a nanocomposite membrane structure which combines the benefits of GO and MOF structure, namely HKUST-1 to develop an advanced membrane structure for desalination.

Most of the desalination systems require upstream processing of feed water and downstream processing of product water. One third of total energy consumption in the modern RO system is due to the upstream and downstream processes rather than the desalination stage [41], which urges the importance of developing a single-stage desalination system, and thus becomes another motivation of this Ph.D. study. Therefore, the underlying ion separation mechanism in an ionized GO membrane is explored to propose a desalination method, that has the capability to develop into a single-stage desalination system, namely the electronanofiltration (ENF). Furthermore, the performance of GE-based materials as a separation membrane or electrode, greatly depends on the operational conditions of the system such as pressure, electric field, temperature and feed concentration. So, this research is intended to investigate the desalination performance of proposed GE-based nanostructures within different operating systems and conditions.

Fluids, confined in nanochannels, exhibit unconventional behaviours due to a close contact with the pore/channel walls that change the interactions among fluid molecules. This can be investigated through either physical experiments or simulations. Naturally, an experimental study is a trial and error process that needs more effort, resources and time. With the advancements in computer science and technology, simulations are much easier to be performed than the experiments when the research is conducted on nanoscale level. Simulations are helpful in predicting, especially the relation between material structure and performance, and understanding phenomena or explaining experimental observations. Many phenomena in nanoscale can be well predicted by using first-principal simulation or molecular dynamics (MD) simulation. Systems with relatively large sizes can be effectively modelled using the MD simulations compared to the first-principle simulation, which provides high accuracy with significantly enhanced computational cost. Hence, in

this dissertation, MD simulations have been conducted to explore the desalination performance of GE-based thin films.

1.3 Objectives

This proposed study would investigate the desalination performance of four GE-based thin films namely, corrugated GE layers, stacked GE sheets, ionized GO layers and GO/MOF nanocomposite using MD simulation. Their performance via a selected desalination technology will be explored. The main objectives of this study are as follows:

- To understand the potential of using GE-based thin films to improve the desalination performances in different technologies, namely, CDI, FO, ENF and PV;
- To study the effects of pore geometry, channel width, entrance configuration, membrane alignment, GE morphology and functional groups on ion separation mechanisms;
- To explore the influences of process operating conditions, including applied pressure, electric field, temperature and concentrations of feed and draw solutions on desalination performance through different technologies;
- To provide guidance on the experimental synthesis of advanced GE-based thin films for seawater desalination.

1.4 Dissertation outline

This Ph.D. dissertation is organized into seven chapters. Following this introduction in Chapter 1, a comprehensive review on advanced desalination technologies, GE-based

thin films and the fundamentals of MD simulation is given in Chapter 2. The study on exploring desalination performances of corrugated GE layers using CDI technology is discussed in Chapter 3. Chapter 4 investigates the effects of pore configuration and membrane structure of stacked GE sheets as an FO membrane on the desalination performance. Chapter 5 presents a method to remove salt from seawater using ionized GO sheets with many large nanopores. In Chapter 6, the desalination performance of a GO/HKUST-1 composite material which combines the advantages of both GO and HKUST-1 MOF in PV desalination is explored. Finally, conclusions and recommended future works are given in Chapter 7.

Chapter 2. Literature Review

Desalination is a physical process that separates salts from water. Thus, it is a thermodynamic process with a minimum required work, known as the minimum thermodynamic energy of separation. The energy efficiency in most desalination processes is controlled by the thermodynamics rather than the rate of operation. In this context, the separation mechanism of the technology used in a desalination process plays a pivotal role. Seawater desalination techniques can be basically classified into thermal, membrane-based separation and chemical separation processes. Membrane-based methods are widely adopted in seawater desalination, and the separation performance of such technologies relies on a semi-permeable membrane. Recently, given the advances in nanotechnology, GE-based structures have been extensively studied as desalination membranes due to their ultra-fast water flux and chemical and mechanical stability. Firstly, this chapter introduces the background of each desalination technology that is commonly used in the industry or has the potential to be used in seawater desalination. Secondly, the structures, fabrication approaches and separation performance of potential GE-based thin films are discussed. Finally, the MD simulation method adopted in this research with its fundamentals is presented.

2.1 Seawater desalination technologies

Desalination is a thermodynamic process with a minimum required energy, known as the minimum thermodynamic energy of separation. Theoretically, a minimum energy of 0.7 kWh/m^3 [5] is required to obtain pure water from seawater, whereas energy in the range of $2\text{--}18 \text{ kWh/m}^3$ is used in existing desalination facilities [6, 9]. Presently, a variety of methods are available for seawater desalination; these methods can be classified into

three categories, based on their operation principle, as shown in Fig. 2.1(a) [7, 8]. In this section, the background of each desalination technology that is commonly used in the industry or has the potential to be used in seawater desalination is introduced.

Fig. 2.1. (a) Classification of desalination technologies [7, 8] (b) Global desalination capacity by technology [61], and (c) Breakdown of operating cost of a seawater RO plant [62, 63].

2.1.1 Thermal driven methods

In thermal processes, the separation of water and salt occurs when feed water undergoes a phase change into vapor or ice. Such processes can be primarily classified into two groups: distillation and crystallization. Liquid-vapor transition is the principle behind distillation systems such as MSFD, MED, membrane distillation and TVC, while liquid-solid transition can be observed in crystallization systems, namely, freezing and hydration. MSFD is the most extensively used distillation method in the industry with a market share of 25% (Fig. 2.1(b)) [61]. Generally, distillation processes require intense

energy and high capital, which hinders their popularity across the globe. Meanwhile, freezing, with a theoretically minimum energy of separation, has been studied as a desalination method since salts preferentially remain in the liquid phase as water is converted into ice. However, the industrial application of freezing as a desalination method is limited due to the complexity of plant design and the contamination of product water [11].

2.1.1.1 MSFD

In MSFD, an evaporator is composed of a series of evaporating chambers called stages, maintained at a decreasing pressure from the first stage (hot) to the last stage (cold) (Fig. 2.2(a)) [10]. Thus, the precise control of pressure in these different stages is essential as some transient time is required to be established before starting the operation of the plant. Generally, steam at a pressure between 0.2 to 0.3 MPa is used as the heating medium, and energy transfer occurs via heat convection. Depending on the temperature applied, there is a tendency towards scale formation and corrosion, as the operating temperature of MSFD is higher than the minimum temperature of 70 °C, at which the occurrence of such phenomena is hindered. Existing commercial MSFD processes are designed with 10 to 30 stages with a 2 °C temperature drop per stage. The overall energy consumption of an MSFD process is approximately 18 kWh/m³ [9]. To lower the energy consumption, large MSFD systems are often combined with a power generation plant in a cogeneration configuration.

2.1.1.2 MED

The MED process consists of a series of evaporators (Fig. 2.2(b)), known as effects, maintained at a reducing ambient pressure, so that the boiling point of water decreasing in

each effect [12]. This aspect of the process allows feed to undergo multiple boiling without the additional heat supply for each effect, except the first one, in which seawater entering into the evaporator is heated by an external heat source. The vapor produced in the first effect acts as the heating medium in the second evaporator, and this process is repeated in each subsequent stage. As a result, MED becomes a low temperature thermal process with an energy consumption of 15 kWh/m³ [9], which is lower than that of the MSFD system.

Fig. 2.2. Schematic representation of desalination methods: (a) MSFD [10] and (b) MED [64].

2.1.1.3 Membrane distillation

Membrane distillation is a thermal driven process in which a hydrophobic porous membrane acts as a barrier for liquid permeation while allowing vapor molecules to pass through it [65]. Since the membrane does not actively contribute to the separation process, this technique is categorized as a thermal driven desalination method. Polytetrafluoroethylene, polypropylene and polyvinylidene fluoride are the most commonly used synthetic polymers in the membrane distillation [66]. These membrane materials are non-polar in nature and thus are not wetted by water with a high dipole. The driving force of this process is the partial pressure difference that can be set off through a

temperature difference. Compared with the MSFD and MED methods, membrane distillation is a low energy process that operates at a relatively low temperature of 50 to 90 °C [65]. Hence, this is a promising method for desalination in places where waste heat, solar power and geothermal heat can be employed as the energy source [67], and it has the potential to be developed into a sustainable desalination solution. Different versions of membrane distillation are available, including direct contact, air gap and vacuum membrane distillation methods.

2.1.2 Membrane separation methods

In membrane-based separation, nearly salt free water is separated from seawater through a semi-permeable membrane, while a highly concentrated brine solution is collected as a retentate (Fig. 2.3(a)). Seawater is forced through the membrane by applying a driving force in terms of pressure or concentration to overcome the osmotic pressure in the seawater. The most widely used separation method in the desalination industry is RO (Fig. 2.1(b)). However, other advanced desalination techniques, such as ED, FO, PV and M/CDI, have demonstrated their potentials for seawater desalination [68-73].

2.1.2.1 RO

In RO, water flows across a membrane via a solution-diffusion mechanism, from a high concentration region to a low concentration region. Accordingly, this method requires a very high pressure, approximately 8 MPa, to overcome the osmotic pressure of seawater, which is typically around 2.5 MPa [6]. The water flux J_w is directly proportional to the applied pressure that can be calculated using the following generalized equation at constant temperature:

$$J_w = A(\Delta P - \Delta \pi), \quad (2.1)$$

where A , ΔP and $\Delta \pi$ are the membrane permeability coefficient, the hydraulic differential pressure across the membrane and the osmotic pressure difference across the membrane, respectively. The desalination performance of RO is mainly governed by the characteristics of the membrane including pore size, thickness, tortuosity, membrane charge and so forth.

Usually, membrane throughput, selectivity, mechanical strength and fouling resistance are important factors to be considered when developing membranes for RO. The membrane lifetime and the water flow rate are often affected by the concentration polarization (CP) and fouling [74]. The accumulation of rejected solutes on the membrane surface is known as the CP. Fouling is an accumulation of materials on the membrane surface and can be classified into the following categories: precipitation fouling, chemical reaction fouling, corrosion fouling, and biological fouling [75]. The CP and fouling are inevitable in RO systems, requiring the use of chemical cleaning agents, such as chlorine, and increasing the cost of water production. Therefore, a membrane should be fouling resistant and able to withstand frequent cleaning and chemical usage.

Fig. 2.3. (a) Simplified membrane separation process and (b) schematic representation of a TFC membrane [6].

In general, RO membranes can be categorized as polymer, inorganic and mixed matrix membranes. Polymer membranes are often made from polyamide or cellulose

acetate. A cellulose acetate membrane has a strong affinity to chlorine compared with a polyamide membrane, which has a good mechanical stability and separation capability. However, the performance of cellulose acetate and polyamide membranes is surpassed by thin-film composite (TFC) membranes [6]. As shown in Fig. 2.3(b), a typical polyamide TFC membrane consists of three layers, namely an active layer (polyamide), a porous supportive layer (polysulfone) and a polyester substrate in which, performance can be enhanced via substrate or polyamide thin film modification. The active layer can be modified to improve the water flux, solute rejection and fouling resistance of the TFC membrane, while its mechanical stability is improved through the development of a defect-free substrate layer. One of the main drawbacks of such polymer membranes is fouling, which can be minimized through the hydrophilization of the membrane surface using hydrophilic additives or grafting functional monomers [6].

Inorganic membranes, such as zeolite, titania and silica are suitable for RO because of their chemical inertness and thermal stability [16-19]. However, these materials are expensive and have a greater thickness compared to polymer membranes. Those inorganic membranes demonstrate good permeability and long-term stability, but also require careful handling due to brittleness, yield low selectivity because of cracks and pin holes, and are generally expensive. Mixed matrix membranes are the third type of RO membrane. This type combines a polymer matrix with an inorganic filler (such as zeolite, alumina, carbon nanotubes (CNT) or TiO_2) [76, 77], demonstrating an enriched desalination performance due to the individual properties of each matrix used in membrane fabrication.

RO systems require more pretreatment of seawater and more maintenance and energy, in the form of electricity and mechanical works. The lower recovery limit of RO depends on the osmotic pressure, while the upper recovery limit is governed by the

chemical composition (scaling) and energy consumption [62, 78]. Most research works in this field have focused on increasing the membrane permeability. Despite the improvements made so far, the desalination energy (2–5 kWh/m³) in an RO system is higher than the theoretical energy requirement [6]. A typical breakdown of the operating cost of a seawater RO plant is presented in Fig. 2.1(c) [62]. In RO, 40% of the flow energy remains in the brine [79], and most of the energy loss occurs as water passes through the membrane due to the large pressure drop. The energy efficiency in RO systems is governed by thermodynamics rather than the rate of the operation. For a recent example, compared to conventional membrane materials, CNT membranes exhibit an ultra-fast water permeability [23] yet do not significantly reduce the energy consumption of the RO system. Thus, it is essential to explore the potential for enhancing the desalination performance of membrane separation by adopting a technology that is less energy intensive than the RO system. The following sections that follow discuss advanced membrane separation processes, and their operation principles, along with the recent progress achieved by modifying membrane structures, especially nanostructured materials.

2.1.2.2 ED

ED is another commercialized membrane separation technology (Fig. 2.1(b)). It consists of an alternate stacking of cation and anion selective membranes, in which ionic flux is driven by an applied electric field (Fig. 2.4(a)). Under the influence of electric potential, ions travel towards the anode (a positively charged electrode) and cations travel towards the cathode (a negatively charged electrode). Cations permeate through the cation exchange membranes that are restricted by the anion exchange membranes. Similarly, anions travel through the anion exchange membrane to reach the anode. As a result, some

compartments are filled with the brine while adjacent chambers are occupied with diluted or purified water. At each electrode, cathode and anode, reactions may take place, depending on the pH and intensity of the applied potential. Consequently, hydrogen and either chlorine or oxygen gases may be generated at the cathodes and anodes, respectively. The desalination efficiency and the energy consumption of an ED cell greatly rely on the current in the cell. Therefore, the applied cell voltage is a critical operating condition.

Fig. 2.4. Schematic representation of (a) ED cell and (b) cation exchange membrane with the fixed and mobile ions [13].

Conventional ion exchange membranes are constructed using polymer chains that contain functional groups such as carboxylic acid (COOH), sulfonic acid (SO_3H) and ammonium hydroxide (NH_4OH) [80]. The net charge of such exchange membranes is determined by the ionization of the functional groups. These charges are named fixed ions and are in equilibrium with the mobile counterions, as illustrated in Fig. 2.4(b) which presents the ion distribution in a cation exchange membrane. In this figure, negatively charged mobile ions represent the coions, which should be zero for an ideal cation exchange membrane. The desired properties of an ion exchange membrane in ED are

selectivity, low electrical resistivity and mechanical and electrical stability. The ED process requires feed pre-treatment, since these ion exchange membranes are prone to suffer from scaling and fouling due to the precipitation of charged particles on the membrane surface. Furthermore, these membranes are incapable of removing uncharged species, requiring a posttreatment stage to assure the quality of potable water.

Diffusion and electromigration are the mechanisms that determine the solute transfer while electroosmosis and osmosis cause the water flow. Owing to its high product recovery, ED is widely used in brackish water desalination, wastewater treatment and desalination of streams from pharmaceutical and food industries. Moreover, ED is more economical for feed solutions consisting of low molecular weighted charged particles of concentration lower than 6000 mg/l [81] and is less applicable in large-scale desalination. As a result, ED is extensively employed in the posttreatment of the permeate of RO systems. A continuous electrochemical process based on the ED method, combining the benefits of both ultra-filtration and continuous electrodeionization, has recently been developed by the Evoqua, and is claimed to reduce the desalination cost of a conventional seawater RO plant by 5 to 15% [15]. Hence, ED would be a good choice in the development of a hybrid desalination system.

2.1.2.3 M/CDI

In CDI, particles with opposite charges are adsorbed into two electrodes under the effect of an external electric field, typically ranging from 1.2–1.5 V [82], and the process continues until the electrodes are saturated with the ions. Saturated electrodes can be regenerated by removing or reversing the external electric field, and then the ions are flushed from the cell. Thus, the CDI process can be divided into two phases, known as adsorption and desorption or deionization. The separation mechanism of a deionization

system is illustrated in Fig. 2.5(a). During the adsorption phase, counterions travel through the pores of the electrode and compensate the charge in the electrode matrix. Meanwhile, the desorption of coions in the electrode matrix may occur. The energy stored during the deionization cycle can be recovered during the regeneration or discharge cycle. Thus, the net energy consumption is the difference between the supplied energy and the recovered energy. For this reason, CDI desalination is an energetically favorable process, whereas effort is needed to perform regeneration effectively.

Since CDI operates at a low pressure and temperature, its operation associates with low investment and infrastructure costs. This method is energy efficient because it removes the salt ions from water, unlike RO, which removes water from the salts. The energy cost of treated water can approximately scale with the number of ions removed; as a result, CDI is a viable method for desalinating low concentration solutions of 10 g/l [83]. Moreover, CDI has a high recovery rate with an ability to remove a wide range of ionic contaminants [82], which makes it an energy-efficient and a cost-effective method compared to a conventional RO system. CDI is a charge-discharge process, whereas ED is a continuous process. Furthermore, CDI is a more energy efficient method for brackish water desalination compared to RO, as shown in Fig. 2.5(b) [84]. However, it is reported that a deionization system with an efficiency above 85% can be a competitor for RO, not only for brackish water but also for seawater desalination [81]. Therefore, more emphasis should be focused on adopting new materials to enhance the energy efficiency of the CDI system.

As per Johnson and Newman's observations, the criteria that determine the efficiency of CDI are fast ion absorption rate, minimal ohmic drop and high applied potential for carbon to behave as an ion exchanger [85]. Electrodes are often made from porous materials, and the process efficiency depends on the characteristics of the materials. The

selection of a suitable material is based on properties such as pore volume, pore size, pore connectivity, electrical conductivity, electrochemical stability and material availability [83]. The most commonly used materials are carbon-based materials, including activated carbon, carbon aerogel, ordered mesoporous carbon and carbon black [83, 86-89]. The use of functionalized carbon with oxygen makes the electrode more responsive to ions as it enhances the surface area and the wettability of the material.

Technological advancements in material science have introduced highly-ordered structures such as CNT, GE and CNT/GE composite [86] into CDI and promoted it as a desalination technique. Among these materials, GE has excellent properties in terms of its high electrical conductivity, surface area, mechanical stability and chemical inertness [31]. It has thus been identified as an exceptional choice for electrosorption. A previous study by Li *et al.* on the electrosorption behavior of GE in a sodium chloride solution has shown that GE has a high capacity of 1.85 mg/g and the electrosorption of NaCl on to GE layers is driven by a physisorption process [30]. Furthermore, Wang *et al.* have used a functional GE nanocomposite as an electrode material and found that this new material has a high deionization capacity in comparison to the electrode of reduced GE oxide and commercially activated carbon [90]. In another study, a GE/CNT composite has been employed to fabricate electrodes: the results revealed that this novel composite material has a higher electrosorption capacity than GE [86].

To improve the performance of the CDI cell, a cation selective membrane is placed to cover the cathode, and an anion selective membrane is placed in front of the anode of the CDI cell. The resultant new system is known as MCDI. As mentioned, during the adsorption phase, coions can discharge from the porous electrode, which lowers the efficiency of the CDI system. By placing an ion exchange membrane facing each electrode, the release of coions from the electrode can be prevented, contributing to

enhancing the ion efficiency of the cell. However, because of the ion exchange membranes, MCDI requires special precautions to minimize the scaling and fouling, as in ED systems. In practical operation, though, this fouling tendency may not be as severe as in RO. However, unlike RO, M/CDI systems do not provide a barrier against microbes. Pretreatment is thus essential to ensure the quality of product water and the longevity of the desalination cell. To improve the potential of CDI for the desalination of seawater, more emphasis should be on the development of electrode materials with a high surface area at fast ion mobility, electrical conductivity, low contact resistance between electrode and current collector, and bio-inertness to avoid biofouling.

Fig. 2.5. (a) Schematic representation of a CDI [83] and (b) the energy necessary to implement RO and CDI technique as a function of feed salinity [84]. The inset in (a) shows an enlarged view of the porous carbon electrode.

2.1.2.4 FO

FO is an advanced separation method that has been reinvigorated by the advancement in materials and engineering concepts. The process associates with the transfer of water through a semi-permeable membrane from a feed solution (FS) with high water chemical potential (low osmotic pressure) to a draw solution (DS) with low water chemical

potential (high osmotic pressure) (Fig. 2.4(a)) [46]. The diluted DS is separated at downstream via some cost-effective separation processes to recover water. Compared to the RO process, FO exhibits various advantages including lower energy consumption, higher fouling resistance and more efficient water recovery [47]. Despite these advantages, FO membranes have a low power density and thus require a large area in practical applications.

The commercially available FO membranes consist of a dense polymer layer, as an active layer, attached to a porous supportive layer (SL). These polymer membranes are fabricated from cellulose acetate, polysulfone, polybenzimidazole, polyamide-imide, polyamide and so on. [91, 92]. In FO, membrane orientation is arranged by directing the feed solution against the active layer. The efficiency of the system depends on the membrane characteristics, such as water permeability, salt retention, CP, and mechanical and chemical stability [91, 93]. CP occurs at the rejecting surface of the membrane as a result of increased solute concentration. In FO, CP, existing on both sides of the membrane surface, significantly reduces the transmembrane osmotic pressure and therefore plays a key role in determining the water flux. This phenomenon is known as external concentration polarization (ECP) and can be mitigated by hydrodynamics, such as mixing or increasing flow rate. Due to the asymmetric structure of FO membranes, as observed in ECP, a boundary layer is developed inside the SL. This phenomenon is known as internal concentration polarization (ICP).

In osmotically driven membrane processes, ICP is mainly responsible for the decline in flux, and the flux reduces significantly at higher solute concentrations [94-96]. The ICP arises because of back diffusion on the membrane surface, a phenomenon that compensates the dilution of the DS due to convective water flow into the DS. For a

symmetric dense membrane, the standard flux equation (Eq. (2.1)) can be modified to include the CP effect as

$$J_w = A \left(\pi_{D,b} \exp \left(-\frac{J_w}{k_D} \right) - \pi_{F,b} \exp \left(\frac{J_w}{k_F} \right) \right), \quad (2.2)$$

where $\pi_{D,b}$, $\pi_{F,b}$, k_D and k_F represent the bulk osmotic pressure of the DS, the bulk osmotic pressure of the FS, the mass transfer coefficient in the DS and the mass transfer coefficient in the FS, respectively. The negative exponential term implies the effect of the dilution of the DS. For an asymmetric FO membrane, where ICP occurs on the DS side and ECP occurs on the FS side, Eq. (2.1) is modified as

$$J_w = A \left(\pi_{D,b} \exp(-J_w K) - \pi_{F,b} \exp \left(\frac{J_w}{k_F} \right) \right), \quad (2.3)$$

where K is the solute transfer resistance to diffusion within the membrane SL.

Fig. 2.6. Schematic representation of desalination methods: (a) FO [46] and (b) PV [97].

Generally, the developments related to FO processes are twofold: (1) development of FO membranes to minimize the CP and (2) development of efficient DSs. Unlike CP, ICP cannot be controlled via hydrodynamics since this process takes place within the SL [98]. The ICP effect can be minimized by reducing the hindrance to the solute diffusion through the modifications to the SL thereby achieving low tortuosity, high porosity and

thin structure [95, 99-103]. Alternatively, the ICP can also be reduced by designing the selective layer to withstand in the FO system without an SL [104, 105]. Therefore, ultra-thin 2D materials such as GE and carbon nitride would play a significant role in the fabrication of FO membranes.

In this context, the ideal DS should have the following characteristics: a high osmotic efficiency, namely high solubility, and low molecular weight that can be separated easily and inexpensively, without being consumed during the process [106]. According to the Van't Hoff equation [107], the osmotic pressure of an ideal dilute solution is given by

$$\pi = n \left(\frac{C}{M} \right) RT, \quad (2.4)$$

where n , C , M , R and T are the number of moles of species formed by dissociation of solutes in solution, the concentration of solutes, the molecular weight of solute, the gas constant and the absolute temperature of the solution, respectively. It is evident that solutes with high water solubility and low molecular mass will yield high osmotic pressure, thereby improving the water flux in the FO process. The diffusion coefficient D_s of the solute has a significant effect on water flux, as a large D_s reduces solute resistance to diffusion, and ultimately reduces the ICP. Increasing temperature reduces the viscosity of the DS and improves mass transfer rate; it therefore has a positive impact on increasing water flux until the temperature reaches a certain critical point at which flux reduces as a result of scaling.

DSs can be classified as volatile, organic, inorganic and novel synthetic solutions. Ammonia and carbon dioxide, as DSs, are tested [106] and have shown good osmotic efficiency due to their water solubility and low molecular weight; however, these substances are corrosive and the regeneration process is energy intensive [93]. Organic compounds, such as glucose, fructose, sucrose and ethanol, display high reverse solute

diffusion in the FO process. Their large molecular weight intensifies the ICP, lowering the water flux. Inorganic salts consisting of organic anion and organic or inorganic cation yield better performances with high diffusion and less ICP. Inorganic solutions are widely used as a DS in the FO process since they enhance the water flux, can be easily recovered by RO or NF and can be used directly without further treatment [69]. NaCl, KCl, MgCl₂, CaCl₂, MgSO₄ and Na₂SO₄ are some commonly tested and used inorganic salts in which monovalent metal chlorides have high flux while divalent metal chlorides have high solubility. Achilli *et al.* have developed a protocol to select a suitable inorganic DS, finding that MgCl₂ is a suitable candidate due to its high performance, potential low cost and reduced risk of scale formation [108]. Ionic liquids and magnetic nanoparticles are some examples of novel synthetic solutions.

2.1.2.5 PV

Permselective evaporation PV is often used for the dehydration and separation of organic mixtures. Recently, this method has been considered as an alternative approach to seawater desalination as it demonstrates high solute rejection, above 99%, due to the non-volatile nature of the salts. In PV applications, the membrane is in direct contact with the feed solution (seawater): as it travels through the membrane, water is partially converted into the vapor phase before it enters the opposite side of the membrane, which is kept under vacuum using a vacuum pump or is purged with a stream of carrier gases (Fig. 2.6(b)) [109]. The advantages of the PV process include its low energy consumption, low cost, high efficiency and, most importantly, its potential to process feed solutions with high salinity, which RO systems cannot handle due to the exceedingly high pressure requirements [48, 49].

Mass transport across the membrane can be divided into 3 steps: (1) the adsorption of the solute onto the membrane surface, (2) the diffusion of preferential components through the membrane, and finally, (3) the desorption of components to the permeate. Among these steps, the solution diffusion is typically the key rate-controlling mechanism in the PV desalination process.

Dense, selective and hydrophilic membranes are utilized in PV separation processes. The characteristics of polymers, inorganic and polymer-inorganic hybrid materials have been explored in the fabrication of PV membranes [48, 71, 97, 110]. Hydrophilic polymer membranes suffer from the trade-off between the membrane flux and separation, high swelling, and low mechanical stability. Inorganic materials, such as zeolites, offer decent permeability and long-term stability, but at the same time require careful handling due to their brittleness, yield low selectivity due to cracks and pin holes, and are generally expensive. In this context, hybrid materials, such as polymer/maleic acid/silica, polymer/MOFs, and polymer/GO), have emerged as the focus of many recent research studies on improving PV desalination systems [48, 49, 111]. The water flux in PV membranes strongly depends on the physicochemical characteristics of the membrane and typically remains low, not exceeding 14 kg/m²/h. Thus, highly hydrophilic materials, such as GO, are significant in the fabrication of PV membranes.

2.2 GE-based thin films

GE is a 2D material with all carbon atoms arranged in a honeycomb lattice structure (Fig. 2.7(a)). It is a building block of all graphitic forms, such as fullerene and CNT, and the thinnest known material with unique properties. Each sp² hybridized carbon atom in GE forms three strong in-plane σ -bonds with an angle of 120° and interatomic bond distance of 1.42 Å, resulting in the outstanding mechanical properties of GE (Fig. 2.7(b)).

Experimental works show that GE has a high Young's modulus of approximately 1100 GPa [35] and a fracture strength of 125 GPa [35]. GE is also an ultra-light weight (0.77 mgm^{-2}) [36] material with a specific surface area of theoretically $2630 \text{ m}^2/\text{g}$ [39], a high thermal conductivity of up to $5300 \pm 0.48 \text{ W/m/K}$ [37] and an electrical conductivity of 200 S/m [38]. A defect-free GE lattice is impermeable to all atoms under ambient conditions as its π -orbitals form a dense delocalized cloud that hinders the gaps within aromatic rings. Some other interesting properties of GE have been reported, including its chemical inertness and feasibility to be chemically functionalized [112, 113]. Although GE is expected to be flat, in nature it exists as a corrugated sheet [114] because of thermal fluctuation-induced ripples, strain-induced wrinkles and crumples, and edge instability-induced ripples and wrinkles [52, 115]. The surface corrugation of GE can also modify its electronic, optical, mechanical and chemical properties [52].

Fig. 2.7. (a) Atomistic configuration of GE and (b) bonds between sp^2 hybridized carbon atoms [31].

Oxidized GE or GO sheets are a widely used derivative of GE in water treatment. GO is an amphiphilic material [116], displays similar properties to GE, and has a high concentration of oxygen containing functional groups such as epoxy and hydroxyl groups on its basal plane, and carboxyl groups at its edges (Fig. 2.8(a)) [26, 117, 118]. GO can

form highly ordered films with nanocapillaries that facilitate fluid flow. These functional groups have reactive sites that enable the synthesis of GE-based composite materials. In contrast to GE, the mass production of GO is economical, and the Brodie, Staudenmaier and Hummers methods are the three commonly used approaches for the fabrication of GO [26]. The degree of the oxidation in GO sheets varies due to the quality of the raw material and reaction conditions, namely pressure and temperature. GO sheets with a low concentration of functional groups are known as rGO (Fig. 2.8(b)) and may have a high concentration of defects, introducing more paths for molecular transport [119].

Fig. 2.8. Structural models of (a) GO and (b) rGO. Red arrows are pointed to defects [120].

Consequently, the physicochemical properties and fabrication techniques of GE have opened up a window for exploring various methods of using GE or GE derivatives in separation processes. Based on the type of GE used, these processes can be mainly categorized as (1) nanoporous GE (NPG), (2) stacked GE laminates, and (3) GE-based nanocomposites (Fig. 2.9) [121]. In this section, the desalination performances of the three representative GE-based thin films are introduced.

2.2.1 NPG

Once perforated, pristine GE can be used for molecule separation. NPG can be formed by perforation employed either from intrinsic defects in the GE lattice or from engineered methods that involve high energy impact with the intent of dislocating tens to thousands of carbon atoms from the GE lattice. Electron bombardment, focused ion beam irradiation, ultraviolet induced oxidative etching, ion bombardment followed by controlled chemical oxidative etching and oxygen plasma etching are different perforation methods used in the synthesis of NPG [118, 122]. Previously, the potential of NPG sheets as desalination membranes has been shown through both experimental and theoretical approaches [22, 23, 28, 40, 123-126].

Fig. 2.9. Main types of GE-based thin films: (a) Nanoporous GE (b) stacked GE laminates and (c) GE-based nanocomposite [121]. Blue arrows indicate possible molecular paths.

Size exclusion is the main mechanism for molecular separation through NPG, which can therefore be effectively used in seawater desalination when pore radius r is approximately around $3.5 \text{ \AA}$ [22, 40] and yield a high water permeability compared to a TFC membrane with water permeability around $3.5 \times 10^{-12} \text{ m}^3/\text{m}^2/\text{s}/\text{Pa}$ [41]. O'Hern *et al.* have tested an NPG by first introducing defects into the GE lattice through ion bombardment and subsequently enlarging the pore size via oxidative etching [126]. The results show that the NPG membrane is cation selective for smaller pore size, while larger pores allow the transport of salt. In another study, a single-layer NPG membrane was

prepared using an oxygen plasma etching process where the pore sizes were altered by controlling the etching time [28]. The experimental results reveal that the water flux increases with the increase of pore size, while also reducing the salt rejection.

GE sheets can withstand high pressures that are ten times more than that possible in a typical seawater RO system [127]. Thus, membranes with relatively large pores can be used as supportive layers in the fabrication of monolayer NPG membranes. Not only because of their high water flux and mechanical strength, but also due to the relative resistance of graphitic carbon to chlorine, GE may facilitate the prevention of fouling by disinfection [127, 128].

At the nanoscale, water molecules form a complex hydrogen bonding network, nanopores, which assist in the formation of favourable geometric orientations and hydrogen bond configurations, enhance the water flow through a membrane [22]. Hence, pore chemistry plays a significant role in desalination processes. In this context, functional groups, such as (H), nitrogen (N), fluorine (F), hydroxyl (OH), carbonyl (COO), COOH and so forth, can be bonded to unsaturated carbon atoms at the pore edges to modify the pore chemistry. Moreover, the ionization of these functional groups in water introduces a net charge to the GE membrane and thus can be adopted as ion selective membranes for nanofiltration, ED and MCDI processes. The passivation of edges and defects in monolayer GE with pyridinic N (N bonds with two carbon atoms) has been experimentally realized by thermal CVD of H and ethylene on Cu foils in the presence of ammonia [129], showing the potential for fabricating N-doped NPG.

GE has also been tested as an electrode material for electrochemical capacitors due to its high conductivity, large surface area and chemical stability [130-133]. The introduction of nanopores into GE electrodes improves the performance of GE-based

capacitors because the GE edges provide much larger specific double layer capacitance than the basal plane of the GE sheet [134].

However, when scaling up the fabrication of GE membranes or electrodes, there exist technical challenges, including (1) synthesis of high quality, large area GE sheets at a low cost and in an environmentally friendly and reproducible manner, (2) perforation to achieve desired pore size, shape and pore distribution while preserving the material's mechanical stability and (3) transferring of GE films onto supportive membranes or layers without the creation of cracks, folds and wrinkles. In this context, assembled GE laminates are considered as effective means to address the above issues. Their respective characteristics and performances are described in the section that follows.

2.2.2 Stacked GE-laminates

Advances in GE chemistry have provided new ways to assemble bulk carbon materials, such as chemically converted GE (CCG) and GO sheets, in a bottom up approach [135]. As a result of corrugation and repulsive forces, individual sheets in the membrane remain separated with an interlayer distance (h) and have pore opening (d) due to interlocked sheets (Fig. 2.9(b)) [135]. Unlike NPG, these thin films can be produced economically in the bulk form [136] and have proven molecular sieving characteristics with ultra-fast water flux [135, 137]. Encouraged by these characteristics, many studies have been focused on exploring new ways to improve the performance of these structures in seawater desalination.

CCG can be synthesized via the chemical and electrochemical exfoliation of graphite or the deoxygenation of GO. At present, exfoliated GE sheets comprise one to three layers of GE with the monolayer and bilayer GE as the dominant products [138, 139]. The nanochannels formed between GE sheets vary in size, because of the trapped

nanoparticles and functional groups that are left between the GE sheets during the fabrication process. These GE structures have a corrugated texture and defects or holes [135, 137], which have significant effects on their physical and chemical characteristics and thus on the desalination performance. Recently, Qiu *et al.* have shown that the corrugation in CCG sheets can be controlled via hydrothermal treatment and that the resultant membrane has potential for use in nanofiltration [137].

GO membranes can be fabricated using different methods, such as vacuum filtration, layer-by-layer deposition (LBL), drop casting and spin coating [118, 140]. Free-standing GO membranes made through these techniques possess different microstructures. For example, the membranes fabricated by pressure, vacuum and evaporation-assisted self-assembly methods exhibit highly ordered, loose and random microstructures, respectively (Fig. 2.10(a)) [141]. Smaller GO sheets have higher number functional groups compared to larger sheets and are attributed to the enlarged interlamellar space in adjacent GO sheets, displaying a random stacking nature [142]. Meanwhile, large GO sheets self-assemble into a compact structure with strong mechanical properties, which is helpful in fabricating well-aligned and strong free-standing GO membranes.

GO nanosheets consist of two regions: pristine GE regions that provide a network of capillaries with nearly frictionless flow and functionalized (oxidized) areas that keep adjacent sheets apart and help water to intercalate between sheets. The ultra-fast water flow between pristine GE sheets breaks down due to a side-pinning effect by water confined amid oxidized regions in GO sheets [143]. Nair *et al.* have fabricated free-standing GO membranes and found that small organic molecules, such as methanol, acetone and hexane, have a permeability several orders of magnitude lower than water [21]. Following their work, many studies have been conducted to further investigate the potential of free-standing GO membranes for water purification [53, 144-146].

An experimental study demonstrates that thick GO membranes with nanochannels of $h = 0.9$ nm are capable of sieving species with a hydrated radius larger than 0.45 nm, whereas ions, such as K^+ , Mg^{2+} and AsO_4^{3-} , permeate with approximately the same rate, showing weak dependence on ion charge [53]. Sun *et al.* have shown that the GO membrane is capable of separating Na^+ from Cu^{2+} due to strong interactions between heavy metal and the functional groups of GO sheets [144]. Furthermore, free-standing GO membranes exhibit a permeability of 12.19 l/m²/hr/bar, with 100% rejection of Evans blue [145]. Dye separation through the GO membranes is mainly ascribed to the size exclusion mechanism and electrostatic interactions between the molecules and the membrane surface, whereas for salt, the Donnan exclusion mechanism determines the separation performance. Moreover, it has been reported that water flux through the GO membranes decreases with the increasing membrane thickness while also enhancing the solute rejection, which is still lower than the rejection through the polymer RO membranes [25, 119]. In addition, GO membranes exhibit good antifouling [56, 57] performances in water purification applications.

The ionization of carboxylic acid and phenol hydroxyl functional groups in the presence of an aqueous solution results in a negative charge on GO sheets and avoids the aggregation of single-layer GO sheets [147]. Once these GO sheets are assembled into membranes, they become interlocked in a parallel manner, forming mechanically robust membranes that can be easily transferred to another substrate. Because of their electric charge, these membranes can be adopted as ion exchange membranes in nanofiltration [45, 148-150] or electrodialysis [151, 152] processes. Nonetheless, such membranes exhibit a much lower rejection of monovalent anions, indicating the necessity of further improvements for seawater desalination. Liu *et al.* have reported the fabrication of an ultra-thin (100 nm), free-standing rGO FO membrane with a high water flux of 57 l/m²/hr

[146]. The FO membrane greatly alleviates the ICP and shows high mechanical stability, which is suitable for FO. In other studies, GO sheets are tested as a PV membrane for organic dehydration, in which the selective diffusion of water determines the molecule separation performance [153, 154].

Meanwhile, feed pressure and concentration have a direct impact on GO membrane performance [145]. At low pH and high pressure, water permeability decreases but achieves a high solute rejection, resulting from the narrowed interlayer distance that is ascribed to lower repulsive forces between negatively charged GO sheets. Nevertheless, free-standing stacked GE laminates require further improvements since in long-term usage, GO may swell in water and increase its interlayer distance, therefore reducing its effectiveness as a molecular sieving membrane, especially in crossflow testing conditions.

Fig. 2.10. (a) Schematic of the assembled GO laminates prepared by different methods: pressure assisted self-assembly, vacuum assisted self-assembly and evaporation assisted self-assembly [141]. (b) Organic linker, metal cluster and structure of MOF-5 [155].

2.2.3 GE-based nanocomposite

GE or GO can be combined with polymers in two ways: (1) surface modification and (2) embedding into a polymer matrix. As the oxygen functional groups of GO provide reactive sites for membrane functionalization (Fig. 2.11(c)), surfaces of polymer membranes are modified via covalently or non-covalently bonding GO using the LBL approach (Fig. 2.11(a) and (b)), thus improving the membranes' fouling and chemical

resistances at a low cost. Depending on the membrane charge, GO sheets can be used either directly or through a bridging material to non-covalently modify the polymer membrane. Amino GO and TiO_2 are commonly adopted nanoparticles for non-covalent bonding, and modified membranes display better antifouling ability, hydrophilicity and chlorine resistance than unmodified polymer membranes [24, 156, 157]. 1,3,5-benzenetricarbonyl trichloride [158], borate [159] and diamine monomers [160] are employed as crosslinkers for the covalent bonding of adjacent GO sheets to provide stability in water and tune the size of the nanochannels.

GO-embedded composite membranes (Fig. 2.11(c)) are extensively tested for ultrafiltration, nanofiltration, pervaporation and gas separation [161-164]. Inside a polymer matrix, GO sheets stack in a random pattern (Fig. 2.6(c)), providing tortuous pathways through parallel-stacked GO nanosheets and more straight and upright pathways through inclined and vertical GO sheets. Vertical GO stacks have a short transport distance of 2–3 orders of magnitude shorter than parallel stacks, helping to achieve high separation permeance [121]. GO composition in the TFC RO membrane exhibits a positive impact in enhancing the water flux, which is attributed to the increased surface hydrophilicity and the facilitated water flow through the interlayer spacing in GO sheets [165]. Moreover, water permeability increases with increasing concentration of GO until a certain critical concentration is reached, after which it then decreases as a result of blockage of pores and reduction of pore size [166].

In addition, the functionalization of GO nanosheets increases the amorphous nature of the polymer membrane. It has been reported that the addition of functionalized GO nanosheets in the phase inversion process enlarges the pore sizes of the modified membrane, yielding an increase in water permeability [165]. Furthermore, irregularly sized GO nanosheets, which can be obtained by tuning the oxidation condition,

centrifugation and sonication time of the fabrication method, have a significant effect on the performance of GE-embedded composite membranes [121]. The incorporation of nanoparticles such as TiO₂, Ag, CNTs or zeolite with GO sheets fixes the interlayer spacings and improves the stability, water flux, rejection and antimicrobial properties of the resulting membranes.

A mixed matrix membrane prepared from dispersing GO in polysulfone [167], a TFC membrane composed of GO and polyamide [27], rGO-embedded phenylenediamine and trimesoyl chloride monomers [168], and GO and polyethersulfone [169] are tested in RO systems and exhibit more enhanced water permeability than the unmodified membranes of each material. Bano *et al.* have demonstrated that the interfacial polymerization of an rGO and polyamide mixture on a polysulfone microfiltration membrane yields an excellent salt rejection of 88% for NaCl and 97% for MgSO₄ [170]. The rejection of NaCl by a GO/TO composite membrane is increased greatly from 5% to more than 30% with water flux around 710 l/m²/hr/bar, which is 70 times more than commercial NF membranes [171]. A nanocomposite is synthesized by interfacial polymerization between piperazine and trimesoyl chloride monomers and a partially rGO/TiO₂ nanocomposite as a hydrophilic modifier [150]. The membrane exhibits an optimum separation performance, including 60.6 l/hr/m² water flux and 93.57% and 36.61% salt rejection of Na₂SO₄ and NaCl solutions, respectively. As per the above observations, the rejection rate of NaCl through these modified membranes is significantly low and thus may affect their application in seawater desalination.

Meanwhile, it has been reported that MOFs, a novel class of nanoporous materials, can be employed to improve the performance of GO membranes in water purification [58-60]. Those MOF/GO composite structures, as desalination membranes, yield attractive performance due to their highly porous structure.

Fig. 2.11. Schematic illustrations of the GO-based membrane surface modification process via (a) Covalent bonding and (b) non-covalent bonding [166]. (c) Schematic representation of the assembly of GO nanosheets in polymer matrix based on the hydrogen bond between functional groups on GO and polyether block amide [161].

MOF

MOFs have outstanding characteristics, including an exceptionally high surface area (up to 7000 m²/g), pore volume, degree of crystallinity and alterable pore functionalities [172-176]. Metal clusters are combined with organic linkers to produce highly porous MOF structures (Fig. 2.10(b)). MOFs have been considered a versatile material that can be used in applications such as gas storage, gas separation, drug delivery, water purification, desalination, sensors, and so on [49, 58, 177]. Thousands of MOFs have been synthesized, and currently several are commercially available (Cu-BTC (BTC: 1,3,5-benzenetricarboxylate), Fe-BTC, Materials of Institute Lavoisier-53 (MIL-53) and Zeolitic Imidazolate Framework-8 (ZIF-8)) [178]. MOFs have been studied either by

incorporating them into a polymer matrix to fabricate mixed matrix membranes [179-181] or by growing them on a supportive layer to develop continuous MOF membranes [49]. In particular, because of their chemical and thermal stability, ZIF-8 and University of Oslo-66 (UiO-66) based membranes are often studied as RO and PV membranes [49, 182-186] for seawater desalination. When compared with the polymer PV membranes, these two PV membranes yield high water flux and ion rejection with ZIF-8 recorded the highest flux among them. However, the water flux from MOF-based membranes is still quite low in general, not exceeding 14 kg/m²/h.

2.3 MD simulation of seawater desalination

2.3.1 Principles

MD simulation can be used to investigate the structure, dynamics and time-dependent properties of many-body systems, by tracking the position and velocity of each atom. Thus, the MD simulation has been widely adopted to study seawater desalination at the nanoscale.

In MD simulation, Newton's law on the motion is used to track the behavior of the system with possible constraints on ensemble, and trajectories of each atom are analyzed to evaluate the system properties and behavior. Therefore, in MD simulation the first objective is to compute the space trajectories of each atom that is obtained by numerically solving Newton's equation:

$$m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i, \quad (2.1)$$

where m_i , $\vec{r}_i$, and $\vec{F}_i$ are the mass of the i -th atom, its position and force vectors, respectively; t is the time. The interactions between atoms are described by a potential function (U) which is used to derive the force $\vec{F}_i$ acting on each atom using:

$$\vec{F}_i = -\frac{\partial U}{\partial \vec{r}_i}. \quad (2.2)$$

The most common method used to solve Eq. (2.1) and predict the position at time $t + \delta t$ is based on the current position at time t and the previous time $t - \delta t$. This integration approach also known as the Verlet algorithm utilizes the Taylor expansion series of $\vec{r}_i$ at both $t + \delta t$ and $t - \delta t$ as

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t)\delta t + \frac{\vec{a}_i(t)}{2}\delta t^2 + \frac{\vec{b}_i(t)}{6}\delta t^3 + O(\delta t^4), \quad (2.3)$$

$$\vec{r}_i(t - \delta t) = \vec{r}_i(t) - \vec{v}_i(t)\delta t + \frac{\vec{a}_i(t)}{2}\delta t^2 - \frac{\vec{b}_i(t)}{6}\delta t^3 + O(\delta t^4), \quad (2.4)$$

where $\vec{v}_i$ is the velocity of the i -th atom. From the summation of Eqs. 2.3 and 2.4, an expression for the position $\vec{r}_i(t + \delta t)$ can be developed in terms of $\vec{r}_i(t)$ and $\vec{r}_i(t - \delta t)$ as

$$\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \vec{a}_i(t)\delta t^2 + O(\delta t^4). \quad (2.5)$$

From the knowledge of the trajectory, the velocity $\vec{v}_i$ can be derived using

$$\vec{v}_i(t) = \frac{\vec{r}_i(t+\delta t) - \vec{r}_i(t-\delta t)}{2\delta t} + O(\delta t^2). \quad (2.6)$$

The estimation of the new position and velocity contains an error that is of the order $O(\delta t^4)$ and $O(\delta t^4)$. This can be eliminated by using improved versions of the Verlet algorithm, such as velocity-Verlet algorithm:

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t)\delta t + \frac{\vec{a}_i(t)}{2}\delta t^2, \quad (2.7)$$

$$\vec{v}_i(t + \frac{\delta t}{2}) = \vec{v}_i(t) + \frac{\vec{a}_i(t)}{2}\delta t, \quad (2.8)$$

$$\vec{a}_i(t + \delta t) = \left(-\frac{1}{m_i}\right) \frac{\partial U}{\partial \vec{r}_i(t+\delta t)}, \quad (2.9)$$

$$\vec{v}_i(t + \delta t) = \vec{v}_i(t + \frac{\delta t}{2}) + \frac{\vec{a}_i(t)}{2}\delta(t + \delta t)\delta t, \quad (2.10)$$

and leap-frog algorithm [187]:

$$\vec{r}_i(t + \delta t) = \vec{r}_i(t) + (t + \frac{\delta t}{2})\delta t, \quad (2.11)$$

$$\vec{v}_i(t + \frac{\delta t}{2}) = \vec{v}_i(t - \frac{\delta t}{2}) + \vec{a}_i(t)\delta t. \quad (2.12)$$

These algorithms are very simple as well as efficient, stable and reasonably accurate, and thus have been extensively applied in MD simulations.

The general MD simulation approach is exemplified in Fig. 2.12. Different types of MD software packages are available, namely Groningen machine for chemical simulations (GROMACS), Large-scale atomic/molecular massively parallel simulator (LAMMPS), Nanoscale molecular dynamics (NAMD), Chemistry at HARvard macromolecular mechanics (CHARMM), Assisted model building and energy refinement (AMBER) and so on. Among these packages, GROMACS and LAMMPS are free, open-source and user-friendly. Thus, in this study, the MD simulation is conducted by using these two MD packages in Nanyang Technological University high performance computer. The software Visual molecular dynamics (VMD) [188] and Open visualization tool (OVITO) [189] are adopted in visualizing trajectories.

2.3.2 Potential Function

In MD studies, the accuracy of the simulation depends on the interatomic potential function. Generally, this can be expressed as

$$U(\vec{r}_i^{3N}) = \sum_i U_1(\vec{r}_i) + \sum_{i<j} U_2(\vec{r}_i, \vec{r}_j) + \sum_{i<j<k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots, \quad (2.13)$$

where U_1 , U_2 and U_3 are the one, two and three-body interactions, respectively. The U_1 represents the external forces applied on the system such as applied pressure, electric or magnetic field. For example, in the pressure-driven desalination process, this value can arise from the net pressure applied on the system. The two-body or non-bonded interactions are usually described by the Van der Waals (vdW) and Coulombic

interactions. In some cases, these are sufficient to describe the atomic interactions. The vdW interaction is described by using the Lennard-Jones (LJ) potential [190] as

$$U_{2,vdW}(\vec{r}_i, \vec{r}_j) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2.14)$$

where ϵ , σ and r_{ij} characterize the energy well that reflects the interaction strength of an atom pair, the equilibrium interatomic distance and the distance between the i th and j th atom, respectively.

The electrostatic interaction between two atoms can be calculated using the Coulomb's Law:

$$U_{2,elec}(\vec{r}_i, \vec{r}_j) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}}, \quad (2.15)$$

where ϵ_0 and ϵ_r are the vacuum and relative permittivity, respectively; the q_i and q_j denote the partial charges of the i th and j th atoms. Since electrostatic interactions consider long-range interactions, a cutoff scheme might result in a significant error in computation. Furthermore, when a periodic boundary condition is applied, the calculation of these electrostatic forces is significantly expensive. Therefore, electrostatic interaction requires special treatment when truncating them in force calculation. A variety of methods such as the Ewald summation, the reaction field and the cell multiple method have been developed to handle the long-range forces. The Ewald summation is developed for efficient calculation of long-range forces in the Fourier space that is computationally expensive to implement. A promising way to tackle this issue is to modify the problem so that the fast Fourier transform can be used to compute the reciprocal space summation. A number of variants of this general theme have been developed; namely particle-mesh Ewald method and the particle-particle-particle-mesh (pppm).

Fig. 2.12. Simplified flowchart of an MD simulation [191].

For a system containing N atoms, $N^2/2$ interatomic forces must be calculated in each time step, so the computation of these forces is generally costly. Therefore, the LJ potential is usually truncated at a cutoff radius which usually ranges from 2.5σ to 5.5σ . However, when long-range electrostatic interactions are involved, it is recommended to use a much greater cutoff, a value of at least $10 \text{ \AA}$. As stated earlier, more comprehensive methods have been devised to handle electrostatic interactions.

Fig. 2.13. Illustration of bond distance r_{ij} , bend angle θ_{ijk} and torsion angle ϕ_{ijkl} in a chain molecule [187].

The three-body interactions U_3 or bonded interactions imply the intramolecular interactions (bond stretching, angle bending, and dihedral and improper torsions) which can evaluate physical and chemical properties for investigating the bond formation and breakage. The bond stretching associates with vibrations in covalent bonds and can be described using the Hooke's Law or harmonic potential as follows:

$$U_{3,bond}(\vec{r}_i, \vec{r}_j) = \frac{1}{2} k_{ij}^b (r_{ij} - r_0)^2, \quad (2.16)$$

where k_{ij}^b is the force constant and r_0 is the equilibrium bond length.

Similarly, the angle bending, deviation of angles from its equilibrium value is often expressed in terms of a harmonic potential using the force constant (k_{ijk}^θ) and the equilibrium bond angle (θ_0):

$$U_{3,angle}(\vec{\theta}_i, \vec{\theta}_j, \vec{\theta}_k) = \frac{1}{2} k_{ijk}^\theta (\theta_{ijk} - \theta_0)^2. \quad (2.17)$$

Torsional terms are generally explained using a cosine function:

$$U_{3,torsion}(\vec{\phi}_i, \vec{\phi}_j, \vec{\phi}_k, \vec{\phi}_l) = k_\phi (1 + \cos(n\phi_{ijkl} + \phi_s)), \quad (2.18)$$

where k_ϕ , n , ϕ_{ijkl} and ϕ_s are the rotational force constant, the number of maxima (or minima) in one full rotation, the angle between the planes containing i, j, k atoms and j, k, l atoms, and the angular offset, respectively.

2.3.3 Water models

Many different potential functions have been developed to model water structure and can be classified as simple interaction-site, flexible and polarizable models. Rigid water models such as SPC (simple point charge) [192], SPC/E (extended simple point charge) [193], the transferable intermolecular potential 3P (TIP3P) [194] and the transferable intermolecular potential 4P (TIP4P) [194] are commonly used in MD simulations. In these models, interactions between water molecules are calculated using pairwise interaction terms which differ from each other. Thus, calculated water properties show a significant difference. Flexible water models such as flexible simple point charge (SPC/FW) [195] and flexible three-center (F3C) [196] permit internal changes in the conformation of the molecule. These models do not capture the polarizability of water. Meanwhile, models have been developed to include the polarizability and many-body effects [197] that may increase the computation effort required for liquid simulation. Recently, Ho and Striolo have demonstrated that polarizability of water has an insignificant effect on water confined in GE channels [198]. Therefore, in this study, the TIP3P water model is selected as it is a widely used water model in MD simulations and is more computational efficient because the model has less (only 3) interaction sites than other models, such as the TIP4P and TIP5P (the transferable intermolecular potential 5P) models [199, 200].

In MD simulations, the time step is limited by bond oscillations which have relatively high frequency and low amplitude. The time step in MD can be increased by a

factor of four by replacing bond vibrations with constraint algorithms such as SHAKE [201], RATTLE [202] and LINear Constraint Solver (LINCS) [159]. The SHAKE algorithm is generally used in rigid water models to constraint the water structure. At the same accuracy, the LINCS algorithm is three to four times faster than the SHAKE algorithm.

2.3.4 Computation of structural and dynamic properties

To characterize the structural and dynamic properties of the simulation system, the radial distribution function (RDF), mean square displacement (MSD) and potential of mean force (PMF) are often estimated in MD studies.

RDF

The RDF represents the atomic density of atom j around one particular atom of type i , known as the reference atom that varies as a function of distance r from the reference atom. The RDF is defined as $g_{ij}(r)$ by

$$g_{ij}(r) = \frac{N_{ij}(r, r + \Delta r)V}{4\pi r^2 \Delta r N_i N_j}, \quad (2.19)$$

where r is the distance between atoms i and j , $N_{ij}(r, r + \Delta r)$ is the number of atom j around i within a shell from r to $r + \Delta r$, V is the system volume, and N_i and N_j are the number of atoms i and j , respectively.

MSD

The MSD measures the deviation of an atom position with respect to a reference position over time. The MSD is defined as the average of square of displacement, which is given by

$$MSD = \langle |r_i(t) - r_i(0)|^2 \rangle, \quad (2.20)$$

where $r_i(t)$ and $r_i(0)$ denote the position of atom i at time t and at a reference point, respectively. The time point of reference does not require to be the starting point of the simulation. Any time point during the simulation can be treated as the reference point as far as the system consists of a large number of atoms and long simulation duration. Linear fitting of the MSD curve gives the diffusion coefficient D based on the relationship:

$$\lim_{t \rightarrow \infty} \langle |r_i(t) - r_i(0)|^2 \rangle \approx 6Dt, \quad (2.21)$$

with t being the simulation time.

PMF

The PMF describes how the free energy varies as a particular coordinate is changed. This may be estimated using techniques such as umbrella sampling or free energy perturbation in the MD simulation. The umbrella sampling method attempts to overcome the sampling difficulty by modifying the PMF so that unfavorable states are sufficiently sampled. An artificial biasing window potential, $w(x)$, is introduced to enhance the sampling in the neighborhood of a chosen value x . A harmonic function is used to describe the $w(x)$ as:

$$w(x) = \frac{1}{2}K(x - x_0)^2, \quad (2.20)$$

where K and x_0 are the force constant and the equilibrium position on the reaction coordinate line, respectively.

2.3.5 Simulation of desalination at the nanoscale

MD simulations are capable of elucidating the underlying mechanisms of water and ion permeation through nanostructures that are difficult to be examined through the experimental approaches. Thus, MD simulation is widely adopted for predicting the desalination performance of nanomaterial-based membranes [22, 104, 105, 182, 200, 203-

206]. In MD simulations, the selectivity [40, 204], diffusivity [200] and dynamics [206, 207] of membranes have been evaluated by observing the molecular trajectories. In addition, the dependence of desalination performance on factors such as membrane morphology, chemical functionalization, and structural and process parameters has been reported.

The computational setup of an RO desalination system usually consists of two water reservoirs separated from the membrane, where water and ion molecules are subjected to the driving force (external pressure), as exemplified in Fig. 2.14(a). Typically, this applied pressure (hundreds of MPa) is higher than the practical values (usually 5.5 MPa [208]), which is common in nonequilibrium MD simulation, reducing the thermal noise and speeding up the simulation process [124, 182, 204, 209]. Water flux through the membrane has a linear relation with the applied pressure and, therefore, the MD results can be extrapolated to approximate the water permeation at pressure employed in a practical desalination process [22, 124].

Cohen-Tanugi and Grossman are the first researchers who elucidated the desalination performance of an NPG membrane using MD simulations, where the membrane could yield a water permeability of 66 l/cm²/day/MPa with a solute rejection of 99% [204]. The results show that the water permeability and pore size have a linear dependency and follow the Hagen-Poiseuille relation. Furthermore, the researchers have demonstrated that such multilayer NPG membranes could enhance the desalination performance of an RO system via enlarged pore misalignment, which improves the salt rejection while maintaining almost constant water permeation [210]. Yilun *et al.* have systematically evaluated the influence of the size, shape and density of nanopores on the mechanical properties of NPG membranes [125]. They have reported that the membrane strength

decreases with the increase of pore size and porosity, whereas the pore shape has a significant influence on the membrane strength since pores are not perfectly circular.

Fig. 2.14. (a) Schematic of the simulation model of an RO system and (b) functionalized NPG with H atoms [211].

The porous structure of the stacked GE membranes is considered as having cascading nanoslits and described in terms of three aspects, namely the height of the nanochannel, the lateral size of nanosheet and the intralayer distance (gap distance between edges of sheets) [135]. Previous studies have focused on investigating the membrane morphology effect on how water and solute flow through the nanochannel formed between GE layers [137, 205-207, 212, 213]. Yoshida *et al.* investigated the flow across a staggered multilayer GE with nanoslits in a staggered alignment, and an inter-layer distance ranging from a few sub-nanometers to several nanometers [213]. Chen *et al.* studied the mechanism of water transport and ion movement through GE oxide membranes in RO systems using MD simulations [207]. They have explored the effects of staggered nanoslits on desalination properties and made a comparison with the infiltration predicted by the continuum model, showing that both predictions are in agreement with each other.

Using MD simulation, it is proven that a GO framework (GOF) membrane, in which GO nanosheets are covalently connected by boronic acid, is an exceptional choice for

seawater desalination with 100% rejection and two orders higher permeation than conventional RO membranes [159]. The dependence of desalination performance on cross-linker concentration, membrane thickness and applied pressure is investigated to tune the performance, and the findings suggest that a GOF membrane with the same thickness as a commercial RO membrane will yield complete salt rejection with two orders magnitude higher water permeability.

The salt rejection in nanoporous membranes is mainly governed by size exclusion, dehydration and charge repulsion, and interactions between solutes and membranes [214]. Molecular sieving is useful in blocking the passage of large ions such as NO_3^- , SO_4^{2-} and NH_4^+ . Simulations suggest that the pore size should be larger than 3.5 Å to facilitate water transport. Hence, for ions with much smaller ionic radii than this value, such as Na^+ and Cl^- , dehydration plays a pivotal role in determining the ionic transport. In wide pores, ions with their complete hydration shell are able to pass through the pore. As the pore becomes narrower, some water molecules may need to peel off from the shell to fit into the pore, which involves a considerable energetic cost. Consequently, the energy barrier for ion permeation increases with reducing pore size. Meanwhile, membrane selectivity is determined by the sizes of the hydrated ions and their hydration energy. For example, narrow membrane pores exhibit a greater rejection rate for small ions with high electric charge.

Many carbon nanopores contain some degrees of chemical functionalization due to oxidation or intentional modification. Simulation results show that water permeability, membrane selectivity and pore stability are affected by the chemical functionalization (Fig. 2.14(b)) [40, 204, 211, 215-217]. It is reported that hydrogenated pores have a lower water permeability and a higher salt rejection than hydroxylated nanopores, as hydrogen passivation makes the pores hydrophobic by restricting the number of hydrogen bond

configurations [204]. Contrastingly, increasing the pore polarity with hydroxyl groups introduces a hydrophilic characteristic, amplifying both water and ionic flux. Recently, Chen *et al.* have shown the potential for using MD simulations to explore the effect of various doping levels of N in NPG membranes functionalized with N, N-H, ammonia, and N-OH [216]. As these functionalized pores are electrically neutral, they are able to successfully reject both Na^+ and Cl^- ions. Among the studied pore configurations, NOH-doped pores exhibit a complete ion rejection with the highest water permeation rate.

Repulsive electrostatic interactions between the membrane and ions help to prevent the passage of ions through the membrane, which is the underlying mechanism for the selectivity of ion exchange membranes. Because of the intensified energetic barrier for coions permeation, coions are effectively excluded from admitting the membrane, while counterions are selectively permeated through the membrane [40, 218]. However, their selectivity depends on the pore size, feed concentration and external electric field and pressure.

In addition, MD simulation can also be used to investigate the structural resilience of GE-based membranes in water desalination, especially in RO systems where high pressure is applied as the driving force [127, 219]. An NPG membrane over a substrate with pores no greater than 1 μm would be expected to withstand hydraulic pressures upward of 57 MPa, which is nearly 10 times higher than in typical seawater RO operations today [127]. It is also possible to evaluate free energy profiles, including for Helmholtz free energy to provide basic information about the driving force behind the desalination process [220-222]. Free energy profiles provide information related to the behaviour in the membrane interface.

As with RO, the osmosis phenomenon is also explored, adopting an MD method [223, 224]. However, the FO desalination performance of GE-based membranes has been

studied in only a few studies [104, 105]. So far, MD simulation studies have been conducted to explore the osmosis phenomena through monolayer NPG membranes with or without pore functionalization. These studies demonstrate that GE membranes are mechanically strong enough to be used in FO systems without an SL, and thus are more efficient than CNT FO membranes [225]. Moreover, the effects of pore diameter, feed temperature and concentration on the desalination performance, along with the interactions between membrane atoms and water molecules and ions, are methodically investigated. However, there is a further opportunity for exploring novel membrane configurations that, unlike NPG membrane, are economically and technologically feasible in large scale fabrication.

Membrane processes with an external electric field are also studied employing MD simulation [218, 226]. The dependence of electroosmotic flow, electrosorption, and ion and water molecule behavior on the electric field are systematically investigated. Most of the previous MD studies on electrosorption are mainly focused on supercapacitors [81], and only a few are related to seawater desalination. Kalluri *et al.* have conducted a simulation study to investigate the structural properties of aqueous electrolytes confined within a GE slit-pore [227]. The study has revealed that under the effect of surface-charged GE layers, ions move toward the electrode because of the counterion condensation effects, at the expense of losing part of their hydration shell. Furthermore, the researchers have studied the pore size dependent accumulation of aqueous electrolytes in slit-shaped graphitic carbon pores of different widths [228]. Ho and Striolo have shown that capacitive enhancement can be achieved by introducing nanoscopic squares and stripes patterns into a flat GE electrode [229]. Based on the findings of this study, a new GE-based composite electrode that manipulates the structural and dynamic properties of

its electric double layer has been developed in the context of a proposed continuous desalination approach [230].

2.4 Summary

The fundamentals of seawater desalination including different desalination methods and their working principles, progress and challenges are reviewed. Among these methods, FO, CDI and PV have recently emerged as potential low energy desalination technologies. Thus, uncovering the fluid transport and separation mechanisms of these methods is essential for the development of next-generation desalination systems.

Due to the advancement in nanotechnology, 2D nanomaterials such as GE-based structures have been extensively studied as desalination membranes because of their ultra-fast water flux and chemical and mechanical stability. Particular attention is devoted in this review to exploring GE-based structures and their desalination performance. In both experimental and theoretical studies, GE-based membranes with lamellar structure have shown great potential for water purification by partially removing ions via nanofiltration and selectively extracting water from solutions. However, a more fundamental understanding of their nanostructures and how to effectively control and design such membranes for advanced desalination processes is needed to exploit this new material for developing a sustainable desalination system.

MD simulation is commonly adopted in seawater desalination studies to investigate the nanoscale fluid behavior, underlying mechanisms of ion rejection and membrane selectivity in different membrane materials. This method is also used to examine the effects of pore structure, chemical functionalization, membrane configuration and operating conditions on the desalination performance. The principles of MD simulation and its application in seawater desalination are presented.

Chapter 3. Corrugated GE Layers for Seawater Desalination via CDI

The surface corrugation of GE can modify its electronic, optical, mechanical, and chemical properties. However, in fundamental analysis, the corrugation effect on the desalination performance of GE-based structures has hardly been studied. This chapter investigates the effect of GE morphology on the CDI process in detail. Furthermore, the dependence of the desalination performance on the electric field and nanochannel entrance configuration is explored.

3.1 Introduction

In most theoretical studies, GE sheets are treated as ideally flat and smooth [205, 231], and lack of attention has been paid to study the corrugation effect on the desalination performance of GE-based membranes or electrodes. The corrugation or ripples in GE is an intrinsic feature that can be controlled in terms of ripple orientation, amplitude, and wavelength and has a strong influence on electronic properties and chemical activity of GE [114, 115, 232]. Qui *et al.* have experimentally shown that the corrugation amplitude of CCG sheets can be controlled through hydrothermal treatment and have demonstrated the potential for enhancing the desalination performance in nanofiltration [137]. Recently, Bo *et al.* investigated the effect of GE morphology on the water transport behaviors through GE bilayers via MD simulations, and the results elucidate that the GE morphology significantly changes the distribution of the water molecules, their orientation and interaction inside the nanochannel [206]. Furthermore, the effect of corrugation on desalination performance through a series of bilayer GE as an RO membrane is explored using MD simulations. The results reveal that the intruding

GE surface has an adverse effect on lowering the water flux, yet has a water permeability of 1020 kg.m/hr/bar, which is three orders higher than the permeability of a commercial RO membrane [233].

No previous research has investigated the dependence of electrosorption separation on the GE morphology. Therefore, the study presented in this chapter intends to evaluate the contribution of GE morphology to CDI using MD simulations.

3.2 Simulation methods

Two corrugated GE layers are placed inside the simulation box to construct a slit pore nanochannel with an entrance width d of 16 Å, as shown in Fig. 3.1. Dimensions of the GE layers along the x and y axes are 120 Å and 20 Å, respectively. According to observations from the study by *Bao et al.*, ripple crests of the GE layers are perpendicular edges of the trench (x -direction) and the out of plane displacement z can be described by a sinusoidal function [114]:

$$z = A \sin\left(\frac{2\pi x}{\lambda}\right), \quad (3.1)$$

where A is the amplitude and λ represents the wavelength. Hence, the corrugation in GE layers is introduced using Eq. (3.1) but the lower layer is set to have a 180° phase shift with respect to the upper layer. Two ends of the GE layers are connected to four vertical GE planes to ensure that water flows only through the channel. At the beginning of the simulation, the left reservoir consists of saline water (27 Na⁺ and 27 Cl⁻ ions solvated with 1175 water molecules) and the right reservoir is filled with pure water (1229 water molecules). As a result, the overall system is retained as electrically neutral with the salinity around 3.5% which is representative of the typical salt concentration in seawater, and the mass density around 1 g/cm³.

Fig. 3.1. Schematic of the simulation model. Cyan, grey and red colours represent C, O and H atoms, respectively. The Na^+ and Cl^- ions are represented by yellow and green colours, respectively.

The simulations are carried out using the LAMMPS package [234]. Periodic boundary conditions are applied in all three directions. The TIP3P water model [235] is adopted to construct water molecules. The CHARMM27 force field [236] is used to describe both the bonded and non-bonded interatomic interactions between the O and H atoms. The particle-mesh Ewald summation technique is applied to compute the long-range electrostatic interactions with a cutoff distance of 12 Å. The vdW interactions between two atoms are described by the LJ potential as in Eq. (2.14).

The interaction between the GE layers and water molecules is modelled as vdW interactions between the C and O atoms, while the interactions among the water molecules and ions are modelled as vdW interactions for all the atom pairs. The vdW interaction parameters are adopted from the literature for the C atoms [237] and the ions [238]. The interaction between species i and j is estimated using the Lorentz-Berthelot mixing rules [123].

All the simulations are performed under the constant volume and temperature (NVT) ensemble with the temperature kept at 300 K. The temperature is calculated with the center-of-mass velocity subtracted. To investigate the effect of the GE morphology on the

deionization performance, the GE layers are treated as rigid walls to prevent out-of-place displacement.

To drive the water molecules to flow through the channel, a high pressure of 500 MPa is applied to the left water reservoir along the x -direction by directly applying a constant force to each water molecules inside it as described in the literature [23]. The high pressure of 500 MPa is adopted to speed up the simulation since a low driving pressure would cause a long time for the simulation to achieve a steady state. An electric field with the intensity amplitude E is applied in the z -direction along the channel region to simulate the electrosorption process. Five different simulation cases are performed by applying different intensities of E (0, 0.25, 0.50, 0.75 and 1.0 V/ Å) to evaluate the effect of an external electrical field on the deionization process. Furthermore, to explore the GE surface morphology effect, different configurations are introduced by varying λ of 20, 30, 40 Å ($A = 2$ Å and $E = 1.0$ V/ Å) and A of 0, 1, 2, 3 Å ($\lambda = 30$ Å and $E = 1.0$ V/ Å). According to the experimental results, the amplitude of GE ripples is taken to be less than 5 Å [239].

The time step of 1 fs is used and the total simulation time in the range of 700 to 800 ps is adopted to achieve a steady state condition. Upon reaching the steady state, the deionization process performance is characterized in terms of the water flux and ion adsorption. A longer simulation time of 2 ns is also tested, and the water flux is obtained to be the same with the water flux at 700 ps. Hence, the simulation time period of 700 to 800 ps is deemed to be long enough to obtain converged results. The simulation results are analyzed by investigating the water density distribution, RDF and ion distribution pattern along the channel. The water density distribution and RDF are captured at different regions, as shown in Fig. 3.2(a). Regions 1 and 3 are named as “narrow” regions which are bounded from troughs of the upper GE layer and crests of the lower GE layer.

Regions 0, 2 and 4 are named as “wide” regions which are bounded from the crests of the upper GE layer and troughs of the lower GE layer.

Fig. 3.2. (a) Representation of different regions inside the channel for capturing the water density and RDF. (b) Closing, (c) opening and (d) concurrent types of entrance configurations.

In nanofluidics, the entrance configuration plays a significant role in affecting the flow behaviors through nanochannels [240]. Hence, the entrance effect on CDI performance is also investigated in this study. Depending on the arrangements of the upper and lower GE layers, three different types of entrance configurations have been identified and depicted in Fig. 3.2. The afore-mentioned GE layer arrangement, as shown in Figs. 3.2(a) and (b), has a “closing” entrance configuration in which one GE layer is a mirror image of the other layer. In the second type, two GE layers are similar to the previous arrangement, but the starting point of the nanochannel is selected such that it has “opening” entrance geometry (Fig. 3.2(c)). The last entrance configuration is named as “concurrent” where two layers are in the same phase (Fig. 3.2(d)).

3.3 Results and discussion

3.3.1 Effect of electric field

The effect of the electric field on ion distribution within the corrugated and flat GE layer channels are firstly investigated, as shown in Fig. 3.3. When the electrical field is not applied, the ions spread all along the channel and their locations present a random pattern (Fig. 3.3(a)).

Fig. 3.3. (a) and (b) Simulation snapshots of corrugated GE channel with electric field intensities of $E = 0.0$ and $1.0 \text{ V/\AA}$, respectively. (c) Simulation snapshot of flat GE channel with an electric field intensity of $E = 1.0 \text{ V/\AA}$.

Contrastingly, when the GE channel exposes to an external field, counter ions move towards the upper and lower GE layers (Figs. 3.3(b) and (c)). These observations are in agreement with the previous study [227]. Further analysis reveals that the corrugated GE channel has a limited area for electrosorption since the ions only distribute at the wide regions near the entrance (Fig. 3.2(a)) due to the anchoring effect caused by the crests of upper layer and troughs of lower GE layer. In the narrow regions, electrostatic force imposed by the external field is not strong enough to anchor the ions at the GE surface. As a result, the ions move with the water stream and enter the wide regions. This ion distribution is significantly different from that in the flat GE layers where the ions almost distribute evenly along the whole channel length direction (x -direction).

Fig. 3.4 illustrates the accumulation of ions (N_i) inside the corrugated GE layers within the simulated time period for an exemplified case of $\lambda = 40 \text{ \AA}$ and $A = 2 \text{ \AA}$. It is

evident that the number of ions increases significantly at the beginning of the simulation. After the initial adsorption stage of 100 ps, ions are adsorbed and concentrated near the entrance of the nanochannel. Therefore, there exists a high energy barrier for the ions in the left reservoir, to further enter into the channel and accumulation of ions slows down. With time, some ions in the R0 region roll over to the next wide region (R2) by chance and create a space near the entrance region so that ions in the left reservoir can enter into the channel. As a result, the number of ions inside the channel increases in a stepwise manner. Moreover, the ions aggregate inside the channel at a faster rate under a weaker electric field intensity ($E = 0.25 \text{ V/\AA}$), and as explained earlier, these ions in the entrance region would lead to a high energy barrier for more ions to penetrate inside the channel. Under a higher external electrical field, this energy barrier is further enhanced and thus blocks the entering of the ions.

Fig. 3.4. Ion accumulation N_i inside the nanochannel ($\lambda = 40 \text{ \AA}$ and $A = 2 \text{ \AA}$) during simulation time span for different intensities of the electric field.

It should be noted that such a phenomenon relies on the small distance between the GE layers. With such a small distance, the entrance of the channel plays a significant role in blocking the entrance of the ions, particularly with the ion accumulation near it. For a

large interlayer distance, the ion can enter the channel without being blocked by the entrance. After they enter the channel, they will be adsorbed at the GE surface and their movement will mainly be constrained by the GE corrugations. As will be evidenced in Fig. 3.8(b), the velocity of the ions inside the channel does not change significantly when the electric field intensity E increases from 0.25 V/Å to 1 V/Å . Hence, it is expected that for a larger interlayer distance, the ion adsorption at the lower $E = 0.25 \text{ V/Å}$ is expected to be close to those at a higher intensity.

The density distribution profiles along the channel thickness (z -direction) direction for the case of $\lambda = 40 \text{ Å}$, $A = 2 \text{ Å}$ and $E = 1.0 \text{ V/Å}$ are displayed in Fig. 3.5. In the regions 1, 3 and 4 (R1, R3 and R4) that are free from anchored ions, density profiles of O and H (Figs. 3.5(a), (c) and (d)) have a qualitatively similar pattern which is close to that observed in systems without the effect of the electric field. In these regions, the density distributions of O and H atoms are similar to each other and symmetric about the middle of the channel along the z -direction. Well-defined water layers can be observed as indicated by the density peaks near the channel walls which is in good agreement with previous studies [227, 241].

For the wide region 2 (R2), the concentrations of the Na^+ and Cl^- ions are observed as proved by their density peaks near the GE layers. Meanwhile, the density distribution of the H and O atoms of water (i.e., HW and OW, respectively) show a significant change, particularly near the concentration of the ions, as compared with those in region R4, and become asymmetric about the center of the channel, indicating rearrangement of water molecules due to the adsorption of ions. As Na^+ ions are trapped inside the troughs of the upper GE layer in response to the electric field, H density peak near the upper GE layer shifted away from it by a distance of around 2.5 Å and a new H density peak appears at the Na^+ ion concentration area. However, there are no significant changes to the H density

distribution near the lower GE layer where Cl^- ions are concentrated, leading to the asymmetry of the H atom distribution. A similar change can be observed for the distribution of the O atoms near the GE layers. The water density varies with the region and indicates the inhomogeneity of water in nanoconfined volume.

Fig. 3.5. Density distributions of the OW and HW atoms, and the Na^+ and Cl^- ions along the channel thickness direction for the configuration of $A = 2 \text{ \AA}$, $\lambda = 40 \text{ \AA}$ and $E = 1.0 \text{ V/\AA}$. (a) - (d) for regions 1, 2, 3 and 4, respectively.

The asymmetric changes at the upper and lower GE layers in region R2 is mainly due to the different energy barrier for the Na^+ and Cl^- ions to lose their hydration shells. For the electric field intensity of $E = 1.0 \text{ V/\AA}$, it is strong enough to peel off the hydration shells of the Na^+ ions and push them close to the upper GE layer, but insufficient for the Cl^- ions to lose their hydration shells. Further simulation results show that under the intensity of $E = 1.0 \text{ V/\AA}$, the average distance of the Na^+ and Cl^- ions to the flat GE surface is around $2.5 \text{ \AA}$ and $3.5 \text{ \AA}$, respectively. When the intensity decreases, these

distances increase (Fig. 3.6), and the distributions of the O and H atoms also get close to those in region R4 without ion concentration. Similar results have been reported in the previous study for confined aqueous NaCl solution within charged carbon slit pore [227].

Fig. 3.6. Dependence of ion concentration in the region R0 on the electric field intensity.

Fig. 3.7. RDFs $g(r)$ for the (a) Na^+ -OW (b) Cl^- -OW atom pairs, in bulk water and the region R2 for the configuration of $A = 2 \text{ \AA}$ and $\lambda = 40 \text{ \AA}$. The vertical green dashed lines indicate the first peak of the distribution functions.

Furthermore, to investigate the peel off of the hydration shells of the Na^+ ions under the electric field intensity of $E = 1.0 \text{ V/\AA}$, RDF for the Na^+ -OW atom pairs in the region R2 is calculated and compared with that for $E = 0 \text{ V/\AA}$ (Fig. 3.7(a)). For reference, the

RDF for the Na^+ -OW atom pairs in bulk water is also calculated. The appearance of the first peak in the RDF function indicates the formation of the first hydration shell around the Na^+ ions. Due to the severe confinement of the corrugated GE layers, the peak heights of the RDF inside the channel are much higher than that in the bulk phase. Moreover, at the electrical field intensity of $E = 1.0 \text{ V/\AA}$, the peak height increases apparently. Bahlakeh *et al.* have shown that with increasing hydration level, the peak height of the RDF would decrease due to the fact that the addition of water molecules around the ion weakens their interaction [242]. Therefore, it is evident that the volume confinement in nanochannel has greatly reduced the hydration shell of Na^+ and is further reduced by the applied electric field. Similarly, Cl^- -OW atom pair interaction is investigated as shown in Fig. 3.7(b). It is evident that the hydration level of Cl^- ions in region R2 does not exhibit a significant variation with the electric field intensity and Cl^- ions have a higher hydration level than Na^+ ions.

The water flow rate, ion adsorption, and water and ion velocities as functions of the applied electric field are depicted in Fig. 3.8. In the absence of an external electrical field, for corrugated GE layer channel, a high water flow rate of around $9 \times 10^{-12} \text{ mol/s}$ can be observed (Fig. 3.8(a)). Ions entering into the channel have similar high velocity as water molecules (Fig. 3.8(b)) and exit from the channel along with the water stream. This observation confirms that no ions are adsorbed on to the GE layers. In contrast, when the channel is exposed to an external electric field perpendicular to the GE layers, the existence of anchoring effect is evidenced by the low velocity of both the water molecules and ions inside the channel. This yields a 77% flow rate reduction in the system with $E = 0.25 \text{ V/\AA}$, and the velocity of ions reduces to also zero. As the field intensity E raises from 0.25 to 0.5 $\text{V/\AA}$, there observes a slight rise in the water flow which attributes to the reduction in adsorbed ions inside the channel. This reduction is caused by the blocking

effect of the entrance at a more intensive electric field which hinders the admittance of ions into the system. Fig. 3.8(a) further elucidates that the water flow rate is not affected by the increasing electric field intensity but is mainly affected by the number of ions adsorbed on the GE surface due to the friction force imposed by the anchored ions.

Fig. 3.8. Dependence of (a, c) the water flow rate, and the number of ions inside the channel, and (b, d) the velocity of water molecules and ions inside the channel along the x -direction on the external electric field intensity E . In (a) and (b), the GE layers have the corrugated surfaces with $A = 2 \text{ \AA}$ and $\lambda = 40 \text{ \AA}$. In (c) and (d), GE layers are flat.

For comparison, the water flow rate, number of ions inside the channel and velocities of water molecules and ions are also investigated for the flat GE layer channel (Figs. 3.8(c) and (d)). At zero electric field, the average number of ions inside the channel is 28 and decreases to the lowest of 23 at the field intensity $E = 0.25 \text{ V}/\text{\AA}$. As the E increases to $1.0 \text{ V}/\text{\AA}$ the number of ions inside the channel increases and recovers to the level recorded at the zero electric field intensity. Different from the nonmonotonic dependence

of the number of ions on the intensity E , the water flow rate decreases monotonically with the increasing intensity E . Moreover, along the x -direction, ions have a similar high velocity as water molecules and exhibit a decreasing trend with rising E (Fig. 3.8(d)).

For the flat GE layers, in the absence of an electric field, ions are distributed randomly inside the channel as observed in the corrugated GE channel. When the channel exposes to the external electric field, ions move towards the GE layers (Fig. 3.3(b)) due to electrostatic attraction. However, the electrostatic force is not strong enough to overcome the force from the moving water stream since no barrier is applied by the GE wall to trap these ions. Therefore, ions move forward along the channel wall and present a high velocity. This indicates that for flat GE layers, the anchoring effect is absent, and the ions can flow through the nanochannel and is not adsorbed at the GE layers though the same external electrical field as for the corrugated GE layers is applied. Moreover, in the flat GE layer channel, ions do not concentrate at the entrance region of the channel and do not block the admittance of more ions. This effect allows more ions to pass through the channel even at high field intensity E .

The different transport behaviors of the ions and water molecules inside the flat and corrugated GE layers suggest that corrugated GE layers have the ability to adsorb ions due to ripples morphology of GE. The main drawback of the corrugated GE channel is that reduced water flow and possibly can increase through methods proposed in previous studies [243, 244].

3.3.2 Effect of wavelength and amplitude

The dependence of the desalination performance on the GE surface corrugation parameters is presented in Fig. 3.9. Fig. 3.9(a) shows that both the water flow rate and ion adsorption increase with the increase of the wavelength λ . As the wavelength λ increases,

the flow resistance arises from the GE ripples depletes and as a result the water flow rate increases, which is consistent with the previous study on the channel morphology effect on the water transport inside GE bilayers [206]. At the same time, for a given amplitude A , the accessible volume at the wide regions increases with the wavelength λ . Therefore, the number of ions that can be adsorbed at each wide region (Fig. 3.2(a)) increases for a larger λ .

Fig. 3.9(b) illustrates the variation of water flow rate and ion adsorption as a function of amplitude A ($\lambda = 30 \text{ \AA}$ and $E = 1.0 \text{ V/\AA}$). As the wave amplitude A increases from $1 \text{ \AA}$ to $3 \text{ \AA}$, the number of ions adsorbed inside the nanochannel decreases significantly. This is because the ions adsorbed at the wide region tend to locate close to the GE layers. Although the total area of the wide region increases as the wave amplitude increases, the effective area for hosting the adsorbed ions reduces, leading to a decrease in the number of adsorbed ions.

Fig. 3.9. Dependence of the water flow rate and the number of ions adsorbed on the (a) wavelength λ and (b) amplitude A . In (a) the amplitude A is $2 \text{ \AA}$, and in (b) the wavelength λ is $30 \text{ \AA}$. For both cases, the electric field intensity is set as $E = 1.0 \text{ V/\AA}$.

In contrast to the monotonic decrease of the number of ions adsorbed, the water flow rate first increases and then decreases as A increases from $1 \text{ \AA}$ to $3 \text{ \AA}$. Such nonmonotonic dependence is the combining result of the blocking effect of the corrugated

GE layers and the flow resisting effect of the ions. As reported in the previous study, the water flow reduces with the increasing amplitude A , which is attributed to the blocked water movement along the channel length (x -direction) by the GE layers due to the extruding of the GE layers inside the water stream [206]. However, the increase of the amplitude A leads to the reduction of the number of ions adsorbed. As a result, the friction force imposed on the water molecules by the ions also decreases. Therefore, the enhancement of the blocking effect of the GE layers is compensated by the weakening of the flow resisting effect of ions, demonstrating the nonmonotonic change of the water flow rate.

Besides affecting the ion adsorption and the water flow rate, the GE corrugation also changes the distribution of the ions and water molecules inside the channel. Figs. 3.10(a) and (b) show the time-average ion distribution along the channel for $\lambda = 20$ and $40 \text{ \AA}$, respectively. At smaller wavelength $\lambda = 20 \text{ \AA}$, the ions are captured from the first three wide regions and for a larger wavelength $\lambda = 40 \text{ \AA}$, the ions are trapped at the first two wide regions in which the total number of adsorbed ions is higher than that for $\lambda = 20 \text{ \AA}$. In the present work, the distance between the GE layers is about $16 \text{ \AA}$. Such a small distance can function to block the entering of the ions inside the nanochannel with the assist of the external electric field as afore-mentioned. Therefore, for a small interlayer distance, the external electric field not only can induce electrosorption but also can help to enhance the nanofiltration, particularly at small wavelength λ . For a practical CDI process, the distance between two electrodes would be much larger and nanofiltration would not occur. Under such conditions, it would be desirable that a relatively large wavelength is presented in the corrugated GE to provide a larger accessible area for electrosorption. Similar ion distribution can be observed for different wave amplitudes as shown in Figs. 3.10(c) and (d). It is evident that the blocking effect of the corrugated GE

layers reduces as amplitude decreases since ions are anchored at the first three wide regions for $A = 1 \text{ \AA}$ but only at the first two wide regions for $A = 3 \text{ \AA}$.

Fig. 3.10. Na^+ ion distribution along the channel for different channel morphology parameters: (a) $\lambda = 20 \text{ \AA}$, $A = 2 \text{ \AA}$, (b) $\lambda = 40 \text{ \AA}$, $A = 2 \text{ \AA}$, (c) $A = 1 \text{ \AA}$, $\lambda = 30 \text{ \AA}$ and (d) $A = 3 \text{ \AA}$, $\lambda = 30 \text{ \AA}$. For all the cases electric field intensity is set at $E = 1.0 \text{ V/ \AA}$.

To characterize the change of the distribution of the water molecules, the RDF for the OW-OW atom pairs is calculated and shown in Fig. 3.11 for different regions inside the channel with $A = 1 \text{ \AA}$ and $\lambda = 30 \text{ \AA}$. For comparison, the RDF for the bulk water is also plotted. The R1 and R3 regions are narrow regions (Fig. 3.2(a)). The R2 and R4 regions are wide regions with and without adsorbed ions, respectively. The first peak of the RDF curves of the water molecules in the channel exhibit higher amplitudes compared to that of the bulk water, which is a direct result of the volume confinement. Moreover, the peak heights for the narrow regions are higher than those of the wide regions, indicating a more

intensive volume confinement effect. For regions R2 and R4 which have the same volume, the peak height in the region R2 is higher than that in the region R4 due to the adsorption of ions in R2 which reduces the accessible volume for the water molecules and enhances the volume confinement. Though the variance of volume confinement, the location of the first peaks are 2.8 Å, in agreement with previous studies [245, 246].

Fig. 3.11. RDF $g(r)$ for the OW-OW atom pairs in different regions inside the channel with configuration of $A = 1$ Å, $\lambda = 30$ Å and $E = 1.0$ V/Å. The vertical green dashed line indicates the first peak of the distribution function.

3.3.3 Effect of entrance configuration

The effects of the closing, opening, and concurrent entrance configurations on the water flow rate and ion adsorption are investigated, and the simulation results are presented in Fig. 3.12. Overall, the water flow rate increases in the order of closing, opening and concurrent entrance configurations (Fig. 3.12(a)), while the number of ions adsorbed increases in the order of opening, concurrent and closing configuration. The effect of the entrance configuration is more prominent at a higher electrical intensity of $E = 1.0$ V/Å than $E = 0.25$ V/Å. For the latter case, the water flow rate and the number of

ions adsorbed show only slight changes as the entrance configuration changes. Moreover, it is observed that the dependence of the water flow rate on the wavelength λ and amplitude A is well preserved despite the change of the entrance configuration. For a larger λ (or larger A), the water flow rate is always higher (or lower). However, the effect of the wave amplitude on the number of ions adsorbed at the GE surface is retained, but the effect of the wavelength disappears. For all entrance configurations considered, the number of ions adsorbed is higher for smaller wave amplitude. For the opening and concurrent entrance, the number of ions adsorbed remains almost the same as the wavelength increases.

Fig. 3.12. Dependence of (a) the water flow rate and (b) the number of ions adsorbed by the channel on different entrance configurations. The default simulation parameter set is $A = 1$ Å, $\lambda = 20$ Å and $E = 1.0$ V/ Å, and the results of this case are shown by the solid triangle as reference data sets, one parameter is changed each time as (indicated by the legend) to show its influence.

To understand the effect of the entrance configuration on the ion adsorption, the distribution of the ions in the simulation system is investigated for different entrance configurations with the case of $A = 3$ Å, $\lambda = 20$ Å and $E = 1.0$ V/ Å, as shown in Fig. 3.13. It is observed that more ions enter the nanochannel for the closing entrance than the other two entrance configurations. This is because of the closing configuration that has the

highest accessible volume near the entrance with the largest effective channel width of 14.6 Å (Fig. 3.13(a)), since the region is formed by the crest and trough of the upper and lower GE layers, respectively. As a result, the closing entrance facilitates the admittance of more ions (Fig. 3.13(b)) into the channel without losing their hydration shell (7.2 and 6.6 Å for Na⁺ and Cl⁻, respectively). After entering the channel, these ions are anchored by the channel walls at the wide region near the entrance. As the ions accumulate near the entrance, they start to block the entering of the water molecules and their movement along the water flow direction, leading to the lower water flow rate than those for the opening and concurrent entrance configurations.

For the opening entrance, the accessible volume near the entrance is much smaller than that for the closing entrance. To enter the nanochannel, the ions have to pass the region with the smallest effective channel width of 10.6 Å, which leads to a much higher energy barrier for the movement of the ions and blocks the entrance of the ions. Similarly, in the concurrent entrance, the water flow is not intensively blocked and presents a higher flow rate than the other two entrance configurations.

Both experimental and theoretical studies [114, 247-249] have demonstrated various ripple manipulation techniques for GE. GE layers placed on the SiO₂ substrate seem to follow the corrugation of the substrates [250]. Furthermore, the periodicity of GE ripples can be manipulated via transferring GE on to pre-strained elastomeric materials, and both the amplitude and periodicity can be reduced with the increase of prestrain on the substrate material [248]. Hence corrugation of GE layers can be controlled by controlling the substrate morphology that is practical to achieve. Therefore, the studied entrance configurations are possible to introduce into real systems, and the results from the present study will be helpful in the design and fabrication of effective nanochannels for CDI.

Fig. 3.13. Ion distribution inside the channel ($A = 3 \text{ \AA}$, $\lambda = 20 \text{ \AA}$ and $E = 1.0 \text{ V/ \AA}$) for different entrance configurations: (a) Closing, (b) opening and (c) concurrent entrance types.

3.4 Summary

MD simulations have been carried out to investigate CDI performances through nanochannels formed by two corrugated GE layers. In contrast to the nanochannel formed by the flat GE layers, the simulation results show that the corrugated GE channels can deplete the water flow rate and greatly enhance the ion removal capacity. Reduced water flow in the corrugated GE channel is attributed to the following reasons: (1) blocked water movement along the x -direction by the extruding of the GE walls and the friction imposed by the adsorbed ions; (2) blocked entrance of the water molecules inside the channel due to the adsorbed ions in the region close to the channel entrance. The enhanced ion removal capacity is due to the strong anchoring effect existing in the wide regions which are bounded by crests and troughs of the upper and lower GE layers, respectively.

Detailed analysis reveals that in corrugated layer GE channels, the water flow rate, and ion removal capacity increase with increasing wavelength λ and decrease with increasing amplitude A . In addition, the ion adsorption is enhanced at a lower electric field intensity E . Inside the channel, ions accumulate in a stepwise increasing pattern. The density distribution profiles along the channel thickness direction (z -direction) and ions

distribution profiles along the channel length direction (x -direction) are used to exemplify the electrosorption characteristics of the corrugated GE channel. Moreover, three different entrance configurations have been studied, namely closing, opening and concurrent, to investigate the entrance effect on CDI performances. The water flow rate increases in the order of closing, opening and concurrent arrangements, while the number of ions adsorbed increases in the order of opening, concurrent and closing configuration. The effect of the entrance configuration on CDI performances is more significant at higher field intensity.

Chapter 4. GE Membranes with Nanoslits for Seawater Desalination via FO

Molecule separation through CCG thin film membrane is influenced by its structural parameters, such as the interlayer distance, pore width and misalignment, and the number of GE layers. However, their effects on FO desalination performance has hardly been studied. This chapter investigates the effects of membrane structural parameters and operating conditions on seawater desalination performance through stacked GE layers as an FO membrane.

4.1 Introduction

Recently, nanomaterials based on carbon such as CNT and GE emerged as excellent platforms for FO membranes fabrication [22, 127, 205, 206, 212]. In practice, CNTs, as FO membranes, are embedded in a polymer matrix and require support from a supportive layer which has an adverse effect on reducing the water flux [251]. Unlike CNTs, stacked CCG layers can withstand not having a supportive layer [252] because of their high mechanical strength [21, 146]. Therefore, CCG thin films can greatly alleviate the ICP observed in conventional FO membranes [146]. The porous structure of those GE membranes is considered to be cascading nanoslits and is described in terms of three aspects, namely, the height of the nanochannel, the lateral size of the nanosheet, and the intralayer distance [135]. Previous studies focused on investigating the membrane morphology effect on how water and solute flow through the nanochannel formed between GE layers as a membrane in pressure driven separation [137, 205-207, 212, 213]. However, the desalination performance of stacked GE laminates, as an FO membrane,

has hardly been investigated. Thus, this study intends to explore the dependence of the desalination performance of stacked GE thin films as an FO membrane.

Filtration is the most heavily exploited technique in the preparation of stacked GE laminates [253]. As reported in the literature, the nanochannel size can be manipulated by controlling the CCG sheet size [142] and stacking of GE sheets using different filtration conditions [135]. As such, the fabrication of stacked GE membranes with desired dimensions is realistic. The bilayer GE membrane is selected as the model membrane because various fabrication approaches of CCG yield a bilayer as the dominant product. The membrane configuration is similar to the dead-end-filtration system, where fluid flows in the direction perpendicular to the membrane. The effects of pore size, pore offset, interlayer separation, and operating conditions such as temperature and DS concentration are systematically investigated to optimize the seawater desalination performance using the FO system.

4.2 Simulation methods

Desalination performance of the bilayer GE membrane in FO systems is studied using the configuration shown in Fig. 4.1(a). The GE membrane consists of two identical GE layers with a width $W = 41 \text{ \AA}$ and a total length $L = 48 \text{ \AA}$ (Fig. 4.1(b)). The membrane has characteristic parameters of pore width d , interlayer distance h , and pore offset distance l . Pristine GE layers are considered as flat to simplify the system. GE membrane is embedded in a water reservoir where the left compartment is filled with the NaCl solution of 0.6 M salinity which is a characteristic of seawater, and the right chamber with the MgCl_2 solution of the concentration of 5.0 M. The MgCl_2 solution is used as DS, because of its high performance, potentially low cost and reduced risk of scale formation

[108]. Initially, the interlayer region between the two GE layers is occupied by pure water as shown in Fig. 4.1(c). Two rigid GE pistons are added at the ends of the reservoir, and they can self-adjust their position during the simulation. Atmosphere pressure is applied to both the pistons by applying a constant force to each of their atoms in the z -direction, as shown by the black arrows (Fig. 4.1(a)). Thus, water diffusion is driven by the chemical potential difference between the two water compartments. A vacuum space with the length $40 \text{ \AA}$ is placed on top of the water reservoir along the z -direction to eliminate the interactions of the system with its images in this direction. Overall, the simulation box size is $x = 49 \text{ \AA}$, $y = 43 \text{ \AA}$ and $z = 130 \text{ \AA}$.

Fig. 4.1. (a) Schematic of the simulation system of the bilayer GE membrane. Cyan, red and white beads represent C, O and H atoms respectively; green, purple and yellow beads represent Na^+ , Mg^{2+} and Cl^- ions respectively. (b) Top view of the GE bilayer membrane. (c) Side view of the bilayer membrane.

The slit-pore GE membrane is fixed and treated as ideal planar during the simulations to prevent out of plane displacement. Hence, the structural parameters of the graphene membrane, including the gap width, the interlayer and offset distances can be well controlled. Good correlations between the membrane structure parameters and the FO performance can thus be obtained. For the effect of distortions in graphene membrane

geometry on the ions and water molecules transport, the readers are recommended to refer our previous works [206, 254]. Carbon atoms are described as uncharged LJ particles using parameters from the AMBER03 force field [255]. The periodic boundary conditions are applied in all directions to mimic an infinitely large membrane. Charged GE sheets are favourable to the interaction with the ions due to the electrostatic interaction. As a result, the ions that enter into the membrane will be trapped in the interlayer region and would largely complicate the water transport through the membrane. as non-polarized and zero charged membrane. Water molecules are modelled using the TIP3P [194] water model and their rigid geometry is maintained by using the constraint algorithm, LINCS [159]. The Na^+ , Mg^{2+} and Cl^- ions are modelled as LJ particles and their interaction parameters are adopted from the AMBER03 force field [255]. The LJ interaction is evaluated with a cutoff of 14 Å and the Coulombic interaction is evaluated using the particle-mesh Ewald method with a grid spacing of 1.2 Å and a fourth-order interpolation.

The system is first subjected to energy minimization using the steepest descent method with a step size of 0.1 Å and converged to a maximum force of 100 kJ/mol/Å. Afterwards, the initial velocities of atoms are assigned using the Maxwell-Boltzman distribution at the temperature of 298K. The temperature is controlled by using the velocity-rescaled Berendsen thermostat [256] with the relaxation time of 0.1 ps. The Leap-frog algorithm is used for integrating Newton's equation of motion with a time step of 2 fs. The simulation is first conducted for 2 ns to achieve the quasi-steady water flow through the GE membrane and is continued for an additional 10 ns to collect data for analysis. All simulations are performed under the NVT ensemble using the GROMACS v5.0.4 package [257].

Parameters of $d = 9$ Å, $h = 8$ Å, $l = 0$ Å, concentration $C = 5$ M and temperature $T = 298$ K are selected as default membrane and process parameters. Several sets of

simulations are performed to evaluate the effects of pore width d (6, 7.5, 9 and 11 Å), interlayer distance h (5, 8, 12 and 16 Å), offset l (0, 5, 10 and 15 Å), concentration C (1, 2, 3 and 5 M) and temperature T (298, 323, 343 and 363 K). Depending on the fabrication approaches and the conditions, stacked GE membranes may have multilayers. Hence the effect of layer number N_l is also investigated by varying it from 1 to 4 using the default membrane configuration.

The FO performance of the slit-pore membrane is compared with its performance in an RO system. The structure parameters of the membrane $d = 9$ Å, $h = 8$ Å and $l = 0$ Å are used for the RO system, and DS is replaced with pure water and the water flow is driven by applying a pressure difference $\Delta P = 100$ MPa to push the water molecules to permeate through the membrane from the NaCl solution to the pure water side. Desalination performances are assessed in terms of the water flux J_w and ion rejection R . The water flux J_w is defined as the mass of water molecules transferred through the membrane from FS to DS per unit time per unit area. The Cl^- ions are common in both FS and DS. Therefore, forward and reverse ion rejection rates are calculated in terms of the Na^+ and the Mg^{2+} concentrations, respectively, on the basis of the following equation [258]:

$$R = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}\right), \quad (4.1)$$

where C_{permeate} and C_{feed} are the ion concentration of the permeate reservoir at the end of the simulation and the initial ion concentration of the feed reservoir, respectively. Simulation results are analyzed by investigating the water density distribution and radial distribution function.

4.3 Results and discussion

To understand the water flow behaviour through the FO membrane, the number N_w of water molecules transferred through the stacked GE layers is monitored as a function of time and the result is presented in Fig. 4.2. For comparison, the result for the RO process is also plotted for the applied pressure difference $\Delta P = 100$ MPa. For the FO process, the number of permeated water molecules increases almost linearly with time. However, for the RO process, the number of permeated water molecules first increases linearly at a much faster speed than that of the FO process. The speed slows down after 4 ns and the permeated water molecules reach a saturation point at around 6 ns, due to the complete permeation of water molecules in the feed reservoir across the membrane. The much slower water permeation in the FO system is due to the fact that osmotic diffusion is a gradual process driven by the osmotic pressure difference across the membrane. The linear fitting of the curve in the FO system gives the water flux J_w . For the default simulation case, the water flux J_w is obtained as $0.0109 \text{ kg/cm}^2/\text{s}$ which is ultra-high as compared to that obtained from the commercial FO membranes. For the other cases, it can be observed that the membrane structure configuration parameters and the operation conditions of the FO system affect the water flux with different extent. A detailed analysis of these effects will be presented later.

It is worth mentioning that a truly steady water flow cannot be achieved and only the quasi-steady water flow can be obtained in a short period that the number of ions does not change. This is because both the water molecules and ions can enter into and diffuse in the interlayer region of the graphene sheets. However, the permeation of the ions into the interlayer region is much slower than the water molecules and follows a random pattern. As the number of the ions inside the interlayer region changes, the permeation of the

water molecules would be affected, and the water flow will also change. It has been found that after the initial 2 ns simulation, the number of ions in the interlayer does not show significant change, particularly for a small gap width and a small interlayer distance, as will be shown in Fig. 4.4. Hence, the number of water molecules shows an overall linear increasing trend with the simulation time, indicating quasi-steady water flow.

Fig. 4.2. Number N_w of water molecules transferred from the FS to the DS through the membrane as a function of time. The default simulation parameter set is $d = 9 \text{ \AA}$, $l = 0 \text{ \AA}$, $h = 8 \text{ \AA}$, $N_l = 2$, $C = 5 \text{ M}$, $T = 298 \text{ K}$ and $\Delta P = 0 \text{ MPa}$, and the results of this case are shown by the solid red line, and one parameter is changed each time (indicated by the legend) to show its influence.

In osmotic pressure driven processes, the solute permeation also plays a significant role in determining the membrane performances, particularly the ion rejection rate. The ions can diffuse from DS to FS due to the concentration gradient and from FS to DS because of the convective water flow. To understand the bidirectional ion diffusion, trajectories of selected Na^+ and Mg^{2+} ions are monitored for the default simulation case, as shown in Fig. 4.3. Since the GE membrane is electrically neutral, size exclusion is the mechanism that determines the ion rejection [259, 260]. Three types of solute moving

behaviours are observed: (1) diffusing through the membrane (2) entering the bilayer region and then returning back to the bulk region and (3) remaining in the bulk region.

Fig. 4.3. Trajectories of selected (a) Na^+ ions and (b) Mg^{2+} ions. Horizontal dash lines indicate the GE layers. One colour represents one individual ion.

As a result, the number $N_{i,m}$ of the ions inside the bilayer region varies with time, as exemplified for the three different cases in Fig. 4.4. It is evident that the number of ions inside the bilayer region shows a significant variation with time and is dependent on the membrane or process configuration. For the default simulation case, the number of ions inside the membrane remains small due to the strong filtration effect at the slit-pore and the small space between the two GE layers. For the RO process, the number of ions inside the membrane can be high. However, this state is transient and does not last for a very long time, indicating that the ions inside the membrane prefer to diffuse through the membrane or return back to FS. For a large interlayer distance $h = 16 \text{ \AA}$, $N_{i,m}$ shows an overall increase with time and such an increase is not observed for other cases. The accumulation of ions inside the membrane is mainly because of the lowered energy state inside the membrane due to the increased interlayer distance. However, if the simulation time continues, it is expected that a quasi-steady behaviour will again be reached.

Fig. 4.4. Number $N_{i,m}$ of ions inside the bilayer region as a function of time for the selected membrane and process configurations. The default simulation parameter set is $d = 9 \text{ Å}$, $l = 0 \text{ Å}$, $h = 8 \text{ Å}$, $N_l = 2$, $C = 5 \text{ M}$, $T = 298 \text{ K}$ and $\Delta P = 0 \text{ MPa}$, and the results of this case are shown by the solid line in red. One parameter is changed each time and is indicated by the legend.

The solute permeation through the membrane depends on the solute diffusion resistance R_D . For the porous membranes, it can be estimated as [107]

$$R_D = \frac{t\tau}{\varepsilon D_s}, \quad (4.2)$$

where t , τ , ε and D_s are the membrane thickness, tortuosity, porosity and bulk diffusion coefficient of solute, respectively. The membrane tortuosity is defined as the ratio between the length of the flow trajectory passing through the medium and straight-line length across the membrane. According to Eq. (4.2), solute diffusion across the stacked GE membrane, i.e., the ion rejection rate, depends on its structure parameters l and h .

4.3.1 Ion rejection

Simulations with a more extended time period of 40 ns have demonstrated that the number of permeated water molecules increases linearly with time first and reaches a plateau at around 30 ns. After 30 ns, the osmosis pressure difference across the membrane

is not high enough to induce apparent water permeation through the membrane. At 30 ns, the solute rejection rate is found to be reduced by around 5%, for the default simulation case. Since the ion rejection rate is time dependent, in this study, the ion concentrations at the end of 12 ns are used to calculate the ion rejection rate. The effects of membrane structural parameters (d , h , l and N_l) and operation parameters (C and T) on the forward and reverse ion rejection R are investigated and the results are shown in Fig. 4.5.

Figs. 4.5(a) and (b) present the effects of pore width d and layer number N_l , respectively. When the pore width d is less than 9 Å, R for the Na^+ and Mg^{2+} ions are 100% for all the ions. As d further increases from 9 Å, R decreases. The rejection rates for Mg^{2+} ions are higher than that of the Na^+ ions since the Mg^{2+} ions move less readily due to their larger hydration radii and divalent charge. Moreover, multilayered membranes demonstrate a higher molecule separation capability than the monolayer GE membrane in FO due to a greater solute diffusion resistance at a larger membrane thickness (Eq. (4.2)). It is worth commenting that the ion rejection rates in the FO process are superb over the results obtained from the simulation of the RO process (76% for Na^+) with the same membrane configuration. This is because in the RO process, the ions are forced to permeate through the membrane due to the large driving force which is a few times greater than the osmotic pressure difference, thus leading to lower ion rejection rates.

Fig. 4.5(c) illustrates the influence of pore offset distance l on the solute permeation through the bilayer membranes with the pore width $d = 9$ Å at a fixed interlayer distance h of 8 Å. The tortuosity of the GE membrane increases with the enlarging l and thus imposes a larger barrier on the solute permeation (Eq. (4.2)). It is observed that the number of ions crossing the interlayer region decreases with the increase in l and thus R increases. Moreover, it is found that at the offset $l = 15$ Å, the permeation of Na^+ and

Mg^{2+} ions into the membrane is completely prohibited and only the Cl^- ions can permeate into the GE membrane. However, these ions then bounce back to their initial resident solution. The increase in both forward and reverse solute rejection rates R with the offset distance l is in agreement with the results from previous studies on the osmosis process [207, 210].

Fig. 4.5(d) illustrates the influence of interlayer separation h on the ion rejection R . The rejection R shows an overall decrease with the increase of h (excluding for the Na^+ ions at $h = 16 \text{ \AA}$ and $d = 9 \text{ \AA}$ with $l = 0 \text{ \AA}$), and the reduction is more prominent for the Na^+ ions. The dependence of R on the interlayer distance h shows that the nanochannel formed by the two GE layers contributes to the molecular sieving by restricting the admittance of the ions into the system. These results are also in agreement with the observations from previously reported experimental studies [252, 261].

The dependence of the ion rejection R on the membrane structural configuration can be explained as follows. To support the discussion, the ion distribution inside the bilayer GE membrane with fully aligned ($l = 0 \text{ \AA}$ and $d = 9 \text{ \AA}$) and offset ($l = 15 \text{ \AA}$ and $d = 9 \text{ \AA}$) pores at separation distances of $h = 8 \text{ \AA}$ and $h = 16 \text{ \AA}$ are illustrated in Fig. 4.6. In fully aligned membranes ($l = 0 \text{ \AA}$), even at a low separation distance $h \leq 8 \text{ \AA}$, the ions pass through the GE membrane as the flow resistance is minimized by the reduced tortuosity (Fig. 4.6(a)). Therefore, the ion rejection R is considerably low compared to that for the larger offset distances at which the permeation of ions through the membrane is largely blocked (Fig. 4.6(b)). As h further increases to be larger than $8 \text{ \AA}$, more ions can enter and pervade through the membrane, which remarkably reduces the ion rejection R . For a small interlayer distance $h \leq 8 \text{ \AA}$, the stacked GE membranes with large offset distance $l > 10 \text{ \AA}$ can present complete solute rejection even at a large slit width $d > 9 \text{ \AA}$. This result

is of guiding significance of the structural design of multilayer GE membranes for seawater desalination.

Fig. 4.5. Dependences of the ion rejection R on various factors: (a) the pore width d , (b) number of layers N_l , (c) offset distance l , (d) interlayer distance h , (e) concentration C , and (f) temperature T .

For small pore width ($d = 9 \text{ \AA}$), when the interlayer distance h increases from 12 to $16 \text{ \AA}$ ($l = 0 \text{ \AA}$ and $l = 15 \text{ \AA}$), the interlayer space is large enough to host the ions. Thus they start to diffuse along the channel and tend to fill in the whole interlayer region rather than concentrate at the entrance region (Figs. 4.6(c) and (d)). Consequently, for larger interlayer distances h , the ions enter into the channel tend to stay inside and only a few will cross the membrane and enter into the DS or FS side. Hence, a higher ion rejection rate can be obtained at a larger h . However, when the pore width becomes large, the energy barrier for the ions entering into the membrane becomes lower. Therefore, for larger pore widths ($d > 9 \text{ \AA}$), more ions enter into the channel and pass through the membrane and thus leading to a significantly lower rejection rate R at $h = 16 \text{ \AA}$.

Fig. 4.6. Ion distribution in the interlayer regions of the membranes with intrinsic parameters: (a) $h = 8 \text{ \AA}$, $l = 0 \text{ \AA}$, (b) $h = 8 \text{ \AA}$, $l = 15 \text{ \AA}$, (c) $h = 16 \text{ \AA}$, $l = 0 \text{ \AA}$, and (d) $h = 16 \text{ \AA}$, $l = 15 \text{ \AA}$. For all the cases, the pore width is set at $d = 9 \text{ \AA}$.

Figs. 4.5(e) and (f) exhibit the effects of concentration C and temperature T on the solute rejection R . For all the cases studied, the bidirectional solute flux shows a very narrow variation with C that has the maximum of 3% reduction for the Na^+ ions at $C = 3 \text{ M}$ in comparison to that at the highest DS concentration $C = 5 \text{ M}$ (Fig. 4.5(e)). Therefore, the ion rejection is almost independent of the DS concentration when the pore width is small. Under this condition, the solute diffusion is mainly governed by the size exclusion

where the membrane structural parameters play a prominent role. The bidirectional ion rejection decreases with the rise in temperature T (Fig. 4.5(f)). These observations are in agreement with the result predicted from the Stokes-Einstein equation for spherical particles, as the ion diffusion rate increases with the increase in T [262].

4.3.2 Water flux

The dependence of the water flux J_w on the structural and process parameters is illustrated in Fig. 4.7. Fig. 4.7(a) exemplifies the influence of pore width d on the water flux J_w . The osmotic water flow increases monotonically with d , which is well consistent with the observations from the previous studies for nanoporous GE membranes in FO systems [104, 105]. Water molecules form a single-layered structure in the pore area at relatively smaller pore widths $d < 9 \text{ \AA}$ and the layering of water increases with d . The increase of the water layer explains the notable flow enhancement with d . Contrary to the impact of d on the water flow, J_w decreases with the GE layers N_l as depicted in Fig. 4.7(b). For example, the bilayer membrane exhibits a 14% flux reduction in comparison to that of the monolayer GE membrane. The monotonic reduction of J_w with the increase in N_l is due to the rise in membrane thicknesses and increased ion concentration in the interlayer region of the GE membrane.

The variation of water flux J_w with the pore offset l is investigated using the bilayer GE membranes with $d = 9 \text{ \AA}$ and $h = 8 \text{ \AA}$ (Fig. 4.7(c)). Overall, J_w decreases with the increase of l and slightly increases at $l = 15 \text{ \AA}$. The decreasing water flow is because of the additional resistance imposed on the water permeation through the membrane due to the change of water movement direction with respect to the locations of the pores [207, 210]. When $l \geq 10 \text{ \AA}$, the pores are completely misaligned with each other and restrict the

ion permeation through the membrane that yields 100% ion rejection (Fig. 4.5(c)). However, as observed in Fig. 4.3, some ions admit into the bilayer region and bounce back to the respective reservoir. Such ion behaviour inside the membrane blocks the water flow. For the offset distance $l = 15 \text{ \AA}$, only the Cl^- ions enter the membrane and move back to the resident water reservoir. Thus, at $l = 15 \text{ \AA}$, the resistance on the water flow due to the ions inside the membrane decreases and thus leading to the water flow increase.

Fig. 4.7(d) depicts the effect of interlayer distance h on the water flux J_w through the GE membranes with fully aligned and offset pores. For the fully aligned pores i.e., $l = 0 \text{ \AA}$, with the width $d = 9 \text{ \AA}$, J_w first decreases as the interlayer distance h increases and then moderately increases when $h = 16 \text{ \AA}$. For the fully offset pores with $l = 15 \text{ \AA}$, almost no water molecules can permeate through the GE bilayer membrane when $h = 5 \text{ \AA}$ because it is too small for both the water molecules and ions to penetrate. As the h increases to $8 \text{ \AA}$, the permeation of water molecules is permitted while the ions are prohibited due to the energy penalty associated with the peeling off their hydration shells. Hence, a sharp increase is observed in the water flux at $h = 8 \text{ \AA}$. As h further increases, the water flux decreases because of the increase of the permeation length for each water molecules diffuse across the membrane.

To understand the effects of interlayer distance h on the water flux J_w , the average permeation time t_p per water molecule and the normalized permeation time t'_p are investigated as a function of h (Fig. 4.8). Here, t_p is obtained by tracking the average time taken by the water molecules to cross the upper GE layer from the FS side and reach the DS side. t'_p is calculated through dividing the t_p by the migration length, which is defined as $(h + l)$. According to Fig. 4.8(a), t_p increases with the increase of h . Contrastingly, t'_p decreases monotonically with the increasing migration length, as shown in Fig. 4.8(b).

The reduction is significant for the membranes with fully aligned pores but is much weaker for the fully offset pores. The results indicate that the permeation velocity or dynamics increases with the increasing h .

Fig. 4.7. Dependences of the water flux J_w on various factors: (a) the pore width d , (b) the number of layers N_l , (c) offset distance l , (d) interlayer distance h , (e) concentration C , and (f) temperature T .

Besides the increase of the permeation or migration path length, the distribution of the ions inside the membrane also changes with the increase of the interlayer distance h , particularly for the case of fully aligned pores, as in the discussion of Fig. 4.6 in Section 4.3.1. Such change would alert the blocking effect of the ions on the water permeation and thus is responsible for the change of the permeation velocity of the dynamics of water molecules.

Fig. 4.8. Dependence of (a) the average permeation time t_p and (b) the normalized permeation time t'_p per water molecule on the interlayer distance h .

Since the total permeation time is determined by both the permeation length and the permeation velocity, they compete with each other in affecting the permeation time. For fully aligned pores, i.e., for the case of $d = 9$ Å and $l = 0$ Å, the increase of the permeation dynamics or velocity due to the blocking effect caused by the ion concentration at the entrance region is prominent and comparable to the increase of the permeation length, thus leading to the nonmonotonic dependence of the water flux on the interlayer distance h . For the fully offset pores, the increase of the permeation velocity is weak, and the permeation time is dominated by the increase of the path length. Thus the water flux decreases with h when it is larger than 8 Å.

Figs. 4.7(e) and (f) exemplify the effects of concentration C and temperature T on the water flux J_w . As shown in Fig. 4.7(f), the water flux J_w for the RO system is also plotted for reference. It is found that J_w increases remarkably with the increase of C and T , which is in agreement with the observations from previous studies [105, 263, 264]. The osmotic pressure difference across the membrane is magnified with the increase of DS concentration C [107], and it intensifies the water flow. Conversely, the concentration polarization effect is profound at a higher level of salinity and adversely affects the water flux J_w . However, for the interlayer distance $h = 8 \text{ \AA}$, the monotonic increase of the water flux J_w with the concentration C indicates that ion concentration polarization effects are less severe in the free-standing GE laminates. This is in agreement with the results from the previous experimental study using reduced GE oxide membranes in FO systems [252]. As the temperature T increases, the viscosity of DS reduces, and the mass transfer rate improves. Thus, the temperature T has a positive impact on amplifying the water flux J_w . Furthermore, in comparison to the performance in the RO system, at a higher temperature, stacked GE membranes in the FO system yield a larger water flux J_w and ion retention (Section 4.3.1). Overall, the performances of multilayer GE membranes with the optimized membrane structure can be further enhanced by elevating the system temperature and DS concentration.

The dependence of the water flux J_w on the temperature can be explained using the Arrhenius activation energy equation [265]:

$$J_w \approx \exp\left(\frac{E_a}{RT}\right), \quad (4.3)$$

where E_a , R and T are the activation energy, gas constant and temperature, respectively. The activation energy for water transport through the bilayer GE membrane ($d = 9 \text{ \AA}$, $h = 8 \text{ \AA}$ and $l = 0 \text{ \AA}$) is calculated by fitting the flux as a function of inverse temperature using

Eq. (4.3) (Fig. 4.9(a)). The activation energy for the slit-pore bilayer GE membrane is obtained as 8.02 kJ/mol which is lower than the values of cellulose acetate membranes [266] and triblock copolymer aquaporin membranes [267]. The lower activation energy well explains the ultra-fast water permeation through the stacked GE membrane. Similarly, the water flux J_w through the corrugated GE channel that is discussed in Section 3.3.1 is calculated for different feed temperatures ($T = 300, 310, 320$ and 330 K). The activation energy E_a for the corrugated GE channel is estimated to be 9.57 kJ/mol (Fig. 4.9(b)). These results indicate that stacked GE membrane is an energetically favourable membrane configuration for seawater desalination via FO compared to corrugated GE channel for CDI.

Fig. 4.9. Water flux J_w as a function of inverse temperature ($1000/T$) for the (a) membrane configuration of $d = 9 \text{ \AA}$, $h = 8 \text{ \AA}$ and $l = 0 \text{ \AA}$ and (b) CDI nanochannel configuration of $d = 16 \text{ \AA}$, $\lambda = 40 \text{ \AA}$ and $A = 2 \text{ \AA}$. Black dashed lines fit to the Arrhenius equation.

The commercially available FO membranes have low water permeability partly due to the concentration polarization effect [268]. Therefore, these membranes have low power densities P_w and require a larger membrane surface for practical applications. P_w of an osmotic pressure driven membrane is defined as the power generated per unit membrane area and is calculated as $P_w = J_w \Delta P$ [268]. It is evident from the present study

that the high water flux renders the slit-pore GE membranes to have high P_w and thus can be effectively used in osmotic pressure driven processes.

Fig. 4.10. Dependence of water density distribution along the membrane axis (z -direction) on (a) number N_l of layers and (b) interlayer distance h for membranes with $d = 9$ Å and $l = 0$ Å.

Fig. 4.11. RDF $g(r)$ for OW-OW atom pairs inside the bilayer regions for different interlayer distance h ($d = 9$ Å and $l = 0$ Å) and in the bulk phase. The vertical black dashed line indicates the first peak of the distribution function.

Nanoconfined water structure plays a substantial role in determining the water flow. The structure of water changes with the interlayer separation h . To investigate the behaviour of water inside the bilayer region, the water density distribution and the radial distribution function are estimated.

Figs. 4.10(a) and (b) show the water density distribution in z -direction for membranes with distinct number N_l of layers and separation distance h . The layering of the water inside the bilayer region is evident by the density profiles as reported in the previous studies [205, 269]. Two density peaks adjacent to the surface of the monolayer GE membrane (Fig. 4.10(a)) indicate the favourable positioning of the water molecule. For the bilayer GE membrane, water inside the interlayer region has a distinct water layer and is denoted by the peak marked in between the two GE layers. As N_l increases, density peak count increases. As the membrane thickness expands with h , multiple density peaks are observed and these peaks merge at a larger h owing to the reduced geometrical confinement (Fig. 4.10(b)).

To characterize the change in the distribution of the water molecules, the radial distribution function $g(r)$ for the OW-OW atom pairs is calculated, as shown in Fig. 4.11 for the membrane configuration of $d = 9 \text{ \AA}$ and $l = 0 \text{ \AA}$. For comparison, the $g(r)$ of bulk water is also plotted. The amplitude of the first peak of the $g(r)$ curve is higher for a narrow interlayer distance which is a direct result of the geometric volume confinement. Highly ordered water structure is evident from the secondary peak heights recorded in the narrow interlayer regions. As h increases, the peak height diminishes notably. The second peak height disappears at large $h > 16 \text{ \AA}$ and emphasizes the collapse of short-range ordered water structure [205].

4.4 Summary

The desalination performance of the stacked GE layers as the FO membrane is studied. The dependence of the desalination performances on the membrane characteristics, such as the pore width, interlayer distance, pore offset and number of layers, and the operating conditions in terms of temperature and DS concentration is investigated. The membrane performances are quantified by calculating the water flux and solute rejection rate. Overall, the GE membranes in FO systems yield a low water flux but an enhanced ion retention capability in comparison to the GE membranes in RO systems. However, when compared with the commercial polymeric membranes in FO systems, the bilayer GE membranes demonstrate a much higher water flow rate and therefore possess a high-power density. Furthermore, the activation energy for the slit-pore bilayer GE membrane is estimated to be 8.02 kJ/mol which is much lower than the typical values of commercially available FO membranes.

The GE membrane structural parameters have a significant effect on controlling the desalination performance. In stacked GE membranes, the size exclusion is the mechanism that mainly determines the solute retention. The monotonic increase of water flux and decrease of ion rejection are observed as the pore width d increases. The complete rejection of ions is observed in the bilayer GE membranes for the pore widths $d < 9 \text{ \AA}$. When the number of layers in the GE membrane increases, the ion rejection increases, and the water flow decreases due to the increase of membrane thickness and ion concentration in the interlayer region. Moreover, desalination performance greatly relies on the interlayer distance h and the offset distance l . At a smaller separation distance of $h < 8 \text{ \AA}$, the nanochannel between two GE layers imposes a great energy barrier on the ions to restrict the ion permeation. Interestingly, the study reveals that the stacked GE

membranes can accomplish a complete ion rejection and maintain a higher water flux even at a large nanoslit width $d > 9 \text{ \AA}$, when an optimum interlayer distance $h = 8 \text{ \AA}$ and a completely misaligned pore configuration are adopted.

Chapter 5. Ionized GO Sheets for Seawater Desalination

Ionization of the functional groups such as carboxylic acid and phenol hydroxyl of the GO sheet introduces a negative charge on the membrane surface. In this chapter, seawater desalination performance of the ionized GO membrane via nanofiltration is studied. Furthermore, this research proposes a method that is more energetically favorable than nanofiltration for enhancing solute rejection through the ionized GO membrane.

5.1 Introduction

Ionization of carboxylic acid and phenol hydroxyl functional groups results in a negative charge on GO sheets and avoids overlapping of single-layer GO sheets [147]. Once these GO sheets are assembled into membranes, they interlock in a parallel manner, forming mechanically robust membranes that can be easily transferred to other substrates. Because of their electric charge, these membranes can be adopted as ion exchange membranes in nanofiltration [45, 148-150] or electrodialysis [151, 152] processes. However, those membranes exhibit a much lower rejection of monovalent anions, indicating the necessity of further improvements for seawater desalination.

Previous studies on GE-based desalination membranes reveal that the nanochannel or nanopore sizes of those membranes should be smaller than 8 Å to effectively be used in seawater desalination [207, 210, 270]. Size exclusion is the main mechanism in solute rejection through those membranes. However, pore sizes of the existing GE-based membranes are larger than this value and solute rejection is considerably low as an RO membrane. Moreover, precise control of interlayer distances of GO membranes is a challenge because of the swelling effect of GO in water. In addition, charged GO membranes with much larger nanocapillaries may not be able to function as ion exchange

membranes because the accumulation of counter ions near the charged functional groups assist in admittance of coions into the membrane region.

Tailoring the chemical structure of GE sheets and nanocapillaries via functionalization with neutral or charged groups or changing GO structure by reducing GO or intercalating chemical groups such as copper hydroxide nanostrands or nanomaterials such as carbon nanotube, carbon dots, and MOFs can improve the selectivity of GO membranes [21, 29, 271-275]. However, these approaches are time and chemical consuming. Thus, there exists a requirement to develop new ways of achieving complete solute rejection in seawater desalination through GO membranes.

In this study, seawater desalination performance of the bilayer ionized GO membrane via nanofiltration is studied using an ionized GO membrane with much larger pore sizes reported in experimental studies. Furthermore, this research proposes a method that is more energetically favorable than nanofiltration for enhancing solute rejection through the ionized GO membrane by exposing the membrane to an external electric field opposite to the direction of water flow. Previously, electrically controlled water permeation through GO was reported to be performed by applying an electric field across the GO membrane [276]. The proposed ENF system is an experimentally feasible approach. In addition, depending on the pore size (nanocapillaries and pinhole defects), ionized GO membranes can separate species that are electrically neutral and thus can be used for developing a single-stage desalination approach. It has been reported that the GO has antifouling characteristics because of the hydrophilic nature. Therefore, these membranes are invulnerable to foulant that enhances the durability of the proposed system.

5.2 Simulation Method

Fig. 5.1(a) shows the simulation model used to study the nanofiltration desalination of the ionized GO membrane. Each GO layer consists of two identical GO sheets with a width $W = 25 \text{ \AA}$ and a length $L = 46 \text{ \AA}$ (Fig. 5.1(c)). The left compartment is filled with NaCl solution of 3.5% salinity (75 Na^+ and 75 Cl^- ions solvated with 6586 water molecules), which is representative of the typical salt concentration in seawater, and the right chamber is filled with pure water (3329 water molecules). Two rigid GE pistons are added at the ends of each chamber. Both pistons can self-adjust their positions during the simulation under pressure P_{left} and P_{right} as indicated in Fig. 5.1(a). A vacuum space with the length $100 \text{ \AA}$ is placed on top of the water reservoir along the z -direction to eliminate the interactions of the system with its images in this direction. The orthogonal dimensions of the computational model are $x = 70 \text{ \AA}$, $y = 56 \text{ \AA}$ and $z = 226 \text{ \AA}$.

The double-layer GO membrane configuration is built as follows. The Lerf–Klinowski model [277], which is consistent with the recent experimental results, is incorporated into the development of the GO structure. According to this model, the chemical composition of the GO nanosheet is set as $\text{C}_{10}\text{O}_1(\text{OH})_1(\text{COOH})_{0.5}$, where an equal number of hydroxyl and epoxy groups are randomly distributed on basal planes (both sides) of the GE sheet and carboxyl groups are placed on the edges of the GE sheets. To study the effect of ionization on the separation performance of GO membrane, in this study, some carboxylic groups are ionized by removing their hydrogen atoms such that each GO sheet used in this study has a negative charge density of $13.5 \text{ \mu C/cm}^2$. GO sheets are then arranged to form a bilayer GO membrane with structural parameters of $d = 10 \text{ \AA}$, $h = 10 \text{ \AA}$ and pore offset $l = 0 \text{ \AA}$ (Fig. 5.1(b)). d and h are based on the prior experimental works [21, 53] and membrane pores are considered as fully aligned, so that

the solute rejection is independent from the pore misalignment. Energy minimization is performed on this GO membrane using the steepest descent method.

Fig. 5.1. (a) Schematic of the simulation model: The left chamber with the feed solution and the right chamber with pure water are separated by an ionized GO membrane. The left piston is exerted by a pressure $P_{left} = 200.1$ MPa, while atmospheric pressure is applied on the right piston ($P_{right} = 0.1$ MPa). Both pistons are allowed to move. Color coding of atoms: C of pistons (grey), C of membrane (cyan), O (red), H (white), Na^+ (yellow) and Cl^- (green). (b) Side view of the membrane. (c) The GO sheet with a pinhole.

The desalination performance of the ionized GO membrane is investigated using the large-scale atomic/molecular massively parallel simulator LAMMPS package [234]. The periodic boundary conditions are applied in all three orthogonal directions. The charge of the ionized groups is balanced by adding extra counterions (Na^+) to maintain the electroneutrality of the system as reported in the previous study [278]. The van der Waals (vdW) interaction between two atoms is described by LJ potential using Eq. (2.4). The ppm summation technique is applied to compute the long-range electrostatic interactions with a cutoff distance of $12 \text{ \AA}$ [279].

The optimized potentials for liquid simulations-all atoms (OPLS-AA) [280] force field parameters are used for GO simulation. The positions of C atoms in the GE lattice are fixed to avoid the out-of-plane displacement, whereas the flexibility of the functional

groups is modelled on the basis of the force field parameters. The sp^2 hybridized C atoms of GO and GE are treated as neutral LJ spheres. The TIP3P [199] model is applied to simulate water, whereas the LJ parameters for Na^+ and Cl^- ions are adopted from a previous work [238]. The SHAKE constraint algorithm is used to maintain the rigid geometry of the water molecules [201]. The atomic interactions among the different species are estimated using the Lorentz–Berthelot mixing rules. There is no explicit interaction between the C of GE and H from water molecules, whereas the values of ϵ and σ for the interaction between C of GE and O from water are set at 0.1031 kcal/mol and 3.34 Å [281].

All the simulations are performed under the NVT ensemble with the temperature kept at 300 K. The temperature is calculated with the center-of-mass velocity subtracted. Initially, a relatively high external force is applied on both the pistons to adjust the densities of the feed and permeate solutions to the desired value. Then, the system is equilibrated at the corresponding desalination temperature T for 100 ps. During this process, a reflecting wall is placed in the left reservoir at a distance of 0.1 Å from the membrane considered. This is required to avoid the interaction of the membrane with the water molecules before achieving the equilibrium state. Once the system reaches the equilibrium state, the reflecting wall is removed to allow the water molecules to penetrate and pass through the membrane to simulate the nanofiltration process. Meanwhile, P_{left} and P_{right} are adjusted again so that the feed and permeate solutions are acted upon by the pressure of 200.1 MPa and standard atmospheric pressure of 0.1 MPa, respectively. The desalination stage itself is conducted for 3 ns with an integration time step of 1 fs. Initially, nanofiltration performances are investigated for seawater and brackish water feed solutions with salinities $C = 3.5\%$ and 1.0% , respectively. Those are the characteristic salinities of seawater and brackish water, respectively.

For both seawater and brackish water systems, an electric field with the intensity amplitude $E = 0.1 \text{ V/Å}$ is applied in the z -direction, across the membrane, opposite to the water flow, to simulate the ENF process. An additional simulation is performed for the seawater feed system where electric field direction is the same as the water flow direction, to evaluate the dependence of ENF performance on the direction of the electric field. Subsequently, for the negative field direction that, as will be shown later, demonstrates the decent desalination performance, MD simulation of its ENF process is then conducted under different electric field intensities ($E = 0.2, 0.4, 0.6$ and 0.8 V/Å) and temperatures ($T = 300, 310, 320, 330$ and 340 K) to investigate the effects of altering these parameters. For simplicity, the effect of corrugation in GO sheets is not considered in this study. An additional simulation is conducted to understand the effect of pinhole defects in GO sheets on nanofiltration performance. For that, pinholes are introduced by creating a nanopore in each GO sheet, as shown in Fig. 5.1(c).

The desalination performance of a membrane is typically evaluated in terms of water flux (J_w) and ion rejection (R). Once water flow reaches the steady-state condition; i.e. the net water flow is from the feed solution to the permeate reservoir, the water flux J_w is calculated as the mass of water molecules transferred through the membrane from feed solution to permeate per unit time per unit area. Solute rejection is estimated on the basis of Eq. (4.1). The selectivity S_i of the membrane towards Na^+ or Cl^- ions can be defined as

$$S_i = \frac{x_{i,feed}/x_{water,feed}}{y_{i,permeate}/y_{water,permeate}}, \quad (5.1)$$

where $x_{i,feed}$ and $x_{water,feed}$ are the molar fraction of either Na^+ or Cl^- ions and water in the feed solution at the beginning of the simulation, respectively. Similarly, $y_{i,permeate}$ and $y_{water,permeate}$ are the molar fraction of either Na^+ or Cl^- ions and water in the permeate solution at the end of the simulation, respectively.

5.3 Results and Discussion

5.3.1 Selectivity of ionized GO membrane

For a membrane with narrow nanopores (cutoff diameter $< 8 \text{ \AA}$), size exclusion is the main mechanism that determines the rejection of ions such as Na^+ and Cl^- . However, electrostatic interactions between the ions and the membrane play a dominant role in controlling the ion permeation through the membrane with wide nanopores. It is reported that nanopores with negatively charged functional groups such as carboxylic and hydroxyl selectively reject the Cl^- ions, whereas membranes with positively charged groups such as ammonium are permeable to the Cl^- ions. To investigate the ion selectivity of the negatively charged GO membrane, solute rejection R , membrane selectivity S , RDF, ion density distribution and PMF are calculated.

Figs. 5.2(a) and (b) show the number of ions inside the membrane region ($N_{i,m}$) and the permeate chamber ($N_{i,p}$), respectively, for both seawater and brackish water systems as a function of the simulation time. The number of mobile coions (Cl^-) inside the membrane region is always lower than that of the counter ions (Na^+). From Fig. 5.2(b), it is evident that the admittance of Cl^- ions to the permeate chamber is initially delayed for about 200 and 700 ps for the seawater and brackish water systems, respectively. These cutoff times are indicated by the black and green dashed lines. Similarly, cutoff time is observed in Fig. 5.2(a) that is noteworthy only for the Cl^- ions in the brackish water system.

Regardless of the nanocapillary sizes (d and h) that are larger than the cutoff pore size ($8 \text{ \AA}$), as will be shown later, the initial blockage of mobile coions is attributed to the noticeably high electrostatic repulsion from the negatively charged oxygen atoms in carboxylate groups and hence those cutoff times are reported. Intensities of those

repulsive forces on the Cl^- ions diminishes as more Na^+ ions are attracted by the oxygen atoms of the carboxylate groups, allowing more Cl^- ions to be admitted into the membrane region. As a result, at the end of the simulation, very low rejection rates are reported for both ions in seawater (R_{Na^+} -55% and R_{Cl^-} -44%) and brackish water (R_{Na^+} -56% and R_{Cl^-} -26%) systems. It is noted that the anion rejection rate is significantly reduced, whereas cation rejection is almost the same for both salinity levels ($C = 3.5\%$ and 1.0%) of feed solution. Furthermore, the water flux through the ionized GO membrane does not demonstrate a significant change with the feed solution salinity (seawater feed system, $0.133 \text{ kg/cm}^2/\text{s}$; and brackish water, $0.139 \text{ kg/cm}^2/\text{s}$). Therefore, ionized GO layers are effective as nanofiltration membranes for seawater desalination. The simulation results for the GO membrane with pinhole defects indicate that defects in GO nanosheets enhance the water flux (by 33%) and simultaneously lower the solute rejection (Na^+ by 4% and Cl^- by 22%) by providing a shorter route for trans-sheet flow. Greatly reduced Cl^- rejection is ascribed to the lower dehydration energy. These observations are in agreement with the results from the previous study [282].

The GO membrane selectivity is calculated using Eq. (5.1). For both cases, the estimated selectivities are S_{Na^+} -2.2 and S_{Cl^-} -1.7 for seawater, and S_{Na^+} -2.3 and S_{Cl^-} -1.4 for brackish water. Consequently, the membrane is highly selective to both ions and not effective as a cation-selective membrane in seawater or brackish water desalination. To further explore the ion selectivity through the GO membrane, the Debye length (λ_d) is calculated on the basis of the equation [283]:

$$\lambda_d = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i (z_i e)^2 C_{i, \text{bulk}}}}, \quad (5.2)$$

where ϵ_0 and ϵ_r are the vacuum and relative permittivity, respectively, k_B is the Boltzmann constant, T is the absolute temperature, z_i is the ionic charge, e is the charge of an electron

and $C_{i,bulk}$ is the number concentration of ion type i in the bulk solution. The λ_d is the distance at which the electrostatic potential of a centre ion reaches to zero due to the net effect of interactions it undergoes with the other mobile charges in the system. The calculated λ_d values are reported as 3.4 and 3.8 Å for seawater and brackish water, respectively. These values are smaller than the nanocapillary size of the GO membrane.

Fig. 5.2. Number of Na⁺ and Cl⁻ ions inside the (a) membrane ($N_{i,m}$) and (b) permeate ($N_{i,p}$) as a function of the simulation time. Black and green dashed lines in (b) indicate the initial cutoff time of seawater and brackish water system, respectively. Number density of (c) Na⁺ and (d) Cl⁻ ions along the z -axis of the GO membrane. Black dashed lines in (c) and (d) indicate the membrane region.

As such, regardless of the membrane surface charge, both ions can permeate through the membrane, elucidating the selectivity of the ionized GO membrane. Furthermore, the

results demonstrate that the λ_d increases when the feed salinity C decreases, in agreement with the previously reported results [284, 285].

Permeation of ions through the membrane is mainly governed by the electrostatic repulsion on Cl^- ions and interaction of Na^+ ions with the carboxylate group at the sheet edges. As a result, the coion (Cl^-) concentration in the membrane region is lower than the bulk solution concentration (Fig. 5.2(d)). Meanwhile, the counter ions concentration (Na^+) in the bulk solution is lower than the counter ion concentration in the membrane region (Fig. 5.2(c)). These results are in agreement with the results predicted by the Donnan exclusion theory [218, 286]. It is reported that for an ion exchange membrane, coion and counter ion rejection rates decrease with increasing solution salinity level [286]. However, in this study, for seawater and brackish water feed solutions, the counter ion rejection rate remains almost the same, whereas coion rejection decreases for the low salinity solution.

The energetic barrier on ion transport through a membrane can be understood by the PMF profile. The PMF profile is calculated using the umbrella sampling discussed in section 2.5. The reaction coordinate is chosen as the z -direction from -5 to 25 Å, which is sufficient to cover the ion permeation from the feed chamber to the permeation chamber. A harmonic bias potential is attached to a randomly selected Na^+ or Cl^- ion in the feed solution. In this study, k is taken as 80 kcal/mol/Å. For each sampling window of 1 Å, the simulation is conducted for 100 ps, in which the first 20 ps are used for the system to reach equilibrium. The following 80 ps are used to record the coordinate of the probe ion and the weighted histogram analysis method (WHAM) is adopted to analyze the data. The results are illustrated in Fig. 5.3.

For both ions, the free energy barriers are shown to emerge at the upstream and downstream membrane surfaces. The PMF calculations reveal that the energetic barrier

on the transport of Cl^- ions through the ionized GO membrane is comparatively higher than the energy barrier on the Na^+ ions. This is attributed to the significantly high repulsive forces acting on the Cl^- ions (by the ionized carboxylic group). The Na^+ ions have a smaller radius and repelled by the hydrogen atoms of functional groups. Therefore, their corresponding energy barriers are small, and valleys are shallow. Thus, with the little energy they can easily move through the membrane while the permeation of Cl^- ions is energetically unfavorable. However, it has been reported that dehydration remains the dominant barrier to pore transport as compared to charge repulsion [287].

Fig. 5.3. The PMF profile for the transport of Na^+ and Cl^- ions through the ionized GO membrane. Upstream side and downstream side GO membrane surfaces are delineated in vertical blue dashed lines.

To further investigate the solute rejection mechanism, the RDFs $g(r)$ between the solute ions and constituent atoms of the water molecules are calculated (Fig. 5.4). The first peaks of the $g(r)$ curves of the ion-water pairs in the membrane exhibit higher amplitudes compared to those of the feed solution, which is a direct result of volume confinement. The first peak locations of Na^+ -HW and Cl^- -OW RDFs provide an estimation of the hydration shell of the cations and anions, respectively. The estimated hydration shell radii of the Na^+ and Cl^- ions are approximately 3.1 and 3.3 Å, respectively.

According to the coordination number curve, there are about six water molecules in the hydration shells of solute ions in the feed solution and five and three water molecules in the hydration shell of the Na^+ and Cl^- ions, respectively, in the membrane region. These results indicate that their hydration structures are altered as they enter the membrane region, to cater to the high energy barrier imposed by the membrane. Because the energy required to remove the hydration radii of the Na^+ ions is greater than that of the Cl^- ions, a decrease of coordination number is notable for the Cl^- ions. Thus, dehydration plays a pivotal role in determining the ionized GO membrane selectivity.

To explore the membrane-ion interactions, the RDFs between ions and membrane atoms are computed, as illustrated in Fig. 5.5. The first peaks of RDFs are attributed to the strong interactions between ions and membrane atoms. The RDFs between the membrane atoms and Na^+ ions reveal that Na^+ ions and oxygen atoms of carboxylate groups (OI) have intense interactions between them (Fig. 5.5(a)). In addition, the oxygen atoms of epoxy groups (OE) and the Na^+ ions exhibit an attractive interaction with each other. However, the amplitude of the first peak height of the OE- Na^+ atom pairs is much lower compared to that of the OI- Na^+ atom pairs, implying a much weaker interaction between OE- Na^+ atom pairs. Meanwhile, the RDFs of the Cl^- ion-membrane atoms (Fig. 5.5(b)) illustrate that Cl^- ions interact with the hydrogen atoms of hydroxyl (HH) and carboxylic (HC) functional groups. The interaction energies between the Cl^- ions and HH or HC atoms are calculated as -6.4 or -5.7 kcal/mol. These attractive energies are not as strong as the repulsive forces between the OI atoms and Cl^- ions (11.4 kcal/mol), reporting a 100% rejection for Cl^- ions during the cutoff time period. As more Na^+ ions attractively interact with the OI atoms, those repulsive forces between the OI atoms and Cl^- ions diminish, which leads to the admittance of Cl^- ions into the membrane region.

Thus, the high selectivity of the ionized GO membrane is due to the strong interaction between OI or OE- Na^+ ions and HC or HH- Cl^- ions.

Fig. 5.4. RDFs $g(r)$ between ions (Na^+ , Cl^-) and atoms (OW, HW) of water molecules in (a and b) feed and (c and d) GO membrane under the default operating conditions of $T = 300$ K and $C = 3.5\%$.

Interactions between the ions and the atoms of functional groups at the edges of GO sheets (carboxylic and carboxylate) are notably higher than other atoms. Consequently, most of the ions prefer to reside near the carboxylic and carboxylate groups, while blocking the molecular permeation paths. This can be verified by comparing the ion density distributions in the xy plane (Fig. 5.6). Because Cl^- ions have lower dehydration energy than the Na^+ ions, some Cl^- ions may lose their hydration shell and squeeze

themselves through those blocked molecular paths. Hence, the Cl^- rejection rate R is lower than the Na^+ rejection rate R . The accumulation of ions at the GO sheet edges is severe for the seawater feed system than the brackish water feed system, resulting in a much lower Cl^- ion rejection for the brackish water feed system. Because of the high dehydration energy and strong interactions with the OI atoms, the Na^+ ion rejection rate is independent of the feed solution salinity level.

Fig. 5.5. RDFs $g(r)$ between the membrane atom and the (a) Na^+ and (b) Cl^- ions inside the ionized GO membranes under the operating conditions of $T = 300$ K and $C = 3.5\%$.

Meanwhile, those ions residing near functional groups may travel further through the membrane with the water flow and get trapped by another functional group or enter into the permeate chamber, reducing its rejection rate R . Initial solute rejection through the GO sheets is mainly attributed to the electrostatic repulsion and attractive interactions between ions and the functional groups of the GO membrane. However, with the time, as ions are trapped by the functional groups at the GO sheet edges, permeation paths of GO membranes are narrowed. Consequently, the ion dehydration also affects the solute rejection through the ionized GO membrane.

Fig. 5.6. Number density distribution of Na^+ ions in (a) seawater and (c) brackishwater, and Cl^- ions (b) seawater and (d) brackishwater, along the xy -plane of the GO membrane.

5.3.2 Effect of electric field

To evaluate ENF performance, initially, the GO membrane is exposed to an external electric field in the negative z -direction (i.e., opposite to the water flow direction) with an intensity of $0.1 \text{ V/\AA}$ (Fig. 5.7(a)). The negative polarity at the cathode side (i.e., the feed side membrane surface), Na^+ ions are attracted towards the membrane, while Cl^- ions are pushed away from the membrane surface. However, some Cl^- ions are admitted to the membrane region along with the water flow. Therefore, regardless of the polarity at the cathode side and the surface charge of the ionized GO membrane, both solute ions are admitted to the membrane region, and the accumulation of Na^+ ions in the membrane region is significantly higher than the accumulation of Cl^- ions (Figs. 5.7(c) and (d)). Because of the positive polarity at the permeate side, Cl^- ions that entered the membrane

region are attracted towards the anode (positive polarity), whereas Na^+ ions are retained inside the membrane region. As a result, the admittance of the Na^+ ions to the permeate chamber is completely hindered. By chance, some Cl^- ions residing near the anode side enter the permeate chamber along with the water stream (Figs. 5.7(d) and (f)). Thus, Cl^- ion rejection rates R of seawater and brackish water systems are reported as 91% and 77%, respectively.

To further explore the dependence of ion rejection R on the electric field direction, the field direction of the seawater system is reversed (Fig. 5.7(b)). Because of the positive polarity at the feed side, a significant number of Cl^- ions enter into the membrane region compared to the negative field direction. These Cl^- ions could not reach the permeate chamber because of the negative polarity of the cathode side. Meanwhile, a noticeably high number of Na^+ ions enter the membrane as a result of electrostatic interactions with the negatively charged GO membrane. These ions accumulate at the cathode side and consequently enter the permeate reservoir along with the water flow. The Na^+ and Cl^- ions rejection rates are recorded as 79 and 100%, respectively. Interestingly, for the positive field direction, the reduction in rejection rate R of Na^+ ion is significant than the increase of Cl^- ion rejection R , with respect to those results observed for system with the negative field direction.

Ion density distributions along the z -direction are analyzed to understand the dependence of solute rejection on the electric field direction (Fig. 5.8). For the positive field direction, density curves of the Na^+ and Cl^- ions have peaks near the permeate side and feed side membrane surfaces, respectively. Coions (Na^+ for cathode side and Cl^- for anode side) tend to move away from the membrane surface, resulting in a lower CP effect. However, because the membrane is negatively charged, some Na^+ ions are able to travel through the membrane and get attracted by the cathode, causing CP at the permeate

side. Those Na^+ ions reside near the downstream side of the membrane blocking the molecular paths for water permeation. Meanwhile, for the system with a negative electric field, the CP effect at the feed side is intensified while the permeate side CP effect is almost negligible. Interestingly, this intense CP effect at the feed side membrane surface has an adverse effect on the water flow, reporting a water flux J_w of $0.0798 \text{ kg/cm}^2/\text{s}$, which is lower than the J_w of the positive field ($0.0960 \text{ kg/cm}^2/\text{s}$). These results are 40 and 28% less than the J_w reported in the absence of the electric field ($0.133 \text{ kg/cm}^2/\text{s}$). Hence, the electric field has an adverse effect on lowering the water flux J_w while enhancing the ion rejection R .

Moreover, it is noticed that when the electric field intensity is raised to $0.6 \text{ V/\AA}$, in the positive field ENF, the Cl^- ion permeation is completely hindered, whereas the Na^+ ion rejection R decreases significantly compared with the R at $E = 0.1 \text{ V/\AA}$. For the negative field ENF, 100% solute rejection is recorded. In the positive field ENF system, despite the feed side field polarity, counter ions (with respect to the membrane charge) are attracted by the membrane and their movement toward the permeate chamber is facilitated by the polarity at the permeate side, lowering the solute retention for high polarity. Because Na^+ ion rejection is more difficult than the Cl^- ion removal, the electric field applied in the direction opposite the water flow appears to be an effective solution in improving the solute rejection through the ionized GO membrane via ENF. To explore the ways to improve the performance of the negative field ENF system, the dependence of desalination performance on the electric field intensity is explored (Fig. 5.9).

Fig. 5.7. (a) and (b) Schematic representation of the negative and positive electric field directions, respectively. The number of Na^+ and Cl^- ions inside the (c and d) membrane ($N_{i,m}$) and (e and f) permeate ($N_{i,p}$) regions as a function of the simulation time in seawater (SW) and brackish water (BW) systems at $T = 300$ K, under the effect of an external electric field.

Figs. 5.9(a) and (b) elucidate the variation of the water flux and ion rejection, respectively, as a function of the electric field intensity. When the field intensity is increased, the water flux J_w decreases, except at $E = 0.6$ V/Å. Overall, Na^+ and Cl^- ions rejection rates R increase with the field intensity. It is expected that attractive forces acting on the Na^+ ions at the feed side increase with increasing field intensity, allowing

more Na^+ ions to be admitted into the membrane region. However, the admittance of Na^+ ions into the membrane decreases with the increasing field intensity, lowering the blocking effect on the water permeation inside the membrane. This could be attributed to the increase in repulsive forces at the anode side that keeps Na^+ ions away from the membrane region. Meanwhile, with the increase in field intensity, repulsive forces acting on the Cl^- ions at the feed side (cathode) increase. When the field intensity is $E > 0.2 \text{ V/\AA}$, these repulsive forces are strong enough to completely block the admittance of Cl^- ions to the membrane region. Furthermore, attractive forces at the anode side hinder the entrance of Cl^- ions into the permeate chamber, reporting an increase in rejection rate with increasing field intensity for $E < 0.2 \text{ V/\AA}$. Consequently, the overall CP effect enhances with the increase in field intensity (Fig. 5.10), blocking the membrane pores at the feed side that enhances the solute rejection while reducing the water flux, except for $E = 0.6 \text{ V/\AA}$.

Fig. 5.8. (a) and (b) Density distribution of Na^+ and Cl^- ions, respectively along the z -axis, under the default operating conditions of $T = 300 \text{ K}$ and $C = 3.5\%$. The two ends of the GO membrane are delineated in vertical black dashed lines.

It can be seen from Fig. 5.10, for the field intensity $E = 0.6 \text{ V/\AA}$, the CP effect at the feed side of the membrane is lower than that of the systems with field intensity $E = 0.4$

and $0.8 \text{ V/\AA}$. This is the main reason for the slight increase in water flow at $E = 0.6 \text{ V/\AA}$. Meanwhile, the water flux at $E = 0.2 \text{ V/\AA}$ is notably lower than the flux at $E = 0.6 \text{ V/\AA}$. This is ascribed to the blocking effect from the ions (for $E = 0.2 \text{ V/\AA}$), travelling through the membrane, on the water permeation that is not significant for $E > 0.2 \text{ V/\AA}$.

Fig. 5.9. (a) and (b) Dependence of the water flux J_w and the solute rejection R on the external electric field intensity E , respectively. Salinity C of the feed solution is 3.5%.

Fig. 5.10. (a) and (b) Density distribution of Na^+ and Cl^- ions, respectively along the z -axis, under the operating conditions of $T = 300 \text{ K}$ and $C = 3.5\%$. The positions of the C planes of the GO membrane are delineated in vertical purple dashed lines.

5.3.3 Effect of temperature

The water flux J_w and R solute rejection as functions of feed temperature are depicted in Fig. 5.11(a) and (b), respectively. As the temperature T increases, the viscosity of feed

solution reduces, and the mass transfer rate improves. Thus, the temperature T has a positive impact on amplifying the water flux J_w . A similar trend has been previously reported for the bilayer GE membrane [270]. For both cases (i.e., nanofiltration system ($E = 0 \text{ V/\AA}$) and ENF system ($E = 0.6 \text{ V/\AA}$)), with the increase in the feed temperature, the number of water molecules and ions (only in nanofiltration) passed through the membrane increases, although the change in water molecules is considerably larger than the increase in ions. Because of this, the CP near the feed side membrane surface increases, as shown in Fig. 5.12. For the range of temperature T studied, the CP at the feed side of the nanofiltration system is lower than that of the ENF system. Hence, the water flux through the nanofiltration system is always higher than the water flux through the ENF system.

Furthermore, with the increase in the feed temperature, the kinetic energy of molecules and their diffusivity increases, and therefore the molecules in the feed solution possess higher kinetic energy [288]. Subsequently, at high feed temperature, water molecules passing through the membrane may have high kinetic energy. To understand the effect of the feed temperature on the water diffusion, the mean square displacement MSD of water inside the membrane is analyzed (Fig. 5.11(c)). A linear fitting of the MSD $\langle \Delta s^2 \rangle(t)$ curve gives the diffusion coefficient D based on the relation shown in Eq. (2.2). In the presence of an external electric field, the diffusion coefficient D increases with the temperature in the order of $T = 300 \text{ K}$ ($4.57 \times 10^{-6} \text{ cm}^2/\text{s}$) $< T = 320 \text{ K}$ ($4.65 \times 10^{-6} \text{ cm}^2/\text{s}$) $< T = 340 \text{ K}$ ($5.21 \times 10^{-6} \text{ cm}^2/\text{s}$). As can be seen from Fig. 5.12(a), in the ENF system, the interlayer region of the GO membrane is free from ions at each temperature, so the resistance from the ions on the water permeation through the membrane is negligible. Hence, D increases as the kinetic energy of the water molecules increase with the temperature.

Fig. 5.11. (a) and (b) Dependence of the water flux J_w and the solute rejection R on the feed temperature T , respectively. Salinity C of the feed solution is 3.5%. (c) MSD of the water molecules in the membrane region at various feed solution temperature T for $E=0$ V/Å and $E=0.6$ V/Å. (d) The Arrhenius plot of the water flux J_w for $E=0$ V/Å and $E=0.6$ V/Å.

However, for $E=0$ V/Å, the diffusion coefficient D increases with the temperature in the order of $T=340$ K (4.64×10^{-6} cm²/s) $<$ $T=300$ K (4.72×10^{-6} cm²/s) $<$ $T=320$ K (4.90×10^{-6} cm²/s). Interactions between water molecules inside the membrane region increase in the order of $T=340$ K $<$ $T=320$ K $<$ $T=300$ K, showing a disordered structure at higher feed temperature because of the increase in kinetic energy (Fig. 5.13). Meanwhile, ionic concentration inside the membrane region increases with the increasing feed temperature (Fig. 5.12(b)), imposing a barrier on the water flow. As a result of these effects, water diffusion in the nanofiltration system exhibits a nonmonotonic behavior with the temperature.

Fig. 5.12. Dependence of ion density distribution on the feed temperature T , along the z -axis of (a) ENF system and (b) nanofiltration, for $C = 3.5\%$. The positions of the C plane of the GO membrane are delineated in vertical purple dashed lines.

With the increase in T , as per the Stokes–Einstein equation for spherical particles [262], the diffusion of ions increases as well, leading to a rise in the number of ions penetrating the membrane that subsequently reduce the solute rejection. As a result, overall solute rejection decreases with the temperature for the nanofiltration system. At certain temperatures, this reduction is not significant, as permeate solute concentration is determined by the number of water molecules and ions in the permeate reservoir, where both quantities increase with the increase in temperature. For the ENF system, as the ionic flux is mainly determined by the field intensity, the solute rejection R is independent of the feed temperature.

The temperature dependency of the water flux through the membrane can be represented by the Arrhenius relation using Eq. (4.3) [265]. The water flux J_w against the reciprocal of temperature is plotted in Fig. 5.11(d) and the linear fitting of the curve gives the apparent activation energy E_a a water molecule needs to overcome as it permeates through the membrane the ionized GO membrane. E_a is estimated to be 12.5 and 13.5 kJ/mol for the ENF and nanofiltration systems, respectively. These values are much lower

than the previously reported reverse osmosis membrane [182]. The positive activation energy implies that the water flux increases with the feed temperature. The relatively low E_a value of the ENF system indicates that the water permeation through the ionized GO membrane in the presence of an external electric field is a more energetically favorable desalination method than nanofiltration. Furthermore, the proposed ENF system yields a 100% solute rejection R , under the given operation conditions, showing its potential as an effective seawater desalination technique. It is demonstrated that pinhole defects in GO nanosheets enhance the water flux by providing a shorter route for trans-sheet flow and could enhance the water flux of the proposed ENF system without altering the solute rejection performance.

Fig. 5.13. RDFs $g(r)$ for the OW-OW pair inside the membrane region at various feed solution temperature T for $E = 0 \text{ V/Å}$.

5.4 Summary

MD simulations are conducted in the present study to explore the desalination performance of the ionized GO as a nanofiltration membrane. In this study, GO oxide sheets have a negative charge because of the ionization of carboxylic groups at the sheet edges, and intra- and interlayer spacings are adopted from the values reported in previous

experimental studies. Meanwhile, nanocapillaries of the GO membrane are larger than the ionic radii of the Na^+ and Cl^- ions and the GO membrane demonstrates low solute rejection rates. The results reveal that electrostatic repulsion or attraction between ions and membrane that blocks or adsorb ions onto the membrane surface and ion dehydration play a pivotal role in controlling the solute rejection. Furthermore, the ionized GO sheets, as a nanofiltration membrane, are effective for seawater desalination (water flux of $0.133 \text{ kg/cm}^2/\text{s}$ and Cl^- ion rejection of 44%) than the brackish water (water flux of $0.139 \text{ kg/cm}^2/\text{s}$ and Cl^- ion rejection of 26%) as Na^+ ion rejection is almost same for both solutions.

When the membrane is exposed to an external electric field, acting along the membrane axis, solute rejection improves significantly at the expense of a reduction in water flux. Coion (with respect to the polarity of the electric field at the permeate side membrane) rejection is reported as 100%, whereas counter ion rejections are 79% (Na^+) and 91% (Cl^-) for positive and negative field directions, respectively. Meanwhile, the reduction of water flux through the ENF system is significantly lower for the negative field direction, which is attributed to the intensified CP effect at the feed side than the CP observed in the positive field direction. Furthermore, the simulation results demonstrate that for the cation selective membrane, solute rejection decreases at high field intensity applied in the positive direction. In practice, the feed flow configuration can be optimized to reduce the CP effect by promoting turbulence between membrane and bulk feed. In this context, opposite field direction could be an effective solution for seawater desalination, because the solute rejection is comparatively higher than that of the positive field ENF system. Interestingly, the ENF system could be an energetically favorable operation with a more excellent solute rejection performance than the nanofiltration system.

Overall, the dependence of water flux on the field intensity shows a nonmonotonic behavior because of the CP effect at the feed side and blocking effect from the ions permeating through the membrane. Contrastingly, because of the activation of water diffusion, the water flux increases with the rise in feed temperature for both nanofiltration and ENF systems.

GO membranes are economical to manufacture in a large scale. However, their applications as desalination membranes are hindered because of comparatively low solute rejection. In this study, an energetically favorable method is proposed that yields a high water flux and complete solute rejection, and membrane fouling does not occur. Hence, the results from the present study are helpful for understanding the desalination performance of a GO membrane and developing a cost effective and efficient advanced desalination method, overcoming the challenges associated with conventional technologies, such as RO.

Chapter 6. GO/HKUST-1 MOF Thin Films for Seawater Desalination via PV

Recent research efforts have been devoted to composite nanomaterials obtained by integrating GE or GO with polymers, MOF or nanomaterials such as CNT. PV membranes made of GO or MOF structures exhibit much lower water flux in general. This chapter focuses on the design of a GO/HKUST-1 nanocomposite material that combines the benefits of both GO and HKUST-1 MOF for the improved water flux and stability of membranes during PV desalination.

6.1 Introduction

Cu-BTC also known as HKUST-1 MOF (Hong Kong University of Science and Technology MOF) is a MOF material widely studied for the fabrication of gas separation membranes [289, 290]. This material was first reported by Chui *et al.* [291], with the metallic group consisting of a pair of Cu^{2+} ions chelated by four carboxylate bridges (benzene-1,3,5-tricarboxylic acid). Subsequently, its wide commercial availability, easy fabrication and high permeability have made Cu-BTC a good candidate for membrane fabrication in general. However, its MOF structure is unstable in pure water and is only moderately stable in steam [292], thereby limiting its potential for water treatment. Such instability in the presence of water is due to the interaction of Cu ions with oxygen in the water molecules causing degradation of the MOF structure. HKUST-1 is found to be stable for months in aqueous solvents (Water: Dimethylformamide (DMF) = 5:1) [293]. Studies have since been carried out to develop HKUST-1 composite materials which are stable in water and can be used for water purification [76, 177, 179, 294-297]. In these structures, the Cu atoms interact with the O atoms in the functional groups of matrix

materials (polymers, graphite, GO) so that the Cu^{2+} ions become stable. Therefore, most of the water molecules will not be able to interact with the Cu atoms and the stability of the MOF structure in water is improved. The present study focuses on the design of a GO/HKUST-1 composite material that combines the benefits of both GO and HKUST-1 for improving the stability of membranes during PV desalination.

Previously reported MOF/graphite oxide composites exhibit a layer-spacing structure due to the growth of the MOF between the graphene layers [297]. The new configuration considered in this study, whereby a unit cell thick HKUST-1 layer is intercalated between GO layers to develop the membrane with a thickness of a few nanometers, can offer an improved material candidate for PV by utilizing the superior performance of HKUST-1 MOF under the protection of the GO layers to improve its stability in water.

6.2 Simulation model

6.2.1 Material of study

Fig. 6.1 shows the simulation model used to study the desalination performance of the HKUST-1 membrane. In the figure, the model for a pure MOF membrane is provided for reference. Two chambers are separated by the MOF membrane with a thickness of 26 Å (Fig. 6.2(a)). The left compartment is filled with NaCl solution of 3.5% salinity (20 Na^+ and 20 Cl^- ions solvated with 1811 water molecules) which is representative of the typical ion concentration in seawater, and the right chamber is a vacuum. Two rigid graphene (GE) pistons are added at the ends of each chamber. The left piston can self-adjust its position during the simulation under the pressure P_{left} , constant at 0.1 MPa (i.e. standard atmospheric pressure) as indicated in Fig. 6.1, while the right piston is fixed in

place. The orthogonal dimensions of the computational model size are: $x = 26 \text{ \AA}$, $y = 208 \text{ \AA}$ and $z = 55 \text{ \AA}$.

Three configurations of the GO/HKUST-1 MOF membranes are explored to study their PV performance. They are referred to as (1) HKUST-1_MOF (a single MOF sheet) membrane, (2) SL-GO_MOF (a MOF sheet with single-layered GO on both sides) membrane and (3) DL-GO_MOF (a MOF sheet with double-layered GO on both sides) membrane (Fig. 6.2). One of the reasons for using the DL-GO_MOF configuration is the ease of their fabrication in practice compared with the SL-GO_MOF membrane configuration [147, 298]. In addition, the swelling of single and double-layered GO must not be so pronounced as expects in the multi-layered GO.

Fig. 6.1. Schematic of the simulation model: The left chamber with the feed solution and the right vacuum chamber are separated by an HKUST-1_MOF membrane. The left piston is exerted by atmospheric pressure ($P_{left} = 0.1 \text{ MPa}$) and is allowed to move, while the right piston is held fixed. Color coding of atoms: C of pistons (grey), C of MOF (cyan), O (red), H (white), Cu (orange), Na^+ (yellow) and Cl^- (green).

The DL-GO_MOF membrane configuration is built as follows. The Lerf–Klinowski model [277], which is consistent with the recent experimental results is incorporated into the development of the GO structure. According to this model, the C:O concentration ratio is set at 5:1, and an equal number of hydroxyl and epoxy groups are randomly distributed on both sides of the GE sheet as shown in Fig. 6.2(d). The single GO sheet consists of 160 C atoms and has the dimensions of $23.5 \times 16.5 \text{ \AA}^2$ in the x - z plane.

Structural optimization of the initial GO and MOF structures is performed on a periodic atomic structure using the density functional theory (DFT) implemented in the Vienna *ab initio* simulation package (VASP) [299]. The interactions between ions and electrons are described by the projector augmented wave (PAW) pseudopotentials [300, 301] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals [302]. The cutoff electron kinetic energy is set to be 400 eV, and k-points of $1 \times 1 \times 1$ are used in this calculation. The conjugate gradient method with a total energy of 1×10^{-4} eV, ionic force convergence criteria of 3×10^{-2} eV/Å for MOF [303] and 1×10^{-2} eV/Å for GO [304] are applied. The optimized GO sheets are then arranged to form a bilayer GO membrane with interlayer and intralayer distances of 10 Å each (Fig. 6.2(c)).

Fig. 6.2. Membrane configurations: (a) HKUST-1 MOF, (b) SL-GO_MOF and (c) DL-GO_MOF. Color coding of atoms: C (cyan), O (red), H (white), Cu (orange). (d) Structure of GO layer after the DFT geometry optimization. Color coding of atoms: C of GO (grey), O (red), H (white).

The HKUST-1 MOF structure is adopted from the Cambridge Crystallographic Data Centre [305]. Two unit cells are placed along the z -direction to allocate sufficient space for the addition of the slit-pore GO membranes to the MOF structure. The equilibrium Cu-O bond length is reported as 1.81 Å [306]. Therefore, the average distance between the Cu atom and the O atom of the epoxy group in the GO layer is set to be 1.81 Å.

6.2.2 Simulation setup

The desalination performance of the three configurations is investigated using the LAMMPS package [234]. The periodic boundary conditions are applied in all three orthogonal directions. The positions of atoms in the membranes are fixed to avoid the out-of-plane displacement. Interactions among the solvent molecules, membrane and pistons are modelled using the vdW interaction combined with the electrostatic interaction. The vdW interaction between two atoms is described by the LJ potential as in Eq. (2.14). The LJ parameters of the C, O and H atoms in the GO membrane are adopted from a previous work [269]. The values of ϵ and σ for the C-O interaction are set at 0.0937 kcal/mol and 3.19 Å [143], respectively. As proposed by Zhao *et al.* [307] the vdW parameters of the MOF atoms (C, O and H) are extracted from the Dreiding force field [308] and those of Cu from the universal force field (UFF) [309]. The TIP3P [199] model is applied to simulate water, while the LJ parameters for Na⁺ and Cl⁻ ions are also adopted from a previous work [238]. The SHAKE constraint algorithm is used to maintain the rigid geometry of the water molecules [201].

The atomic interactions among the different species are estimated using the Lorentz-Berthelot mixing rules. The sp² hybridized C atoms of GO and GE are treated as neutral, while the partial charges of the functional groups in the GO and MOF atoms are adopted from research works [310] and [311], respectively. The particle-mesh Ewald summation

technique is applied to compute the long-range electrostatic interactions with a cutoff distance of 14 Å [279].

All simulations are performed under the NVT ensemble. Initially, a relatively high external force is applied on the left piston to adjust the density of the feed solution. Then, the system is equilibrated at the corresponding desalination temperature T for 10 ps. Meanwhile, P_{left} is adjusted again so that the feed solution is acted upon by the standard atmospheric pressure of 0.1 MPa. During this process, a reflecting wall is placed in the left reservoir at a distance of 0.1 Å from the membranes considered. This is required in order to avoid the interaction of the membranes with the water molecules before achieving the equilibrium state. Once the system reaches the equilibrium state, the reflecting wall is removed to allow the water molecules to penetrate and pass through the membrane to simulate the PV desalination process. The desalination stage itself is conducted for 10–14 ns depending on the operating conditions and membrane size with an integration time step of 1 fs. When a water molecule from the feed solution permeates through the membrane into the vacuum chamber, an extra force would be applied to it to drive it towards the right piston to maintain the right chamber to be approximately vacuum [221].

The desalination performance of a membrane is typically evaluated in terms of water flux (J_w) and ion rejection (R). The water flux is defined as the number of water molecules transferred across the membrane from the feed to permeate reservoirs per unit area and unit time. The rejection rate is defined using Eq. (4.1).

The desalination performances of the three types of membranes are first evaluated under the default operating conditions, namely the feed salinity $C = 3.5\%$ that is characteristic of seawater concentration and temperature $T = 348$ K. The PV performance of GO_MOF composite membranes are compared with that of a bilayer GO membrane

with a thickness of 13.5 Å and inter and intra layer distances of 10 Å each (similar to the bilayers shown in Fig.3(c)). Subsequently, for the SL-GO_MOF membrane that, as will be shown later, demonstrates the decent desalination performance under the default operating conditions, MD simulation of its PV process is then conducted under different feed solution salinities ($C = 3.5\%$, 5.0% , 7.5% and 10%) and temperatures ($T = 318$, 333 , 348 and 363 K) in order to investigate the effects of altering these parameters.

6.3 Results and discussion

The MOF, SL-GO_MOF and DL-GO_MOF membranes are first investigated under the default conditions as mentioned earlier (Section 6.2.2). Fig. 6.3(a) shows the number of water molecules inside the permeate chamber (N_w) as a function of the simulation time. The desalination performance is analyzed only after the systems have reached a steady state, i.e. when the water molecules have filled the entire void space in the membranes. It is observed that for the pure MOF membrane, the time required for this preliminary process is less than 3 ns, while for the SL-GO_MOF and DL-GO_MOF configurations, it takes approximately 4 and 7.5 ns, respectively. Therefore, for the pure MOF and SL-GO_MOF configurations, the measurements are only deemed significant after the first 5 ns (indicated by the blue vertical dashed line in Fig. 6.3(a)). In the case of the DL-GO_MOF membrane, this cutoff time is extended to the first 8 ns of the PV process (indicated by the red vertical dashed line in Fig.6.3(a)).

The simulation results show that the pure MOF membrane demonstrates the highest water flux of $0.0056 \text{ kg/cm}^2/\text{s}$ among the three types of membranes under the conditions $C = 3.5\%$ and $T = 348 \text{ K}$. The SL-GO_MOF and DL-GO_MOF configurations yield lower values of J_w of $0.0031 \text{ kg/cm}^2/\text{s}$ and $0.0014 \text{ kg/cm}^2/\text{s}$, respectively. For all three

configurations, the ion rejection rates R are recorded at 100% at the end of the simulations.

To explore the effects of membrane rigidity on ion rejection, an additional simulation has been conducted for a flexible membrane. The membrane atoms are constrained to their initial positions by tethering a spring to each atom with the spring constant of 1 kcal/mol/Å. This treatment helps to reduce lateral drifting of membrane atoms while maintaining its atomic structure and introduce some degree of flexibility while keeping the computational time low. The water permeability (P_w) of a membrane is taken to assess its desalination performance. It is calculated by assuming a perfect vacuum on the permeate side and using the equation:

$$P_w = h * J_w / \Delta P, \quad (6.1)$$

where h denotes the membrane thickness and ΔP the pressure difference between the feed and permeate sides.

It is found that the water permeability of the flexible MOF membrane is increased by 35% in comparison with its rigid counterpart, while its solute rejection rate is also 100% (Fig. 6.3(c)). Zhao *et al.* [307] have shown that the HKUST-1 MOF is less flexible than the well-studied MOF-5 and its framework flexibility is insignificant in the adsorption of CO₂. Furthermore, their results suggest that the force field parameters used in their study can be adopted to study the intense interactions between adsorbate and MOF membrane. As will be discussed later, the ion rejection occurs mainly due to the intense interactions between the ions and membrane atoms that adsorbed them. Moreover, NaCl is non-volatile and unlikely to be converted to the vapor phase after reaching the upper membrane surface (at the permeate side), which enables a high solute rejection in the PV process [71, 111]. Thus, we believe that the force field parameters used in this study and

the treatment of the membranes as rigid structures are valid to simulate a PV desalination system.

Due to the presence of the GO layers (Fig. 6.2(b)) that impede the molecules from penetrating the MOF, the effective opening area of GO layered membranes for permeation is smaller than that of the pure MOF membrane. The water molecules and the solute ions can only penetrate the MOF membrane through the slits on the surface GO layer and subsequently, the gaps between the adjacent GO layers. Therefore, the rate of molecule sorption (desorption) from the feed reservoir to the MOF membrane (from the MOF membrane to the permeate reservoir) is reduced compared with the pure MOF membrane. Thus, the water flux J_w through the SL-GO_MOF and DL-GO_MOF membranes are 43% and 75% lower than that of the pure MOF membrane, respectively. Naturally, the reduction of water flux can be attributed to the increase of membrane resistance to the penetration of water molecules concomitant with an increase in its thickness (Fig. 6.2). In addition, most slit positions in the GO layers are offset with one another, causing tortuosity and the prolongation of molecule trajectories as well as the ion accumulation inside the membrane (Fig. 6.3(b)) that also impinge the water flux. A similar trend has been reported in the literature for PV membranes made from GO/polyacrylonitrile [48] and GO/polydopamine/alumina [54]. At the same time, as will be discussed later, increasing the number of GO layers reduces the interactions between the Cu atoms of the MOF structure and water molecules, ensuring better stability of the structure compared with the single-layered model. Therefore, minimizing the number of GO layers while maintaining the overall structural stability is paramount in the design of GO/HKUST-1 membrane for PV.

Fig. 6.3. (a) Number of water molecules transferred from the feed solution to the permeate reservoir through the membrane (N_w), as a function of the simulation time. (b) Number of Na^+ and Cl^- ions inside the membrane (N_i) as a function of the simulation time. (c) Number of water molecules N_w and ions N_i transferred from the feed solution to the permeate as a function of time for the flexible MOF membrane under the default operating conditions of $T = 348$ K and $C = 3.5\%$.

To further investigate the water permeation, the transport diffusion coefficient of water (D_w) through the membrane is calculated based on Fick's law from the following equation [312]:

$$D_w = \frac{J_w h}{c_{w,m}}, \quad (6.2)$$

where h is the membrane thickness and $C_{w,m}$ is the water concentration at the membrane surface on the feed side. As more GO layers are added to the MOF membrane, the value of $C_{w,m}$ increases much more rapidly than h , and as expected, the estimated diffusivity D_w decreases, similar to the water flux J_w (Table 6.1).

Table 6.1. Water flux J_w and diffusion coefficient D_w of three types of membranes

	MOF	SL-GO_MOF	DL-GO_MOF
h (Å)	26	36.25	56.25
J_w (kg/cm ² .s)	0.0056	0.0031	0.0014
D_w (10 ⁻⁶ cm ² /s)	1.26	0.74	0.44

RDFs between the solute ions and constituent atoms of the water molecules are computed to understand the hydration structure of the ions in the feed and MOF membrane (Fig. 6.4). The first peaks of the RDF curves of the ion-water pairs in the membrane exhibit higher amplitudes compared to those of the feed solution, which is a direct result of volume confinement. The first peak locations of Na⁺-HW and Cl⁻-OW RDF curves provide an estimation of the hydration shell radii of the cations and anions, respectively. Hence, the estimated hydration shell radii of Na⁺ and Cl⁻ ions are approximately 3.2 and 3.4 Å, respectively. These values are in agreement with previously reported values in related literature [207, 313].

According to the coordination number curve, there are about six water molecules in the hydration shells of solute ions in both the feed solution and MOF membrane, indicating no change in their hydration structure as they enter the membrane region. The pore sizes of the HKUST-1 MOF (radii of 7 and 5.5 Å) and GO (slit width of 10 Å) are much larger than the hydration radii of ions, so the solute ions can penetrate the

membranes easily. However, the trajectories of the ions (Fig. 6.5(a)) reveal that they have a propensity of accumulating inside the membranes (Fig. 6.3(b)), showing that the adsorption of ions by the membrane is the main mechanism for desalination. It is noted that the ion accumulation is most prominent in the double-layered GO composite membrane, while for the single-layered GO membrane, it is not so pronounced and even slightly less noticeable than the pure MOF membrane. Adsorbed ions can still interfere with the water diffusion.

Fig. 6.4. RDFs $g(r)$ between ions (Na^+ , Cl^-) and atoms (OW, HW) of water molecules in (a and c) feed and (b and d) MOF membrane under the default operating conditions of $T = 348$ K and $C = 3.5\%$.

Fig. 6.5. (a) Trajectories of selected Na^+ ions and Cl^- ions. Blue dashed lines indicate the upper membrane region. (b) A fragmental cluster of HKUST-1 MOF.

To further understand the effect of ions on the water diffusion, the ion density distributions along the y -axis (see Fig. 6.1) at the end of the PV simulations are analyzed (Fig. 6.6). In the pure MOF membrane, most of the Cl^- ions reside at the feed side (Fig. 6.6(a)), while Na^+ ions diffuse deeper into the membrane before being adsorbed. In order to explain this, RDFs between the ions and membrane atoms are plotted (Fig. 6.7). The first peak of the Cl^- -Cu RDF curve (Fig. 6.7(b)) is attributed to the intense interactions between the Cl^- ions and the Cu atoms of the MOF structure. Thus, the Cu atoms on the surface of the left side of the MOF structure hinder the admittance of Cl^- ions into the membrane. The first peak of the Na^+ -O11 (Fig. 6.5(b)) RDF curve (Fig. 6.7(a)) is at a short distance of around $2.75 \text{ \AA}$ and reveals the affinity of Na^+ ions towards the O11 atoms of the MOF. The peaks of the Na^+ ions with the rest of the MOF atoms are flat and broad, indicating weak interactions between them. The above observations imply that the adsorption of ions by the MOF membrane is due to the intense interactions between the MOF and ions.

Fig. 6.6. Density distribution of solute ions of the (a) MOF (b) SL-GO_MOF and (c) DL-GO_MOF membranes along the y -axis, at the end of the simulation under the default operating conditions of $T = 348$ K and $C = 3.5\%$. The two ends of the membrane are delineated in vertical black dashed lines. (d) Ion distribution inside the DL-GO_MOF membrane. Color coding of atoms: C (cyan), O (red), H (white), Cu (orange), Na^+ (yellow) and Cl^- (green).

As stated earlier, due to the coverage of the MOF structure by the GO layers, the ion sorption inside the SL-GO_MOF membrane is lower than that of the pure MOF membrane (Figs. 6.3(b) and 6.6(b)). Meanwhile, for the SL-GO_MOF and DL-GO_MOF membranes, the Na^+ ion concentration on the feed side is noticeably higher than the Cl^- ion concentration as the Na^+ ions interact more intensely with the functional groups of the GO sheets ((Fig. 6.7(d) and (f)). The DL-GO_MOF membrane has the highest ion density inside the membrane region (Fig. 6.6(c)) since the interlayer and intralayer distances of

the bilayer GO are sufficiently large for both Na^+ and Cl^- ions to enter the composite membrane easily. These ions interact preferentially with the GO and most of them are located inside the bilayer region (Figs. 6.6(d)), acting as a blockage to the permeation path and imposing additional resistance on the transportation of water molecules. This impinges the water flux through the DL-GO_MOF membrane.

In principle, the adverse effects can be reduced by controlling the interlayer and intralayer distances of the GO membrane to hinder ion permeation, where size exclusion is the key mechanism that rejects the solute ions. However, ions can still concentrate at the surface of the membrane on the feed side and enhance the external concentration polarization effect on the membrane surface on the feed side.

In this study, the relationship between the water flux J_w and membrane configurations is further analyzed using RDF for OW-OW pairs between water molecules ($g(r)_{\text{ow-ow}}$) inside the membrane region (Fig. 6.8(a)). The water contact angles for HKUST-1 and GO are found to be 34.7° [314] and 26.8° [315], respectively; ergo, GO is more hydrophilic than the HKUST-1 MOF. Consequently, the interactions between the GO and water molecules are more intense than those of the MOF structure and water molecules. This can be evidenced by the increasing intensity of the first peak of the RDF curves $g(r)_{\text{ow-ow}}$ for the membranes in the order of DL-GO_MOF $\rightarrow$ SL-GO_MOF $\rightarrow$ MOF. The more pronounced fluctuations noticed in the RDF of the pure MOF membrane are due to the enhancement of short-range order of the water structure and intensified interactions among the water molecules.

To understand the effect of the interaction energy on water mobility, the MSD of water inside the membrane is analyzed (Fig. 6.9). A linear fitting of the MSD $\langle \Delta s^2 \rangle(t)$ curve gives the diffusion coefficient D based on the relation shown in Eq. (2.2). This approximation has been commonly applied in MD simulations to study the diffusion

coefficient through membranes. Unlike D_w , diffusivity D decreases in the order of DL-GO_MOF ($4.33 \times 10^{-6} \text{ cm}^2/\text{s}$) $\rightarrow$ SL-GO_MOF ($2.64 \times 10^{-6} \text{ cm}^2/\text{s}$) $\rightarrow$ MOF ($0.85 \times 10^{-6} \text{ cm}^2/\text{s}$), which indicates that the water molecules move more easily in the DL-GO_MOF membrane. It should be noted that intense interactions between the water molecules in the same order (Fig. 6.8(a)) is the main contributor in slowing down the water diffusion. However, the water flux J_w for the membranes decreases in the order MOF $\rightarrow$ SL-GO_MOF $\rightarrow$ DL-GO_MOF implying that the pore size, membrane thickness and the ion accumulation inside the membrane due to the GO layer(s) significantly affect the water flux J_w .

In PV membranes, evaporation may occur inside the membrane or at its surface due to a difference in the partial pressures of the components on both sides. Hence transport through the membrane can be divided into two zones: the liquid zone and vapor zone. To explore the region where phase transition takes place, water density distributions along the y-axis of SL-GO_MOF and DL-GO_MOF membranes are analyzed. For clarity, the density distributions of water molecules near the upper membrane regions of the SL-GO_MOF and DL-GO_MOF membranes are shown in Fig.6.10. It is evident that the evaporation takes place inside the membrane since the water density decreases to zero gradually within the membrane region. Thus, an absence of water molecules is observed near the downstream side within the membranes.

It has been reported that the low stability of HKUST-1 in water is due to the strong affinity of Cu atoms towards water molecules [177, 316, 317]. To investigate the interactions between the Cu atoms of MOF and the water molecules, the RDFs for the pair Cu-OW ($g(r)_{\text{Cu-OW}}$) are plotted for the membrane configurations considered (Fig. 6.8(b)). The first peak is located at 2.35 Å, and its intensity drops notably with an increasing number of GO layers, indicating that GO layers have lowered the water

affinity of Cu. This is attributed to the interactions between the Cu atoms on the HKUST-1 surfaces and the O atoms of the GO layers, which significantly reduce the number of Cu atoms available to interact directly with the water molecules. Meanwhile, functional groups hinder the water molecules reaching the Cu atoms. The average number of Cu-OW bonds per surface Cu atoms are calculated to be five for the pure MOF and two for the SL-GO_MOF membrane, showing that clustering of water is reduced around the Cu atoms (Fig. 6.11). Since the surface Cu atoms are greatly isolated from the water molecules by the GO layer(s), the structural stability of the MOF structure is protected. Furthermore, the GO layers on the side of the permeate chamber are exposed to a less humid environment, which also assures membrane structural stability.

The Cu-OW interaction energy is calculated to further verify the results. The magnitude of the interaction energy decreases in the order of MOF (−56 kcal/mol) → SL-GO_MOF (−50 kcal/mol) → DL-GO_MOF (−32 kcal/mol) and indicates that the interactions between the water molecules and the Cu atoms in the MOF structure are reduced as more GO layers are added. In the DL-GO_MOF case, such behavior results in the increased density of water ($> 1 \text{ g/cm}^3$) in the region between the two GO layers (Fig. 6.10) and indicates that the water molecules interact more intensely in this constrained area, which does not apply in the case of the SL-GO_MOF membrane. Moreover, the incorporation of GO creates a more hydrophobic environment surrounding the metallic sites that protect the coordination bonds from interactions with water molecules [297].

Fig. 6.7. RDFs $g(r)$ between ions-membrane atom pairs inside (a,b) MOF, (c,d) SL-GO_MOF and (e,f) DL-GO_MOF membranes under the default operating conditions of $T = 348$ K and $C = 3.5\%$.

Fig. 6.8. RDFs $g(r)$ for the (a) OW-OW pair and (b) Cu-OW pair inside the MOF, SL-GO_MOF and DL-GO_MOF membranes under the default operating conditions of $T = 348$ K and $C = 3.5\%$.

Fig. 6.9. Mean square displacement MSD of water molecules inside the membrane region of three types of membranes studied.

When this nanocomposite structure is combined with a polymer matrix, a further decrease in the clustering of the water molecules near the Cu atoms can be expected because of the interaction between Cu atoms and the oxygen functional groups in the polymer. Meanwhile, the addition of a polymer matrix can further enhance the structural stability of MOF in water, and thus can be effectively utilized in the fabrication of

composite membranes for PV. Moreover, it is observed that when the feed salinity is raised to 10%, the Cu-OW interactions for the same membrane configuration (in particular, for SL-GO_MOF) would be reduced due to the lower number of water molecules in the feed solution. Thus, the composite structures can withstand highly saline environments (e.g. highly concentrated brine solution).

Fig. 6.10. Density distribution of water molecules along the y-axis of (a) SL-GO_MOF and (b) DL-GO_MOF membranes. Downstream surfaces of the membranes are delineated in red vertical dashed lines.

Furthermore, the PV performances of GO_MOF composite membranes are analyzed and compared with the performance of a bilayer GO membrane, in terms of water permeability. The bilayer GO membrane yield a permeability of 2.5×10^{-4} kg.m/m²/hr/bar at 348 K which is 40% and 10% lower than those of the SL-GO_MOF (4.2×10^{-4} kg.m/m²/hr/bar) and DL-GO_MOF (2.8×10^{-4} kg.m/m²/hr/bar) membranes, respectively. Furthermore, the GO/HKUST-1 composite structure in this study has a higher water permeability compared with the ZIF-8 PV membrane (7.5×10^{-6} kg.m/m²/hr/bar at 348 K) reported in previous literature [49], which can be attributed to the large pore sizes and hydrophilicity of the GO/HKUST-1 composite membrane surface. Also, its enhanced

water flux may be ascribed to a facilitated transfer mechanism described in ref [318], that will also be discussed in our future work. It has also been reported that the experimental fabrication of these composite structures is simple and economical [76]. Hence, the proposed new composite membrane is an efficient and economical candidate for PV desalination of seawater.

Fig. 6.11. Clustering of the water molecules around feed side surface Cu atoms in (a) MOF and (b) SL-GO-MOF membranes. Results are visualized using OVITO software [185]. Color coding of atoms: O (blue), Cu (orange), Na^+ (yellow) and Cl^- (green). In panel (b) GO layer is not shown for clarity. Red lines indicate bonds between the surface Cu atoms (feed side) and O of water molecules.

6.3.1 Effect of feed temperature

Furthermore, the effects of the feed temperature on the membrane performance during PV is analyzed (Fig. 6.12(a)). As expected, the water flux J_w increases with the increase of feed temperature T . A similar trend is also reported in previous literature [48, 49, 111, 221]. The water flux increases significantly when the temperature is raised from 318 K to 333 K. However, at higher temperatures, this trend slows down noticeably. With increasing feed temperature, the kinetic energies of the water molecules and their

diffusivity increase, and therefore the water molecules near the surface of and within the membrane possess a high mean kinetic energy, resulting in high water flux. As per the Stokes-Einstein equation for spherical particles [262], the diffusion of ions increases as well with increasing feed temperature, leading to an increase in the number of ions penetrating the membrane and subsequently get adsorbed, thus blocking the water permeation paths and retarding the water flux. Such an effect becomes more prominent at higher temperatures and accounts for the declining rate of increase of the water flux. Despite this phenomenon, the water flux reported in the present study is still much higher than the water flux of the GO/polyacrylonitrile membrane (65.1 kg/m²/hr) [48] and GO/polydopamine/alumina membrane (48.4 kg/m²/hr) [54].

To explore the effects of temperature on the diffusivity of water molecules, their MSD in the feed solution and the apparent water diffusion coefficient D_w through the membrane are estimated (Figs. 6.12(b) and (c), respectively). As seen from the MSD curves, the mass transfer coefficient of water in the feed solution increases with the temperature. Due to the high mobility of the molecules, the mass transport of water molecules across the membrane increases, as denoted by the monotonically increasing apparent diffusion coefficient of water D_w with temperature.

In general, for water desalination, the temperature dependency of the water flux through the membrane can be represented by the Arrhenius relation using Eq. (4.3) [265]. The water flux J_w against the reciprocal of temperature is plotted in Fig. 6.12(d) and the linear fitting of the curve gives the apparent activation energy for the water permeation through the membrane. To improve the accuracy of the fitted curve, an additional simulation at 310 K is conducted. From the gradient of the Arrhenius plot, E_a is estimated to be 12.49 kJ/mol. The positive activation energy implies that the water flux increases with the feed temperature while its relatively low value (compared to E_a of

GO/polyacrylonitrile membranes and GO/polydopamine/alumina of 22.19 [48] and 26.5 kJ/mol [54], respectively) is attributed to the membrane structure that facilitates the water diffusion.

Fig. 6.12. (a) Dependence of the water flux J_w on feed temperature T . (b) MSD of the water molecules inside the feed solution at various feed solution temperatures T . (c) Dependence of the apparent water diffusion coefficient D_w on feed temperature T . (d) The Arrhenius plot of the water flux J_w .

For water desalination, E_a can be interpreted as a compound parameter that characterizes the overall effect of temperature as a driving force for permeation and permeability coefficient [319]. Thus, it can be represented as the sum of the heat of evaporation ΔH_{eva} and activation energy characterizing the membrane permeability E_p . Since ΔH_{eva} of water at 25 °C is 44.0 kJ/mol [320], E_p of the SL-GO_MOF membrane at

this temperature is estimated to be -31.5 kJ/mol. The negative sign of E_p indicates that the water sorption process is the most dominant among the three steps associated with the PV separation. Moreover, it implies that the membrane permeability coefficient decreases with increasing temperature, which can be reconciled with the decline in the rate of increase of the water flux (with respect to increasing feed temperature) at higher temperatures due to enhanced ion diffusion mentioned earlier. However, the high kinetic energies and therefore high thermally activated diffusivity of water molecules would still lead to an overall increase in the water flux.

6.3.2 Effect of feed concentration

Fig. 6.13(a) shows the effect of feed salinity on the performance of the GO_MOF membrane during PV at 348 K. The water flux J_w decreases as the feed salinity increases and the results are in agreement with previous literature [48, 49, 111]. The increase of water content in the feed solution results in a sharp increase in water and solute flux due to the enhanced driving force for PV desalination [321]. This can be further investigated by analyzing the diffusion behavior of water in the feed solution, as presented in the following discussion.

The RDF for OW-OW atom pairs in the feed solution, $g(r)_{\text{OW-OW}}$, is plotted at different feed salinities to understand the effects of the solutes on the water structure (Fig. 6.13(b)). In pure water, $g(r)_{\text{OW-OW}}$ is characterized by its first peak at ~ 2.8 Å and the second peak at ~ 4.5 Å. It is noticeable that under pressure, the second peak shifts from ~ 4.5 Å to ~ 3.4 Å [322]. Similarly, in this study, due to the collapse of the second coordination shell with the increase of the feed concentration, the second peak moves closer to the first peak. This can be explained by the fact that the water at high salinity

levels has a more compact structure and tends to transform from low-density liquid to high-density liquid, so to speak, characterized by its disordered structure.

The transformation of the structure of water at higher levels of salinity is due to the competition between ion-water interactions and water-water interactions [323]. These interactions are dominated by the charge density effect and hydrogen-bonding, respectively. Because of the asymmetric distribution of charge in water molecules, anions are more prominent in ordering the water structure than the cations. The pairwise interaction energies for the water molecule-water molecule and water molecule- Cl^- ion interactions in the feed solution are calculated for different salinity levels (Fig. 6.14). It is noted that with the increasing ion concentration, the interactions of the water molecules among themselves decrease while the water molecule- Cl^- interactions increase. Such an increase in the water-ion interactions changes the nature of the bonds between water molecules and results in reduced water flux J_w .

The sorption of water molecules and ions through the liquid-membrane interface is also affected by the feed concentration. To verify this, the ion density distribution along the y-axis is analyzed for different feed salinities (Fig. 6.13(c)). The results show that at the liquid-membrane interface, the value of the ion density peaks increases with the increased solute concentration, indicating that the ion concentration polarization effect at the membrane surface is more pronounced. Such polarization reduces the driving force for water flowing through the membrane while increasing the driving force for the ion permeation. As a result, the number of ions penetrating and residing within the membrane increases, worsening the blockage of the membrane pores, imposing additional frictional forces and hindering the water flow.

Fig. 6.13(d) shows the apparent water diffusion coefficient D_w calculated using Eq. (6.2) as a function of the feed salinity level. Interestingly, the D_w function demonstrates a

nonmonotonic behavior with the feed salinity. When the feed salinity C is raised from 3.5% to 5%, D_w is drastically reduced. With a further increase in the salinity to 10%, the diffusion coefficient D_w increases monotonically. For feed salinity $C \leq 5\%$, a similar trend has been observed by Xie *et al.* [111] who have reported that for ion concentration in the range of 0.2%–5.0% and at a relatively high temperature (338 K), the D_w for polymer-inorganic membrane decreases monotonically with increasing feed concentration.

Fig. 6.13. (a) Dependence of the water flux J_w on feed salinity C . (b) RDF $g(r)_{OW-OW}$ of water molecules in the feed solution for different feed salinities C . (c) Ion density distribution along the y -axis for feed salinities of 3.5% and 10%. Green dashed lines indicate the membrane region. (d) Dependence of the apparent water diffusion coefficient D_w on the feed salinity C . The inset in (b) shows an enlarged view of the inward shift of the second peak as delineated by the dashed rectangle.

For a fixed thickness of the SL-GO_MOF membrane ($h = 36.25 \text{ \AA}$), both J_w and $C_{w,m}$ decrease with the increasing ion concentration. The intensities of the first two peaks of the RDF decrease significantly, especially for the second peak, indicating that there is more disordered liquid at a higher salinity (Fig. 6.13(b)). Therefore, the increased diffusivity at $C > 5\%$ is probably due to the reduced interactions among the water molecules (Fig. 6.14) (decreased intermolecular hydrogen bonds). In this case, because of the reduced interactions, the water molecules have increased diffusivity, while the water flux is reduced due to the blockage of membrane pores by the ions and the ion concentration polarization effect.

Fig. 6.14. Dependence of the interaction energy (for water molecules and water- Cl^-) on the feed salinity C , at a fixed temperature $T = 348 \text{ K}$.

Previous studies on GO membranes for seawater desalination have demonstrated a complete rejection of ions by controlling the interlayer and intralayer distances within the GO layers (complete offset pores and interlayer distance $< 8 \text{ \AA}$) [207, 270, 324]. In the present study, the impact of accumulated ions on the water flux inside the membrane can be lowered by densely packing the GO layers to impose a large energy barrier against the penetration of ions. However, such an increase of ion rejection near the membrane

surface also significantly enhances the concentration polarization and would therefore result in decreased water flux. Generally, by increasing the feed flow rate, the concentration polarization can be lowered [321], reducing the transport resistance in the liquid boundary layer and increasing the water flux. Hence, by controlling the feed flow rate, the desalination performance of densely packed GO_MOF membranes can be optimized for the fabrication of effective PV membranes for the desalination of highly concentrated brine solutions.

6.4 Summary

MD simulations are conducted to explore the performance of the GO/HKUST-1 membrane used for PV. It is revealed that for the SL-GO_MOF membrane, a high water flux of $0.0032 \text{ kg/cm}^2/\text{s}$ could be achieved at a desalination temperature of 368 K. The DL-GO_MOF possesses the lowest flux of $0.0014 \text{ kg/cm}^2/\text{s}$, but it is still higher than that of GO-based membranes reported in previous literature. For all membrane configurations and operating conditions, the solute rejection remains at 100% due to the non-volatile nature of NaCl and the adsorption of ions by the MOF membrane. The apparent activation energy for water permeation is estimated to be 12.5 kJ/mol, which is much lower than the typical values of commercially available membranes.

Due to the activation of water molecule diffusion, the water flux increases monotonically with the temperature. Despite the nonmonotonic behavior of water diffusivity with respect to the feed salinity observed in the study, the water permeation through the membrane decreases monotonically with the increasing feed salinity due to the blockage of the membrane pores by the ions and the ion concentration polarization effect. Furthermore, with increasing feed salinity, the ions suppress the motion of water

molecules (similar to the high-pressure effect), while the increase in diffusivity at $C > 5\%$ can be attributed to the reduction of some intermolecular interactions caused by the enhanced water-ion interactions. Thus, the study reveals that water diffusion is significantly affected by the feed salinity during the PV process.

The simulation results also show that the structural stability of the GO/HKUST-1 membrane can be improved by increasing the number of GO layers and operating within a highly saline feed solution. However, with increasing concentration of the feed, the accumulated ions within and at the surface of the membrane increase and reduce the overall water flux. This can be mitigated by packing the GO layers densely to restrict the diffusion of ions into the membrane, but such a method may also adversely impact the overall membrane performance due to the increased concentration polarization on the membrane surface. To use the proposed membrane configurations in the desalination of highly concentrated brine solutions, the feed flow configuration can be optimized to reduce the concentration polarization effect by promoting turbulence between membrane and bulk feed.

Chapter 7. Conclusions and Recommendations

This chapter presents the main conclusions from the research carried out in this Ph.D. study and recommendations for future research.

7.1 Conclusions

MD simulations have been conducted to investigate the desalination performance of GE-based thin films via different desalination technologies that have the potential to lower energy consumption. The effects of GE morphology, membrane structural parameters and functional groups on ion separation mechanisms have been investigated. Furthermore, the dependence of the desalination performance on the operating parameters has been explored to further improve the performance of the studied thin-film structures. A desalination performance comparison between different membrane configurations with their default structural parameters is presented in Table 7.1. The main conclusions from this study are listed as follows:

- Corrugation of GE sheets greatly enhances the ion adsorption capacity while adversely affecting the water flow rate in the CDI system. The reduction of the water flow rate can be explained by the following reasons: (1) blocked water movement by the extruding of the GE walls and the friction imposed by the adsorbed ions; (2) blocked entrance of the water molecules inside the channel because of the adsorbed ions in the region close to the channel entrance. The enhanced ion removal capacity is due to the strong anchoring effect existing in the regions that are bounded by crests and troughs of the upper and lower GE layers, respectively. Both water flow rate and ion adsorption increase with increasing wavelength and decreasing amplitude. In addition, ion adsorption is enhanced at a

lower electric field intensity. Moreover, the desalination performance of such a system depends on the entrance configuration and the entrance effect becomes significant at higher electric field intensity. Among the three types of entrance configurations considered, the water flow rate increases in the order of closing, opening and concurrent arrangements, while the number of ions adsorbed increases in the order of opening, concurrent and closing configuration.

- The desalination performance through the stacked GE laminates greatly depends on the membrane structural parameters such as pore size, pore offset, interlayer distance, and the number of GE layers. The complete rejection of ions is observed in the bilayer GE membranes for the nanoslit widths $d < 9 \text{ \AA}$. When the number of layers in the GE membrane increases, the ion rejection increases, and the water flow decreases because of the increase in membrane thickness and ion concentration in the interlayer region. Moreover, desalination performance greatly relies on the interlayer distance h and the offset distance l . The study reveals that the stacked GE membrane can accomplish a complete ion rejection and maintain a high water flux even at a large nanoslit width $d > 9 \text{ \AA}$ when an optimum interlayer distance h is set to $8 \text{ \AA}$ and a completely misaligned pore configuration are adopted. Overall, the GE membranes in FO systems yield a low water flux but an enhanced ion retention capability in comparison to the GE membranes in RO systems. However, when compared with the commercial polymeric membranes in FO systems, the bilayer GE membranes demonstrate a much higher water flow rate, and thus possessing a high-power density. Most importantly, internal concentration polarization effects are less severe in the free-standing GE laminates. The performances of the stacked GE membrane can be further

enhanced by operating the FO system at an elevated temperature and draw solute concentration.

Table 7.1. Comparison between different membrane configurations with their default structural parameters.

Technology	Structure	Material	ΔP (bar)	P_w (kg.cm/cm ² /s/bar)	R (%)	E_a (kJ/mol)
CDI		GE	5000	2.8E-10	94*	9.57
FO		GE	0.109**	8.0E-09	97-Na ⁺ 100-Mg ²⁺	8.02
RO		GE	1000	1.4E-12	76-Na ⁺	NC
Nanofiltration		Ionized GO	2000	9.7E-12	55-Na ⁺ 44-Cl ⁻	13.52
ENF		Ionized GO	2000	5.2E-12	100	12.49
PV		GO	1	6.1E-10	100	NC
	SL_GO/HKUST-1	1	1.2E-09	100	12.57
	DL_GO/HKUST-1	1	7.8E-10	100	NC

NC- not calculated in this study

*Calculation is based on the equation from ref [231]

**Calculation is based on Eq. (2.4)

- Ionization of the carboxylic acid group of the GO sheet introduces a negative charge on the membrane surface. The ionized GO membrane is selective for both Na⁺ and Cl⁻ ions for nanocapillaries much larger (10 Å) than the maximum pore size of 7 Å, which allows 100% solute rejection in RO. The electrostatic repulsions and attractions

between ions and membrane and ion dehydration are the mechanisms that drive the ion rejection through the ionized GO sheets as a nanofiltration membrane. The negatively charged membrane is more effective as a nanofiltration membrane for the seawater desalination than the brackish water desalination. Furthermore, the ENF system with an electric field opposite to the water flow direction is an energetically favourable method that greatly enhances the ion rejection through the ionized GO membrane, compared with the nanofiltration. For the ENF system, the water flux shows a nonmonotonic dependence on the electric field intensity, whereas the solute rejection increases with the increase of field intensity. At the field intensity of $E = 0.6 \text{ V/Å}$, a complete rejection of solute can be realized with a water flux as high as $0.071 \text{ kg/cm}^2/\text{s}$.

- Cu atoms of the HKUST-1 MOF structure can interact with O atoms of the functional groups in GO to form a GO/HKUST-1 composite structure. The structural stability of the GO/HKUST-1 nanocomposite can be improved by increasing the number of GO layers and operating within a highly saline feed solution. The increase in the number of GO layers diminishes the permeate flux because of the presence of additional barriers in the molecular paths. The nanocomposite membranes demonstrate excellent water flux higher than that of ZIF-8 and GO membranes reported earlier in PV desalination. The salt rejection of the composite membrane configurations for all operating conditions remains at 100% because of the non-volatile nature of NaCl and the adsorption of ions by the HKUST-1 MOF. Due to the activation of water molecule diffusion, the water flux increases monotonically with the feed temperature. The water permeation through the membrane decreases monotonically with the increasing feed

salinity due to the blockage of the membrane pores by the ions and the ion concentration polarization effect.

- The apparent activation energy E_a of the bilayer GE structure, as an FO membrane, is 8.02 kJ/mol, which is much lower than the E_a of other nanostructures investigated in this study and is therefore an energetically favourable membrane configuration for seawater desalination via FO. Meanwhile, the ENF method proposed in this study is more effective, as the ionized GO membrane demonstrates a higher water flux and ion rejection performance at a comparatively lower energy requirement ($E_a = 12.49$ kJ/mol) which is significantly lower than the previously reported E_a for RO membrane.

7.2 Recommendations

This study is based on unsupported GE-based structures that are easy to construct and can perform simulations at a lower computational cost. However, in real world applications such as nanofiltration, RO and PV, GE-based nanostructures have been combined with appropriate supportive layers to fabricate TFC membranes that adversely affect the desalination performance because the water flux reduces with the increasing membrane thickness. In addition, GE-based thin films have been used as additives to polymers for fabricating mixed matrix membranes. These new TFC or mixed matrix membranes should be tested for their desalination performance, structural stability under various desalination conditions, and material compatibility between the GE film and supportive layer or polymer matrix. In this context, MD simulations can be performed to determine their underlying transport mechanisms and assess structural stability to further improve their desalination performance for commercialization.

Meanwhile, different fabrication approaches have been proposed in the literature to control the interlayer distances in stacked GO membranes using cross-linkers. Depending on the cross-linker structure and concentration, pore size and accessible surface area of the composite structure can be tuned and therefore cross-linkers may impose a different level of effects on the desalination performance and structural stability of the composite material. MD simulations can be adopted to investigate the relation between cross-linker composition and desalination performance or material stability to develop a simulation database that will be helpful for the experimental synthesis of thin-film membranes with the optimized performance at a minimum effort.

Fouling is an inevitable phenomenon in membrane separation processes that adversely affect the membrane performances of those composite structures. Hence, it is recommended that the fouling of GE-based nanostructures in various desalination systems can be studied in future work. The dependence of fouling on the membrane properties, operating conditions, and types of foulants can be investigated to determine the underlying fouling mechanism of different types of foulants. Similarly, the CP effect in composite structures can be studied using MD simulations. This will provide guidance for understanding the ways to minimize fouling and CP such as appropriate membrane design and selection of operating conditions.

Process engineering modelling can be conducted to assess thermal and electrical energy requirements for seawater desalination via different technologies. Furthermore, a full cost estimation of desalination will be useful for understanding the economic feasibility of GE-based structures as separation membranes or electrodes in their respective desalination systems.

In this study, the proposed ENF method is tested on the ionized GO. In addition, many other functional groups such as Br, Cl, F and SO₃H can also be adopted to

functionalize GE and explored to understand the dependence of desalination performance on the chemical functionalization. Meanwhile, the effects of concentration level and distribution patterns of functional groups on the solute rejection can be evaluated. This desalination approach can also be tested using materials such as MOFs to promote them for various water purification applications.

Finally, experimental studies can be carried out to fabricate GE-based membrane structures to evaluate their commercial viability. In addition, the proposed ENF method can be further designed to develop a single-stage portable nanofluidic device for water desalination or purification applications.

References

- [1] A.M. Gilau, M.J. Small, *Designing cost-effective seawater reverse osmosis system under optimal energy options*, Renewable Energy, 33 (2008) 617-630.
- [2] S.M. Rao, P. Mamatha, *Water quality in sustainable water management*, Current Science, 87 (2004) 942-947.
- [3] S. Karavoltsos, A. Sakellari, N. Mihopoulos, M. Dassenakis, M.J. Scoullas, *Evaluation of the quality of drinking water in regions of Greece*, Desalination, 224 (2008) 317-329.
- [4] G.N. Tiwari, H.N. Singh, R. Tripathi, *Present status of solar distillation*, Solar Energy, 75 (2003) 367-373.
- [5] M. Schiffler, *Perspectives and challenges for desalination in the 21st century*, Desalination, 165 (2004) 1-9.
- [6] S.S. Shenvi, A.M. Isloor, A. Ismail, *A review on RO membrane technology: Developments and challenges*, Desalination, 368 (2015) 10-26.
- [7] T.-x. He, L.-j. Yan, *Application of alternative energy integration technology in seawater desalination*, Desalination, 249 (2009) 104-108.
- [8] G.D. Gebreeyessus, *Status of hybrid membrane-ion-exchange systems for desalination: A comprehensive review*, Applied Water Science, 9 (2019) 135.
- [9] M. Al-Sahali, H. Ettouney, *Developments in thermal desalination processes: Design, energy, and costing aspects*, Desalination, 214 (2007) 227-240.
- [10] S.A. Kalogirou, "Chapter 8 - Solar Desalination Systems.", *Solar Energy Engineering*, edited by S.A. Kalogirou, Second Edition, Academic Press, Boston, (2014) 431-479.
- [11] T. Humplik, J. Lee, S. O'hern, B. Fellman, M. Baig, S. Hassan, M. Atieh, F. Rahman, T. Laoui, R. Karnik, *Nanostructured materials for water desalination*, Nanotechnology, 22 (2011) 292001.
- [12] A.D. Khawaji, I.K. Kutubkhanah, J.-M. Wie, *Advances in seawater desalination technologies*, Desalination, 221 (2008) 47-69.
- [13] H. Strathmann, A. Grabowski, G. Eigenberger, *Ion-exchange membranes in the chemical process industry*, Industrial & Engineering Chemistry Research, 52 (2013) 10364-10379.
- [14] T. Xu, *Ion exchange membranes: State of their development and perspective*, Journal of Membrane Science, 263 (2005) 1-29.

- [15] N. Voutchkov, *Energy use for membrane seawater desalination—current status and trends*, Desalination, 431 (2018) 2-14.
- [16] L. Li, J. Dong, T.M. Nenoff, R. Lee, *Desalination by reverse osmosis using MFI zeolite membranes*, Journal of Membrane Science, 243 (2004) 401-404.
- [17] T. Tsuru, D. Hironaka, T. Yoshioka, M. Asaeda, *Titania membranes for liquid phase separation: Effect of surface charge on flux*, Separation and Purification Technology, 25 (2001) 307-314.
- [18] R. Xu, J. Wang, M. Kanezashi, T. Yoshioka, T. Tsuru, *Development of robust organosilica membranes for reverse osmosis*, Langmuir, 27 (2011) 13996-13999.
- [19] A. Kayvani Fard, G. McKay, A. Buekenhoudt, H. Al Sulaiti, F. Motmans, M. Khraisheh, M. Atieh, *Inorganic membranes: Preparation and application for water treatment and desalination*, Materials, 11 (2018) 74.
- [20] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Electric field effect in atomically thin carbon films*, Science, (2004) 666.
- [21] R. Nair, H. Wu, P. Jayaram, I. Grigorieva, A. Geim, *Unimpeded permeation of water through helium-leak-tight graphene-based membranes*, Science, 335 (2012) 442-444.
- [22] D. Cohen-Tanugi, J.C. Grossman, *Nanoporous graphene as a reverse osmosis membrane: Recent insights from theory and simulation*, Desalination, 366 (2015) 59-70.
- [23] M.E. Suk, N.R. Aluru, *Water transport through ultrathin graphene*, The Journal of Physical Chemistry Letters, 1 (2010) 1590-1594.
- [24] W. Choi, J. Choi, J. Bang, J.-H. Lee, *Layer-by-layer assembly of graphene oxide nanosheets on polyamide membranes for durable reverse-osmosis applications*, ACS Applied Materials & Interfaces, 5 (2013) 12510-12519.
- [25] Y. Han, Z. Xu, C. Gao, *Ultrathin graphene nanofiltration membrane for water purification*, Advanced Functional Materials, 23 (2013) 3693-3700.
- [26] K.A. Mahmoud, B. Mansoor, A. Mansour, M. Khraisheh, *Functional graphene nanosheets: The next generation membranes for water desalination*, Desalination, 356 (2015) 208-225.
- [27] H.-R. Chae, J. Lee, C.-H. Lee, I.-C. Kim, P.-K. Park, *Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance*, Journal of Membrane Science, 483 (2015) 128-135.
- [28] S.P. Surwade, S.N. Smirnov, I.V. Vlassiouk, R.R. Unocic, G.M. Veith, S. Dai, S.M. Mahurin, *Water desalination using nanoporous single-layer graphene*, Nature Nanotechnology, 10 (2015) 459-464.

- [29] H. Huang, Z. Song, N. Wei, L. Shi, Y. Mao, Y. Ying, L. Sun, Z. Xu, X. Peng, *Ultrafast viscous water flow through nanostrand-channelled graphene oxide membranes*, Nature Communications, 4 (2013).
- [30] H. Li, T. Lu, L. Pan, Y. Zhang, Z. Sun, *Electrosorption behavior of graphene in NaCl solutions*, Journal of Materials Chemistry, 19 (2009) 6773-6779.
- [31] A.K. Geim, K.S. Novoselov, *The rise of graphene*, Nature Materials, 6 (2007) 183-191.
- [32] W. Choi, J.-w. Lee, "Graphene: Synthesis and applications." *Nanomaterials and their applications*, Boca Raton : CRC Press ; London : Taylor & Francis, (2012).
- [33] J.S. Bunch, S.S. Verbridge, J.S. Alden, A.M. van der Zande, J.M. Parpia, H.G. Craighead, P.L. McEuen, *Impermeable Atomic Membranes from Graphene Sheets*, Nano Letters, 8 (2008) 2458-2462.
- [34] S. Hu, M. Lozada-Hidalgo, F.C. Wang, A. Mishchenko, F. Schedin, R.R. Nair, E.W. Hill, D.W. Boukhvalov, M.I. Katsnelson, R.A.W. Dryfe, I.V. Grigorieva, H.A. Wu, A.K. Geim, *Proton transport through one-atom-thick crystals*, Nature, 516 (2014) 227-230.
- [35] C. Lee, X. Wei, J.W. Kysar, J. Hone, *Measurement of the elastic properties and intrinsic strength of monolayer graphene*, Science, 321 (2008) 385-388.
- [36] J.d.L.Fuente, *Graphenea*, <http://www.graphenea.com/pages/graphene-properties>. Accessed 24-03-2016.
- [37] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, *Superior thermal conductivity of single-layer graphene*, Nano Letters, 8 (2008) 902-907.
- [38] Y. Zhang, L. Zou, Y. Wimalasiri, J.-Y. Lee, Y. Chun, *Reduced graphene oxide/polyaniline conductive anion exchange membranes in capacitive deionisation process*, Electrochimica Acta, 182 (2015) 383-390.
- [39] A. Peigney, C. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset, *Specific surface area of carbon nanotubes and bundles of carbon nanotubes*, Carbon, 39 (2001) 507-514.
- [40] D. Konatham, J. Yu, T.A. Ho, A. Striolo, *Simulation insights for graphene-based water Desalination Membranes*, Langmuir, 29 (2013) 11884-11897.
- [41] M. Elimelech, W.A. Phillip, *The future of seawater desalination: Energy, technology, and the environment*, Science, 333 (2011) 712-717.
- [42] D.H. Seo, S. Pineda, Y.C. Woo, M. Xie, A.T. Murdock, E.Y. Ang, Y. Jiao, M.J. Park, S.I. Lim, M. Lawn, *Anti-fouling graphene-based membranes for effective water desalination*, Nature Communications, 9 (2018) 683.

- [43] A. Aghigh, V. Alizadeh, H.Y. Wong, M.S. Islam, N. Amin, M. Zaman, *Recent advances in utilization of graphene for filtration and desalination of water: A review*, *Desalination*, 365 (2015) 389-397.
- [44] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y.I. Song, *Roll-to-roll production of 30-inch graphene films for transparent electrodes*, *Nature Nanotechnology*, 5 (2010) 574-578.
- [45] A. Akbari, P. Sheath, S.T. Martin, D.B. Shinde, M. Shaibani, P.C. Banerjee, R. Tkacz, D. Bhattacharyya, M. Majumder, *Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide*, *Nature Communications*, 7 (2016) 10891.
- [46] M. Darwish, H. Abdulrahim, A. Hassan, A. Mabrouk, A. Sharif, *The forward osmosis and desalination*, *Desalination and Water Treatment*, 57 (2016) 4269-4295.
- [47] T.Y. Cath, A.E. Childress, M. Elimelech, *Forward osmosis: Principles, applications, and recent developments*, *Journal of Membrane Science*, 281 (2006) 70-87.
- [48] B. Liang, W. Zhan, G. Qi, S. Lin, Q. Nan, Y. Liu, B. Cao, K. Pan, *High performance graphene oxide/polyacrylonitrile composite pervaporation membranes for desalination applications*, *Journal of Materials Chemistry A*, 3 (2015) 5140-5147.
- [49] Y. Zhu, K.M. Gupta, Q. Liu, J. Jiang, J. Caro, A. Huang, *Synthesis and seawater desalination of molecular sieving zeolitic imidazolate framework membranes*, *Desalination*, 385 (2016) 75-82.
- [50] A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini, A. Cipollina, *Electrodialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications*, *Desalination*, 434 (2018) 121-160.
- [51] Y. Oren, *Capacitive deionization (CDI) for desalination and water treatment—past, present and future (a review)*, *Desalination*, 228 (2008) 10-29.
- [52] S. Deng, V. Berry, *Wrinkled, rippled and crumpled graphene: An overview of formation mechanism, electronic properties, and applications*, *Materials Today*, 19 (2016) 197-212.
- [53] R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A.K. Geim, R.R. Nair, *Precise and ultrafast molecular sieving through graphene oxide membranes*, *Science*, 343 (2014) 752-754.
- [54] K. Xu, B. Feng, C. Zhou, A. Huang, *Synthesis of highly stable graphene oxide membranes on polydopamine functionalized supports for seawater desalination*, *Chemical Engineering Science*, 146 (2016) 159-165.
- [55] S.A. Kiran, Y.L. Thuyavan, G. Arthanareeswaran, T. Matsuura, A. Ismail, *Impact of graphene oxide embedded polyethersulfone membranes for the effective treatment of distillery effluent*, *Chemical Engineering Journal*, 286 (2016) 528-537.

- [56] L. Yu, Y. Zhang, B. Zhang, J. Liu, H. Zhang, C. Song, *Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties*, Journal of Membrane Science, 447 (2013) 452-462.
- [57] W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang, C. Fan, *Graphene-based antibacterial paper*, ACS Nano, 4 (2010) 4317-4323.
- [58] J. Ma, X. Guo, Y. Ying, D. Liu, C. Zhong, *Composite ultrafiltration membrane tailored by MOF@ GO with highly improved water purification performance*, Chemical Engineering Journal, 313 (2017) 890-898.
- [59] J. Wang, Y. Wang, Y. Zhang, A. Uliana, J. Zhu, J. Liu, B. Van der Bruggen, *Zeolitic imidazolate framework/graphene oxide hybrid nanosheets functionalized thin film nanocomposite membrane for enhanced antimicrobial performance*, ACS Applied Materials & Interfaces, 8 (2016) 25508-25519.
- [60] Y. Ying, D. Liu, W. Zhang, J. Ma, H. Huang, Q. Yang, C. Zhong, *High-flux graphene oxide membranes intercalated by metal-organic framework with highly selective separation of aqueous organic solution*, ACS Applied Materials & Interfaces, 9 (2017) 1710-1718.
- [61] J.E. Miller, *Review of water resources and desalination technologies*, Sandia National Laboratories, Albuquerque, NM 49 (2003): 2003-0800.
- [62] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, *Reverse osmosis desalination: Water sources, technology, and today's challenges*, Water Research, 43 (2009) 2317-2348.
- [63] Voutchkov, Nikolay, and Raphael Semiat. "Seawater desalination." *Advanced membrane technology and applications*, (2008) 47-86. <https://doi.org/10.1002/9780470276280.ch3>.
- [64] M. Eldean (2011), *Design and simulation of solar desalination systems* (Doctoral thesis, Suez Canal University, Egypt). Retrieved from <https://www.researchgate.net>.
- [65] M. Bhadra, S. Roy, S. Mitra, *Desalination across a graphene oxide membrane via direct contact membrane distillation*, Desalination, 378 (2016) 37-43.
- [66] L. Song, B. Li, K.K. Sirkar, J.L. Gilron, *Direct contact membrane distillation-based desalination: Novel membranes, devices, larger-scale studies, and a model*, Industrial & Engineering Chemistry Research, 46 (2007) 2307-2323.
- [67] F. Banat, N. Jwaied, *Economic evaluation of desalination by small-scale autonomous solar-powered membrane distillation units*, Desalination, 220 (2008) 566-573.
- [68] L.J. Banasiak, T.W. Kruttschnitt, A.I. Schäfer, *Desalination using electrodialysis as a function of voltage and salt concentration*, Desalination, 205 (2007) 38-46.
- [69] S. Phuntsho, H.K. Shon, T.C. Zhang, R.Y. Surampalli, " *Introduction: Role of membrane science and technology and forward osmosis processes.*" *Forward*

- osmosis: Fundamentals and applications*, American Society of Civil Engineers (ASCE), (2015). <https://doi.org/10.1061/9780784414071.ch1>.
- [70] T.C. Zhang, Y. Yuan, R.Y. Surampalli, "Forward osmosis processes for desalination: evolution, case studies, and future directions." *Forward osmosis: Fundamentals and applications*, American Society of Civil Engineers (ASCE), (2015). <https://doi.org/10.1061/9780784414071.ch14>.
- [71] C.H. Cho, K.Y. Oh, S.K. Kim, J.G. Yeo, P. Sharma, *Pervaporative seawater desalination using NaA zeolite membrane: Mechanisms of high water flux and high salt rejection*, Journal of Membrane Science, 371 (2011) 226-238.
- [72] R. Zhao, S. Porada, P.M. Biesheuvel, A. van der Wal, *Energy consumption in membrane capacitive deionization for different water recoveries and flow rates, and comparison with reverse osmosis*, Desalination, 330 (2013) 35-41.
- [73] X. Xu, L. Pan, Y. Liu, T. Lu, Z. Sun, D.H. Chua, *Facile synthesis of novel graphene sponge for high performance capacitive deionization*, Scientific Reports, 5 (2015) 8458.
- [74] E. Matthiasson, B. Sivik, *Concentration polarization and fouling*, Desalination, 35 (1980) 59-103.
- [75] M.Z. Abedin, N.-H. Kim, *An experimental study on accelerated fouling of aluminum oxide and ferric oxide particles in internally enhanced tubes*, Journal of Mechanical Science and Technology, 30 (2016) 5707-5714.
- [76] X. Li, Y. Liu, J. Wang, J. Gascon, J. Li, B. Van der Bruggen, *Metal-organic frameworks based membranes for liquid separation*, Chemical Society Reviews, 46 (2017) 7124-7144.
- [77] W.-g. Kim, S. Nair, *Membranes from nanoporous 1D and 2D materials: A review of opportunities, developments, and challenges*, Chemical Engineering Science, 104 (2013) 908-924.
- [78] L. Malaeb, G.M. Ayoub, *Reverse osmosis technology for water treatment: State of the art review*, Desalination, 267 (2011) 1-8.
- [79] C. Liu, K. Rainwater, L. Song, *Energy analysis and efficiency assessment of reverse osmosis desalination process*, Desalination, 276 (2011) 352-358.
- [80] V.V. Nikonenko, A.B. Yaroslavtsev, G. Pourcelly, "Ion transfer in and through charged membranes: Structure, properties, and theory." *Ionic interactions in natural and synthetic macromolecules*, (2012) 267-335. <https://doi.org/10.1002/9781118165850.ch9>.
- [81] M.A. Anderson, A.L. Cudero, J. Palma, *Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?*, Electrochimica Acta, 55 (2010) 3845-3856.

- [82] L. Weinstein, R. Dash, *Capacitive deionization: Challenges and opportunities*, Desalination & Water Reuse, 23 (2013) 34-37.
- [83] S. Porada, R. Zhao, A. van der Wal, V. Presser, P.M. Biesheuvel, *Review on the science and technology of water desalination by capacitive deionization*, Progress in Materials Science, 58 (2013) 1388-1442.
- [84] J.J. Urban, *Emerging scientific and engineering opportunities within the water-energy nexus*, Joule, 1 (2017) 665-688.
- [85] A. Johnson, J. Newman, *Desalting by means of porous carbon electrodes*, Journal of the Electrochemical Society, 118 (1971) 510-517.
- [86] D. Zhang, T. Yan, L. Shi, Z. Peng, X. Wen, J. Zhang, *Enhanced capacitive deionization performance of graphene/carbon nanotube composites*, Journal of Materials Chemistry, 22 (2012) 14696-14704.
- [87] B. Jia, L. Zou, *Wettability and its influence on graphene nanosheets as electrode material for capacitive deionization*, Chemical Physics Letters, 548 (2012) 23-28.
- [88] L. Zou, L. Li, H. Song, G. Morris, *Using mesoporous carbon electrodes for brackish water desalination*, Water Research, 42 (2008) 2340-2348.
- [89] M.-W. Ryoo, G. Seo, *Improvement in capacitive deionization function of activated carbon cloth by titania modification*, Water Research, 37 (2003) 1527-1534.
- [90] Z. Wang, B. Dou, L. Zheng, G. Zhang, Z. Liu, Z. Hao, *Effective desalination by capacitive deionization with functional graphene nanocomposite as novel electrode material*, Desalination, 299 (2012) 96-102.
- [91] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, *Forward osmosis processes: Yesterday, today and tomorrow*, Desalination, 287 (2012) 78-81.
- [92] I.L. Alsvik, M.-B. Hägg, *Pressure retarded osmosis and forward osmosis membranes: Materials and methods*, Polymers, 5 (2013) 303-327.
- [93] Y. Zhong, X. Feng, W. Chen, X. Wang, K.-W. Huang, Y. Gnanou, Z. Lai, *Using UCST ionic liquid as a draw solute in forward osmosis to treat high-salinity water*, Environmental Science & Technology, 50 (2015) 1039-1045.
- [94] G.T. Gray, J.R. McCutcheon, M. Elimelech, *Internal concentration polarization in forward osmosis: Role of membrane orientation*, Desalination, 197 (2006) 1-8.
- [95] X. Song, Z. Liu, D.D. Sun, *Nano gives the answer: Breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate*, Advanced Materials, 23 (2011) 3256-3260.
- [96] L. Chekli, H. Shon, S. Phuntsho, J. Kim, J. Cho, *"Draw solutes in forward osmosis processes."* *Forward osmosis: Fundamentals and applications*, American Society of Civil Engineers (ASCE), (2015). <https://doi.org/10.1061/9780784414071.ch5>.

- [97] M. Drobek, C. Yacou, J. Motuzas, A. Julbe, L. Ding, J.C.D. da Costa, *Long term pervaporation desalination of tubular MFI zeolite membranes*, Journal of Membrane Science, 415 (2012) 816-823.
- [98] J.R. McCutcheon, M. Elimelech, *Modeling water flux in forward osmosis: Implications for improved membrane design*, AIChE Journal, 53 (2007) 1736-1744.
- [99] S. You, C. Tang, C. Yu, X. Wang, J. Zhang, J. Han, Y. Gan, N. Ren, *Forward osmosis with a novel thin-film inorganic membrane*, Environmental Science & Technology, 47 (2013) 8733-8742.
- [100] D. Emadzadeh, W.J. Lau, T. Matsuura, M. Rahbari-Sisakht, A.F. Ismail, *A novel thin film composite forward osmosis membrane prepared from PSf-TiO₂ nanocomposite substrate for water desalination*, Chemical Engineering Journal, 237 (2014) 70-80.
- [101] Y. Wang, R. Ou, Q. Ge, H. Wang, T. Xu, *Preparation of polyethersulfone/carbon nanotube substrate for high-performance forward osmosis membrane*, Desalination, 330 (2013) 70-78.
- [102] Y. Wang, R. Ou, H. Wang, T. Xu, *Graphene oxide modified graphitic carbon nitride as a modifier for thin film composite forward osmosis membrane*, Journal of Membrane Science, 475 (2015) 281-289.
- [103] M.J. Park, S. Phuntsho, T. He, G.M. Nisola, L.D. Tijing, X.-M. Li, G. Chen, W.-J. Chung, H.K. Shon, *Graphene oxide incorporated polysulfone substrate for the fabrication of flat-sheet thin-film composite forward osmosis membranes*, Journal of Membrane Science, 493 (2015) 496-507.
- [104] J.-G. Gai, X.-L. Gong, *Zero internal concentration polarization FO membrane: Functionalized graphene*, Journal of Materials Chemistry A, 2 (2014) 425-429.
- [105] J.-G. Gai, X.-L. Gong, W.-W. Wang, X. Zhang, W.-L. Kang, *An ultrafast water transport forward osmosis membrane: Porous graphene*, Journal of Materials Chemistry A, 2 (2014) 4023-4028.
- [106] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, *Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance*, Journal of Membrane Science, 278 (2006) 114-123.
- [107] J.H. van't Hoff, *Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen*, Zeitschrift für Physikalische Chemie, 1 (1887) 481-508.
- [108] A. Achilli, T.Y. Cath, A.E. Childress, *Selection of inorganic-based draw solutions for forward osmosis applications*, Journal of Membrane Science, 364 (2010) 233-241.
- [109] J. Neel, "Pervaporation." *Membrane Science and Technology*, Elsevier, (1995) 143-211.

- [110] B. Liang, K. Pan, L. Li, E.P. Giannelis, B. Cao, *High performance hydrophilic pervaporation composite membranes for water desalination*, Desalination, 347 (2014) 199-206.
- [111] Z. Xie, D. Ng, M. Hoang, T. Duong, S. Gray, *Separation of aqueous salt solution by pervaporation through hybrid organic–inorganic membrane: Effect of operating conditions*, Desalination, 273 (2011) 220-225.
- [112] D.C. Elias, R.R. Nair, T. Mohiuddin, S. Morozov, P. Blake, M. Halsall, A.C. Ferrari, D. Boukhvalov, M. Katsnelson, A. Geim, *Control of graphene's properties by reversible hydrogenation: Evidence for graphane*, Science, 323 (2009) 610-613.
- [113] K.P. Loh, Q. Bao, P.K. Ang, J. Yang, *The chemistry of graphene*, Journal of Materials Chemistry, 20 (2010) 2277-2289.
- [114] W. Bao, F. Miao, Z. Chen, H. Zhang, W. Jang, C. Dames, C.N. Lau, *Controlled ripple texturing of suspended graphene and ultrathin graphite membranes*, Nature Nanotechnology, 4 (2009) 562-566.
- [115] A. Fasolino, J.H. Los, M.I. Katsnelson, *Intrinsic ripples in graphene*, Nature Materials, 6 (2007) 858-861.
- [116] F. Kim, L.J. Cote, J. Huang, *Graphene oxide: Surface activity and two-dimensional assembly*, Advanced Materials, 22 (2010) 1954-1958.
- [117] D. Gu, J.B. Fein, *Adsorption of metals onto graphene oxide: Surface complexation modeling and linear free energy relationships*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 481 (2015) 319-327.
- [118] L. Huang, M. Zhang, C. Li, G. Shi, *Graphene-based membranes for molecular separation*, The Journal of Physical Chemistry Letters, 6 (2015) 2806-2815.
- [119] M. Fathizadeh, W.L. Xu, F. Zhou, Y. Yoon, M. Yu, *Graphene oxide: A novel 2-dimensional material in membrane separation for water purification*, Advanced Materials Interfaces, 4 (2017) 1600918.
- [120] N. Kim, G. Xin, S.M. Cho, C. Pang, H. Chae, *Microwave-reduced graphene oxide for efficient and stable hole extraction layers of polymer solar cells*, Current Applied Physics, 15 (2015) 953-957.
- [121] G. Liu, W. Jin, N. Xu, *Graphene-based membranes*, Chemical Society Reviews, 44 (2015) 5016-5030.
- [122] M. Becton, L. Zhang, and X. Wang, *Molecular Dynamics study of programmable nanoporous graphene*, Journal of Nanomechanics and Micromechanics, 4 (2014) B4014002.
- [123] C. Zhu, H. Li, S. Meng, *Transport behavior of water molecules through two-dimensional nanopores*, The Journal of Chemical Physics, 141 (2014) 18C528.

- [124] D. Cohen-Tanugi, J.C. Grossman, *Water permeability of nanoporous graphene at realistic pressures for reverse osmosis desalination*, Journal of Chemical Physics, 141 (2014) 1-4.
- [125] Y. Liu, X. Chen, *Mechanical properties of nanoporous graphene membrane*, Journal of Applied Physics, 115 (2014) 034303.
- [126] S.C. O'Hern, M.S.H. Boutilier, J.-C. Idrobo, Y. Song, J. Kong, T. Laoui, M. Atieh, R. Karnik, *Selective ionic transport through tunable subnanometer pores in single-layer graphene membranes*, Nano Letters, 14 (2014) 1234-1241.
- [127] D. Cohen-Tanugi, J.C. Grossman, *Mechanical strength of nanoporous graphene as a desalination membrane*, Nano Letters, 14 (2014) 6171-6178.
- [128] H. Wendt, S. Dermeik, A. Ziogas, *Chlorine corrosion of graphites and technical carbons—I. Reaction with gaseous chlorine at elevated temperatures*, Materials and Corrosion, 41 (1990) 457-463.
- [129] Z. Luo, S. Lim, Z. Tian, J. Shang, L. Lai, B. MacDonald, C. Fu, Z. Shen, T. Yu, J. Lin, *Pyridinic N doped graphene: Synthesis, electronic structure, and electrocatalytic property*, Journal of Materials Chemistry, 21 (2011) 8038-8044.
- [130] G. Ning, Z. Fan, G. Wang, J. Gao, W. Qian, F. Wei, *Gram-scale synthesis of nanomesh graphene with high surface area and its application in supercapacitor electrodes*, Chemical Communications, 47 (2011) 5976-5978.
- [131] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, *Carbon-based supercapacitors produced by activation of graphene*, Science, 332 (2011) 1537-1541.
- [132] Z. Fan, Q. Zhao, T. Li, J. Yan, Y. Ren, J. Feng, T. Wei, *Easy synthesis of porous graphene nanosheets and their use in supercapacitors*, Carbon, 50 (2012) 1699-1703.
- [133] L.L. Zhang, X. Zhao, M.D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, R.S. Ruoff, *Highly conductive and porous activated reduced graphene oxide films for high-power supercapacitors*, Nano Letters, 12 (2012) 1806-1812.
- [134] W. Yuan, J. Chen, G. Shi, *Nanoporous graphene materials*, Materials Today, 17 (2014) 77-85.
- [135] C. Cheng, G. Jiang, C.J. Garvey, Y. Wang, G.P. Simon, J.Z. Liu, D. Li, *Ion transport in complex layered graphene-based membranes with tuneable interlayer spacing*, Science Advances, 2 (2016) e1501272.
- [136] V.C. Tung, M.J. Allen, Y. Yang, R.B. Kaner, *High-throughput solution processing of large-scale graphene*, Nature Nanotechnology, 4 (2009) 25-29.

- [137] L. Qiu, X. Zhang, W. Yang, Y. Wang, G.P. Simon, D. Li, *Controllable corrugation of chemically converted graphene sheets in water and potential application for nanofiltration*, Chemical Communications, 47 (2011) 5810-5812.
- [138] K. Parvez, R. Li, S.R. Puniredd, Y. Hernandez, F. Hinkel, S. Wang, X. Feng, K. Müllen, *Electrochemically exfoliated graphene as solution-processable, highly conductive electrodes for organic electronics*, ACS Nano, 7 (2013) 3598-3606.
- [139] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, *Exfoliation of graphite into graphene in aqueous solutions of inorganic salts*, Journal of the American Chemical Society, 136 (2014) 6083-6091.
- [140] B. Mi, *Graphene oxide membranes for ionic and molecular sieving*, Science, 343 (2014) 740-742.
- [141] C.-H. Tsou, Q.-F. An, S.-C. Lo, M. De Guzman, W.-S. Hung, C.-C. Hu, K.-R. Lee, J.-Y. Lai, *Effect of microstructure of graphene oxide fabricated through different self-assembly techniques on 1-butanol dehydration*, Journal of Membrane Science, 477 (2015) 93-100.
- [142] X. Lin, X. Shen, Q. Zheng, N. Yousefi, L. Ye, Y.-W. Mai, J.-K. Kim, *Fabrication of highly-aligned, conductive, and strong graphene papers using ultralarge graphene oxide sheets*, ACS Nano, 6 (2012) 10708-10719.
- [143] N. Wei, X. Peng, Z. Xu, *Understanding water permeation in graphene oxide membranes*, ACS Applied Materials & Interfaces, 6 (2014) 5877-5883.
- [144] P. Sun, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Z. Xu, H. Zhu, *Selective ion penetration of graphene oxide membranes*, ACS Nano, 7 (2013) 428-437.
- [145] H. Huang, Y. Mao, Y. Ying, Y. Liu, L. Sun, X. Peng, *Salt concentration, pH and pressure controlled separation of small molecules through lamellar graphene oxide membranes*, Chemical Communications, 49 (2013) 5963-5965.
- [146] H. Liu, H. Wang, X. Zhang, *Facile fabrication of freestanding ultrathin reduced graphene oxide membranes for water purification*, Advanced Materials, 27 (2015) 249-254.
- [147] H. Huang, Y. Ying, X. Peng, *Graphene oxide nanosheet: An emerging star material for novel separation membranes*, Journal of Materials Chemistry A, 2 (2014) 13772-13782.
- [148] Z. Jia, W. Shi, *Tailoring permeation channels of graphene oxide membranes for precise ion separation*, Carbon, 101 (2016) 290-295.
- [149] G.S. Lai, W.J. Lau, P.S. Goh, A.F. Ismail, N. Yusof, Y.H. Tan, *Graphene oxide incorporated thin film nanocomposite nanofiltration membrane for enhanced salt removal performance*, Desalination, 387 (2016) 14-24.
- [150] M. Safarpour, V. Vatanpour, A. Khataee, M. Esmaeili, *Development of a novel high flux and fouling-resistant thin film composite nanofiltration membrane by*

- embedding reduced graphene oxide/TiO₂*, Separation and Purification Technology, 154 (2015) 96-107.
- [151] S. Gahlot, P.P. Sharma, H. Gupta, V. Kulshrestha, P.K. Jha, *Preparation of graphene oxide nano-composite ion-exchange membranes for desalination application*, RSC Advances, 4 (2014) 24662-24670.
- [152] G. Shukla, R.P. Pandey, V.K. Shahi, *Temperature resistant phosphorylated graphene oxide-sulphonated polyimide composite cation exchange membrane for water desalination with improved performance*, Journal of Membrane Science, 520 (2016) 972-982.
- [153] R. Liu, G. Arabale, J. Kim, K. Sun, Y. Lee, C. Ryu, C. Lee, *Graphene oxide membrane for liquid phase organic molecular separation*, Carbon, 77 (2014) 933-938.
- [154] K. Huang, G. Liu, Y. Lou, Z. Dong, J. Shen, W. Jin, *A graphene oxide membrane with highly selective molecular separation of aqueous organic solution*, Angewandte Chemie International Edition, 53 (2014) 6929-6932.
- [155] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Design and synthesis of an exceptionally stable and highly porous metal-organic framework*, Nature, 402 (1999) 276.
- [156] S.G. Kim, D.H. Hyeon, J.H. Chun, B.-H. Chun, S.H. Kim, *Novel thin nanocomposite RO membranes for chlorine resistance*, Desalination and Water Treatment, 51 (2013) 6338-6345.
- [157] Y. Gao, M. Hu, B. Mi, *Membrane surface modification with TiO₂-graphene oxide for enhanced photocatalytic performance*, Journal of Membrane Science, 455 (2014) 349-356.
- [158] M. Hu, B. Mi, *Enabling graphene oxide nanosheets as water separation membranes*, Environmental Science & Technology, 47 (2013) 3715-3723.
- [159] A. Nicolai, B.G. Sumpter, V. Meunier, *Tunable water desalination across graphene oxide framework membranes*, Physical Chemistry Chemical Physics, 16 (2014) 8646-8654.
- [160] W.-S. Hung, C.-H. Tsou, M. De Guzman, Q.-F. An, Y.-L. Liu, Y.-M. Zhang, C.-C. Hu, K.-R. Lee, J.-Y. Lai, *Cross-linking with diamine monomers to prepare composite graphene oxide-framework membranes with varying d-spacing*, Chemistry of Materials, 26 (2014) 2983-2990.
- [161] J. Shen, G. Liu, K. Huang, W. Jin, K.R. Lee, N. Xu, *Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient CO₂ capture*, Angewandte Chemie, 127 (2015) 588-592.
- [162] K. Cao, Z. Jiang, J. Zhao, C. Zhao, C. Gao, F. Pan, B. Wang, X. Cao, J. Yang, *Enhanced water permeation through sodium alginate membranes by incorporating graphene oxides*, Journal of Membrane Science, 469 (2014) 272-283.

- [163] A. Huang, Q. Liu, N. Wang, Y. Zhu, J.r. Caro, *Bicontinuous zeolitic imidazolate framework ZIF-8@ GO membrane with enhanced hydrogen selectivity*, Journal of the American Chemical Society, 136 (2014) 14686-14689.
- [164] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, J. Niu, B. Zhou, X. Qian, *Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes*, Journal of Membrane Science, 458 (2014) 1-13.
- [165] J. Yin, G. Zhu, B. Deng, *Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification*, Desalination, 379 (2016) 93-101.
- [166] H.M. Hegab, L. Zou, *Graphene oxide-assisted membranes: Fabrication and potential applications in desalination and water purification*, Journal of Membrane Science, 484 (2015) 95-106.
- [167] B. Ganesh, A.M. Isloor, A.F. Ismail, *Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane*, Desalination, 313 (2013) 199-207.
- [168] M. Safarpour, A. Khataee, V. Vatanpour, *Thin film nanocomposite reverse osmosis membrane modified by reduced graphene oxide/TiO₂ with improved desalination performance*, Journal of Membrane Science, 489 (2015) 43-54.
- [169] S. Zinadini, A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, H. Zangeneh, *Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates*, Journal of Membrane Science, 453 (2014) 292-301.
- [170] S. Bano, A. Mahmood, S.-J. Kim, K.-H. Lee, *Graphene oxide modified polyamide nanofiltration membrane with improved flux and antifouling properties*, Journal of Materials Chemistry A, 3 (2015) 2065-2071.
- [171] P. Sun, Q. Chen, X. Li, H. Liu, K. Wang, M. Zhong, J. Wei, D. Wu, R. Ma, T. Sasaki, *Highly efficient quasi-static water desalination using monolayer graphene oxide/titania hybrid laminates*, NPG Asia Materials, 7 (2015) e162.
- [172] Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, *Metal-organic framework nanosheets as building blocks for molecular sieving membranes*, Science, 346 (2014) 1356-1359.
- [173] O.K. Farha, I. Eryazici, N.C. Jeong, B.G. Hauser, C.E. Wilmer, A.A. Sarjeant, R.Q. Snurr, S.T. Nguyen, A.O.z.r. Yazaydin, J.T. Hupp, *Metal-organic framework materials with ultrahigh surface areas: Is the sky the limit?*, Journal of the American Chemical Society, 134 (2012) 15016-15021.
- [174] S.M. Cohen, *Postsynthetic methods for the functionalization of metal-organic frameworks*, Chemical Reviews, 112 (2011) 970-1000.

- [175] M. Shah, M.C. McCarthy, S. Sachdeva, A.K. Lee, H.-K. Jeong, *Current status of metal–organic framework membranes for gas separations: Promises and challenges*, *Industrial & Engineering Chemistry Research*, 51 (2012) 2179-2199.
- [176] M.S. Denny Jr, J.C. Moreton, L. Benz, S.M. Cohen, *Metal–organic frameworks for membrane-based separations*, *Nature Reviews Materials*, 1 (2016) 16078.
- [177] L. Li, X.L. Liu, H.Y. Geng, B. Hu, G.W. Song, Z.S. Xu, *A MOF/graphite oxide hybrid (MOF: HKUST-1) material for the adsorption of methylene blue from aqueous solution*, *Journal of Materials Chemistry A*, 1 (2013) 10292-10299.
- [178] J. Jiang, *Molecular simulations in metal–organic frameworks for diverse potential applications*, *Molecular Simulation*, 40 (2014) 516-536.
- [179] S. Sorribas, A. Kudasheva, E. Almendro, B. Zornoza, Ó. de la Iglesia, C. Téllez, J. Coronas, *Pervaporation and membrane reactor performance of polyimide based mixed matrix membranes containing MOF HKUST-1*, *Chemical Engineering Science*, 124 (2015) 37-44.
- [180] J.-Y. Lee, C.Y. Tang, F. Huo, *Fabrication of porous matrix membrane (PMM) using metal-organic framework as green template for water treatment*, *Scientific Reports*, 4 (2014) 3740.
- [181] Y. He, Y.P. Tang, D. Ma, T.-S. Chung, *UiO-66 incorporated thin-film nanocomposite membranes for efficient selenium and arsenic removal*, *Journal of Membrane Science*, 541 (2017) 262-270.
- [182] Z. Hu, Y. Chen, J. Jiang, *Zeolitic imidazolate framework-8 as a reverse osmosis membrane for water desalination: Insight from molecular simulation*, *The Journal of Chemical Physics*, 134 (2011) 134705.
- [183] K.M. Gupta, K. Zhang, J. Jiang, *Water desalination through zeolitic imidazolate framework membranes: Significant role of functional groups*, *Langmuir*, 31 (2015) 13230-13237.
- [184] L. Wan, C. Zhou, K. Xu, B. Feng, A. Huang, *Synthesis of highly stable UiO-66-NH₂ membranes with high ions rejection for seawater desalination*, *Microporous and Mesoporous Materials*, 252 (2017) 207-213.
- [185] X. Liu, N.K. Demir, Z. Wu, K. Li, *Highly water-stable zirconium metal–organic framework UiO-66 membranes supported on alumina hollow fibers for desalination*, *Journal of the American Chemical Society*, 137 (2015) 6999-7002.
- [186] M. Miyamoto, K. Hori, T. Goshima, N. Takaya, Y. Oumi, S. Uemiya, *An organoselective zirconium-based metal–organic-framework UiO-66 membrane for pervaporation*, *European Journal of Inorganic Chemistry*, 2017 (2017) 2094-2099.
- [187] M. González, *Force fields and molecular dynamics simulations*, *École Thématique de la Société Française de la Neutronique*, 12 (2011) 169-200.

- [188] W. Humphrey, A. Dalke, K. Schulten, *VMD: Visual molecular dynamics*, Journal of Molecular Graphics, 14 (1996) 33-38.
- [189] A. Stukowski, *Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool*, Modelling and Simulation in Materials Science and Engineering, 18 (2009) 015012.
- [190] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, *The Lennard-Jones equation of state revisited*, Molecular Physics, 78 (1993) 591-618.
- [191] L. Bo (2015), *Thermal properties of two-dimensional nanomaterials*, (Doctoral thesis, Nanyang Technological University, Singapore). Retrieved from <https://hdl.handle.net/10356/65403>.
- [192] H.J. Berendsen, J.P. Postma, W.F. van Gunsteren, J. Hermans, "Interaction models for water in relation to protein hydration." *Intermolecular forces*, Springer, (1981) 331-342.
- [193] H. Berendsen, J. Grigera, T. Straatsma, *The missing term in effective pair potentials*, Journal of Physical Chemistry, 91 (1987) 6269-6271.
- [194] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, M.L. Klein, *Comparison of simple potential functions for simulating liquid water*, The Journal of Chemical Physics, 79 (1983) 926-935.
- [195] Y. Wu, H.L. Tepper, G.A. Voth, *Flexible simple point-charge water model with improved liquid-state properties*, The Journal of Chemical Physics, 124 (2006) 024503.
- [196] M. Levitt, M. Hirshberg, R. Sharon, K.E. Laidig, V. Daggett, *Calibration and testing of a water model for simulation of the molecular dynamics of proteins and nucleic acids in solution*, The Journal of Physical Chemistry B, 101 (1997) 5051-5061.
- [197] P. Barnes, J. Finney, J. Nicholas, J. Quinn, *Cooperative effects in simulated water*, Nature, 282 (1979) 459.
- [198] T.A. Ho, A. Striolo, *Polarizability effects in molecular dynamics simulations of the graphene-water interface*, The Journal of Chemical Physics, 138 (2013) 054117.
- [199] D.J. Price, C.L. Brooks III, *A modified TIP3P water potential for simulation with Ewald summation*, The Journal of Chemical Physics, 121 (2004) 10096-10103.
- [200] E. Harder, D.E. Walters, Y.D. Bodnar, R.S. Faibish, B. Roux, *Molecular dynamics study of a polymeric reverse osmosis membrane*, The Journal of Physical Chemistry B, 113 (2009) 10177-10182.
- [201] J.-P. Ryckaert, G. Ciccotti, H.J. Berendsen, *Numerical integration of the cartesian equations of motion of a system with constraints: Molecular dynamics of n-alkanes*, Journal of Computational Physics, 23 (1977) 327-341.

- [202] H.C. Andersen, *Rattle: A “velocity” version of the shake algorithm for molecular dynamics calculations*, Journal of Computational Physics, 52 (1983) 24-34.
- [203] Z.E. Hughes, J.D. Gale, *A computational investigation of the properties of a reverse osmosis membrane*, Journal of Materials Chemistry, 20 (2010) 7788-7799.
- [204] D. Cohen-Tanugi, J.C. Grossman, *Water desalination across nanoporous graphene*, Nano Letters, 12 (2012) 3602-3608.
- [205] B. Liu, R. Wu, J.A. Baimova, H. Wu, A.W.-K. Law, S.V. Dmitriev, K. Zhou, *Molecular dynamics study of pressure-driven water transport through graphene bilayers*, Physical Chemistry Chemical Physics, 18 (2016) 1886-1896.
- [206] B. Liu, R. Wu, A.W.-K. Law, X.-Q. Feng, L. Bai, K. Zhou, *Channel morphology effect on water transport through graphene bilayers*, Scientific Reports, 6 (2016) 38583.
- [207] B. Chen, H. Jiang, X. Liu, X. Hu, *Molecular insight of water desalination across multilayer graphene oxide membranes*, ACS Applied Materials & Interfaces, (2017).
- [208] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, *State-of-the-art of reverse osmosis desalination*, Desalination, 216 (2007) 1-76.
- [209] F. Zhu, E. Tajkhorshid, K. Schulten, *Pressure-induced water transport in membrane channels studied by molecular dynamics*, Biophysical Journal, 83 (2002) 154-160.
- [210] D. Cohen-Tanugi, L.-C. Lin, J.C. Grossman, *Multilayer nanoporous graphene membranes for water desalination*, Nano Letters, 16 (2016) 1027-1033.
- [211] K. Sint, B. Wang, P. Král, *Selective ion passage through functionalized graphene nanopores*, Journal of the American Chemical Society, 131 (2009) 9600-9600.
- [212] X. Yang, X. Yang, S. Liu, *Molecular dynamics simulation of water transport through graphene-based nanopores: Flow behavior and structure characteristics*, Chinese Journal of Chemical Engineering, 23 (2015) 1587-1592.
- [213] H. Yoshida, L. Bocquet, *Labyrinthine water flow across multilayer graphene-based membranes: Molecular dynamics versus continuum predictions*, The Journal of Chemical Physics, 144 (2016) 234701.
- [214] B. Corry, *Designing carbon nanotube membranes for efficient water desalination*, The Journal of Physical Chemistry B, 112 (2008) 1427-1434.
- [215] Z. He, J. Zhou, X. Lu, B. Corry, *Bioinspired graphene nanopores with voltage-tunable ion selectivity for Na^+ and K^+* , ACS Nano, 7 (2013) 10148-10157.
- [216] Q. Chen, X. Yang, *Pyridinic nitrogen doped nanoporous graphene as desalination membrane: Molecular simulation study*, Journal of Membrane Science, 496 (2015) 108-117.

- [217] Y. Wang, Z. He, K.M. Gupta, Q. Shi, R. Lu, *Molecular dynamics study on water desalination through functionalized nanoporous graphene*, Carbon, 116 (2017) 120-127.
- [218] S. Zhao, J. Xue, W. Kang, *Ion selection of charge-modified large nanopores in a graphene sheet*, The Journal of Chemical Physics, 139 (2013) 114702.
- [219] X. Zhang, S. Liu, H. Liu, J. Zhang, X. Yang, *Molecular dynamics simulation of the mechanical properties of multilayer graphene oxide nanosheets*, RSC Advances, 7 (2017) 55005-55011.
- [220] J.C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R.D. Skeel, L. Kale, K. Schulten, *Scalable molecular dynamics with NAMD*, Journal of Computational Chemistry, 26 (2005) 1781-1802.
- [221] Z. Hu, B. Liu, M. Dahanayaka, A.W.-K. Law, J. Wei, K. Zhou, *Ultrafast permeation of seawater pervaporation using single-layered C₂N via strain engineering*, Physical Chemistry Chemical Physics, 19 (2017) 15973-15979.
- [222] H. Zhang, B. Liu, H.T. Kieu, M.S. Wu, K. Zhou, A.W.-K. Law, *Coarse-grained molecular dynamics study of membrane distillation through meso-size graphene channels*, Journal of Membrane Science, 558 (2018) 34-44.
- [223] S. Murad, J.G. Powles, *Computer simulation of osmosis and reverse osmosis in solutions*, Chemical Physics Letters, 225 (1994) 437-440.
- [224] A. Kalra, S. Garde, G. Hummer, *Osmotic water transport through carbon nanotube membranes*, Proceedings of the National Academy of Sciences, 100 (2003) 10175-10180.
- [225] Y.-x. Jia, H.-l. Li, M. Wang, L.-y. Wu, Y.-d. Hu, *Carbon nanotube: Possible candidate for forward osmosis*, Separation and Purification Technology, 75 (2010) 55-60.
- [226] J. Azamat, *Functionalized graphene nanosheet as a membrane for water desalination using applied electric fields: Insights from molecular dynamics simulations*, The Journal of Physical Chemistry C, 120 (2016) 23883-23891.
- [227] R.K. Kalluri, D. Konatham, A. Striolo, *Aqueous NaCl solutions within charged carbon-slit pores: Partition coefficients and density distributions from molecular dynamics simulations*, The Journal of Physical Chemistry C, 115 (2011) 13786-13795.
- [228] R.K. Kalluri, M.M. Biener, M.E. Suss, M.D. Merrill, M. Stadermann, J.G. Santiago, T.F. Baumann, J. Biener, A. Striolo, *Unraveling the potential and pore-size dependent capacitance of slit-shaped graphitic carbon pores in aqueous electrolytes*, Physical Chemistry Chemical Physics, 15 (2013) 2309-2320.
- [229] T.A. Ho, A. Striolo, *Capacitance enhancement via electrode patterning*, Journal of Chemical Physics, 139 (2013) 204708.

- [230] T.A. Ho, A. Striolo, *Promising performance indicators for water desalination and aqueous capacitors obtained by engineering the electric double layer in nano-structured carbon electrodes*, The Journal of Physical Chemistry C, 119 (2015) 3331-3337.
- [231] H. Zhang, B. Liu, M.-S. Wu, K. Zhou, A.W.-K. Law, *Transport of salty water through graphene bilayer in an electric field: A molecular dynamics study*, Computational Materials Science, 131 (2017) 100-107.
- [232] D.W. Boukhvalov, M.I. Katsnelson, *Enhancement of chemical activity in corrugated graphene*, The Journal of Physical Chemistry C, 113 (2009) 14176-14178.
- [233] Q. Shi, H. Gao, Y. Zhang, Z. Meng, D. Rao, J. Su, Y. Liu, Y. Wang, R. Lu, *Bilayer graphene with ripples for reverse osmosis desalination*, Carbon, 136 (2018) 21-27.
- [234] S. Plimpton, *Fast parallel algorithms for short-range molecular dynamics*, Journal of Computational Physics, 117 (1995) 1-19.
- [235] M. Xue, H. Qiu, W. Guo, *Exceptionally fast water desalination at complete salt rejection by pristine graphyne monolayers*, Nanotechnology, 24 (2013) 505720.
- [236] A.D. MacKerell Jr, D. Bashford, M. Bellott, R.L. Dunbrack Jr, J.D. Evanseck, M.J. Field, S. Fischer, J. Gao, H. Guo, S. Ha, *All-atom empirical potential for molecular modeling and dynamics studies of proteins†*, The journal of Physical Chemistry B, 102 (1998) 3586-3616.
- [237] S. Rikhtehgaran, A. Lohrasebi, *Water desalination by a designed nanofilter of graphene-charged carbon nanotube: A molecular dynamics study*, Desalination, 365 (2015) 176-181.
- [238] I.S. Joung, T.E. Cheatham, *Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations*, The Journal of Physical Chemistry B, 112 (2008) 9020-9041.
- [239] N. Abedpour, M. Neek-Amal, R. Asgari, F. Shahbazi, N. Nafari, M.R.R. Tabar, *Roughness of undoped graphene and its short-range induced gauge field*, Physical Review B, 76 (2007) 195407.
- [240] S. Gravelle, L. Joly, C. Ybert, L. Bocquet, *Large permeabilities of hourglass nanopores: From hydrodynamics to single file transport*, The Journal of Chemical Physics, 141 (2014) 18C526.
- [241] X. Xia, M.L. Berkowitz, *Electric-field induced restructuring of water at a platinum-water interface: A molecular dynamics computer simulation*, Physical Review Letters, 74 (1995) 3193-3196.
- [242] G. Bahlakeh, M.M. Hasani-Sadrabadi, K.I. Jacob, *Exploring the hydrated microstructure and molecular mobility in blend polyelectrolyte membranes by quantum mechanics and molecular dynamics simulations*, RSC Advances, 6 (2016) 35517-35526.

- [243] J. Kou, J. Yao, H. Lu, B. Zhang, A. Li, Z. Sun, J. Zhang, Y. Fang, F. Wu, J. Fan, *Electromanipulating water flow in nanochannels*, *Angewandte Chemie*, 127 (2015) 2381-2385.
- [244] X. Gong, J. Li, H. Lu, R. Wan, J. Li, J. Hu, H. Fang, *A charge-driven molecular water pump*, *Nature Nanotechnology*, 2 (2007) 709-712.
- [245] S. Imberti, A. Botti, F. Bruni, G. Cappa, M.A. Ricci, A.K. Soper, *Ions in water: The microscopic structure of concentrated hydroxide solutions*, *The Journal of Chemical Physics*, 122 (2005) 194509.
- [246] A. Soper, F. Bruni, M. Ricci, *Site-site pair correlation functions of water from 25 to 400 C: Revised analysis of new and old diffraction data*, *The Journal of Chemical Physics*, 106 (1997) 247-254.
- [247] N. Bowden, S. Brittain, A.G. Evans, J.W. Hutchinson, G.M. Whitesides, *Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer*, *Nature*, 393 (1998) 146-149.
- [248] Y. Wang, R. Yang, Z. Shi, L. Zhang, D. Shi, E. Wang, G. Zhang, *Super-elastic graphene ripples for flexible strain sensors*, *ACS Nano*, 5 (2011) 3645-3650.
- [249] A. Smolyanitsky, V. Tewary, *Manipulation of graphene's dynamic ripples by local harmonic out-of-plane excitation*, *Nanotechnology*, 24 (2013) 055701.
- [250] L. Brey, J. Palacios, *Exchange-induced charge inhomogeneities in rippled neutral graphene*, *Physical Review B*, 77 (2008) 041403.
- [251] Z. Song, Z. Xu, *Ultimate osmosis engineered by the pore geometry and functionalization of carbon nanostructures*, *Scientific Reports*, 5 (2015).
- [252] F. Yan, C. Yu, B. Zhang, T. Zou, H. Zhao, J. Li, *Preparation of freestanding graphene-based laminar membrane for clean-water intake via forward osmosis process*, *RSC Advances*, 7 (2017) 1326-1335.
- [253] C. Cheng, D. Li, *Solvated graphenes: An emerging class of functional soft materials*, *Advanced Materials*, 25 (2013) 13-30.
- [254] M. Dahanayaka, B. Liu, Z. Hu, Z. Chen, A.W.-K. Law, K. Zhou, *Corrugated graphene layers for sea water desalination using capacitive deionization*, *Physical Chemistry Chemical Physics*, 19 (2017) 8552-8562.
- [255] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, P.A. Kollman, *A second generation force field for the simulation of proteins, nucleic acids, and organic molecules*, *Journal of the American Chemical Society*, 117 (1995) 5179-5197.
- [256] G. Bussi, D. Donadio, M. Parrinello, *Canonical sampling through velocity rescaling*, *The Journal of Chemical Physics*, 126 (2007) 014101.

- [257] D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A.E. Mark, H.J. Berendsen, *GROMACS: Fast, flexible, and free*, Journal of Computational Chemistry, 26 (2005) 1701-1718.
- [258] D. Emadzadeh, W. Lau, T. Matsuura, A. Ismail, M. Rahbari-Sisakht, *Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization*, Journal of Membrane Science, 449 (2014) 74-85.
- [259] N.T. Hancock, T.Y. Cath, *Solute coupled diffusion in osmotically driven membrane processes*, Environmental Science & Technology, 43 (2009) 6769-6775.
- [260] N.T. Hancock, W.A. Phillip, M. Elimelech, T.Y. Cath, *Bidirectional permeation of electrolytes in osmotically driven membrane processes*, Environmental Science & Technology, 45 (2011) 10642-10651.
- [261] Q. Wang, C. Aubry, Y. Chen, H. Song, L. Zou, *Insights on tuning the nanostructure of rGO laminate membranes for low pressure osmosis process*, ACS Applied Materials & Interfaces, (2017).
- [262] J.T. Edward, *Molecular volumes and the Stokes-Einstein equation*, Journal of Chemical Education, 47 (1970) 261.
- [263] W. Wang, Y. Zhang, M. Esparra-Alvarado, X. Wang, H. Yang, Y. Xie, *Effects of pH and temperature on forward osmosis membrane flux using rainwater as the makeup for cooling water dilution*, Desalination, 351 (2014) 70-76.
- [264] S.-J. You, X.-H. Wang, M. Zhong, Y.-J. Zhong, C. Yu, N.-Q. Ren, *Temperature as a factor affecting transmembrane water flux in forward osmosis: Steady-state modeling and experimental validation*, Chemical Engineering Journal, 198 (2012) 52-60.
- [265] C.W. Saltonstall, *Practical aspects of sea water desalination by reverse osmosis*, Desalination, 18 (1976) 315-320.
- [266] H. Mehdizadeh, J.M. Dickson, P.K. Eriksson, *Temperature effects on the performance of thin-film composite, aromatic polyamide membranes*, Industrial & Engineering Chemistry Research, 28 (1989) 814-824.
- [267] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, *Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z*, Proceedings of the National Academy of Sciences, 104 (2007) 20719-20724.
- [268] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, *Recent developments in forward osmosis: Opportunities and challenges*, Journal of Membrane Science, 396 (2012) 1-21.
- [269] H. Dai, Z. Xu, X. Yang, *Water permeation and ion rejection in layer-by-layer stacked graphene oxide nanochannels: A molecular dynamics simulation*, The Journal of Physical Chemistry C, 120 (2016) 22585-22596.

- [270] M. Dahanayaka, B. Liu, Z. Hu, Q.-X. Pei, Z. Chen, A.W.-K. Law, K. Zhou, *Graphene membranes with nanoslits for seawater desalination via forward osmosis*, *Physical Chemistry Chemical Physics*, 19 (2017) 30551-30561.
- [271] P. Sun, F. Zheng, M. Zhu, Z. Song, K. Wang, M. Zhong, D. Wu, R.B. Little, Z. Xu, H. Zhu, *Selective trans-membrane transport of alkali and alkaline earth cations through graphene oxide membranes based on cation- π interactions*, *ACS Nano*, 8 (2014) 850-859.
- [272] W.L. Xu, C. Fang, F. Zhou, Z. Song, Q. Liu, R. Qiao, M. Yu, *Self-assembly: A facile way of forming ultrathin, high-performance graphene oxide membranes for water purification*, *Nano Letters*, 17 (2017) 2928-2933.
- [273] Y. Li, V.r. Alain-Rizzo, L. Galmiche, P. Audebert, F. Miomandre, G. Louarn, M. Bozlar, M.A. Pope, D.M. Dabbs, I.A. Aksay, *Functionalization of graphene oxide by tetrazine derivatives: A versatile approach toward covalent bridges between graphene sheets*, *Chemistry of Materials*, 27 (2015) 4298-4310.
- [274] S. Mallakpour, A. Abdolmaleki, S. Borandeh, *Covalently functionalized graphene sheets with biocompatible natural amino acids*, *Applied Surface Science*, 307 (2014) 533-542.
- [275] I. Roppolo, A. Chiappone, K. Bejtka, E. Celasco, A. Chiodoni, F. Giorgis, M. Sangermano, S. Porro, *A powerful tool for graphene functionalization: Benzophenone mediated UV-grafting*, *Carbon*, 77 (2014) 226-235.
- [276] K.-G. Zhou, K. Vasu, C. Cherian, M. Neek-Amal, J.C. Zhang, H. Ghorbanfekr-Kalashami, K. Huang, O. Marshall, V. Kravets, J. Abraham, *Electrically controlled water permeation through graphene oxide membranes*, *Nature*, 559 (2018) 236.
- [277] A. Lerf, H. He, M. Forster, J. Klinowski, *Structure of graphite oxide revisited*, *The Journal of Physical Chemistry B*, 102 (1998) 4477-4482.
- [278] C. Fang, H. Wu, S.-Y. Lee, R.L. Mahajan, R. Qiao, *The ionized graphene oxide membranes for water-ethanol separation*, *Carbon*, 136 (2018) 262-269.
- [279] A.D. MacKerell Jr, D. Bashford, M. Bellott, R.L. Dunbrack Jr, J.D. Evanseck, M.J. Field, S. Fischer, J. Gao, H. Guo, S. Ha, *All-atom empirical potential for molecular modeling and dynamics studies of proteins*, *The Journal of Physical Chemistry B*, 102 (1998) 3586-3616.
- [280] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, *Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids*, *Journal of the American Chemical Society*, 118 (1996) 11225-11236.
- [281] F.d.r. Leroy, S. Liu, J. Zhang, *Parametrizing nonbonded interactions from wetting experiments via the work of adhesion: Example of water on graphene surfaces*, *The Journal of Physical Chemistry C*, 119 (2015) 28470-28481.

- [282] A. Gogoi, A. Koneru, K.A. Reddy, *Role of graphene oxide (GO) nanosheet sizes, pinhole defects and non-ideal lamellar stacking on the performance of layered GO membranes: An atomistic investigation*, Nanoscale Advances, (2019).
- [283] M.M. Kohonen, M.E. Karaman, R.M. Pashley, *Debye length in multivalent electrolyte solutions*, Langmuir, 16 (2000) 5749-5753.
- [284] P. Gaddam, W. Ducker, *Electrostatic screening length in concentrated salt solutions*, Langmuir, 35 (2019) 5719-5727.
- [285] H. Ma, K. Wang, Z. Gao, H. Wang, S. Wang, C. Zhang, G. Wang, J. Bai, *Current characteristic signals of aqueous solution transferring through microfluidic channel under non-continuous DC electric field*, AIP Advances, 4 (2014) 107139.
- [286] F. Fornasiero, H.G. Park, J.K. Holt, M. Stadermann, C.P. Grigoropoulos, A. Noy, O. Bakajin, *Ion exclusion by sub-2-nm carbon nanotube pores*, Proceedings of the National Academy of Sciences, 105 (2008) 17250-17255.
- [287] L.A. Richards, A.I. Schäfer, B.S. Richards, B. Corry, *The importance of dehydration in determining ion transport in narrow pores*, Small, 8 (2012) 1701-1709.
- [288] M. Dahanayaka, R. Babicheva, Z. Chen, A. Wing-Keung Law, M. See Wu, K. Zhou, *Atomistic simulation study of GO/HKUST-1 MOF membranes for seawater desalination via pervaporation*, Applied Surface Science, (2019) 144198.
- [289] K.-S. Lin, A.K. Adhikari, C.-N. Ku, C.-L. Chiang, H. Kuo, *Synthesis and characterization of porous HKUST-1 metal organic frameworks for hydrogen storage*, International Journal of Hydrogen Energy, 37 (2012) 13865-13871.
- [290] E. Adatoz, A.K. Avci, S. Keskin, *Opportunities and challenges of MOF-based membranes in gas separations*, Separation and Purification Technology, 152 (2015) 207-237.
- [291] S.S.-Y. Chui, S.M.-F. Lo, J.P. Charmant, A.G. Orpen, I.D. Williams, *A chemically functionalizable nanoporous material [Cu₃ (TMA) ₂ (H₂O) ₃]_n*, Science, 283 (1999) 1148-1150.
- [292] J. Canivet, A. Fateeva, Y. Guo, B. Coasne, D. Farrusseng, *Water adsorption in MOFs: Fundamentals and applications*, Chemical Society Reviews, 43 (2014) 5594-5617.
- [293] K.A. Cychosz, A.J. Matzger, *Water stability of microporous coordination polymers and the adsorption of pharmaceuticals from water*, Langmuir, 26 (2010) 17198-17202.
- [294] C. Petit, J. Burrese, T.J. Bandoz, *The synthesis and characterization of copper-based metal-organic framework/graphite oxide composites*, Carbon, 49 (2011) 563-572.

- [295] F. Ke, L.-G. Qiu, Y.-P. Yuan, F.-M. Peng, X. Jiang, A.-J. Xie, Y.-H. Shen, J.-F. Zhu, *Thiol-functionalization of metal-organic framework by a facile coordination-based postsynthetic strategy and enhanced removal of Hg^{2+} from water*, Journal of Hazardous Materials, 196 (2011) 36-43.
- [296] K.Y. Jee, J.S. Kim, J. Kim, Y.T. Lee, *Effect of hydrophilic $\text{Cu}_3(\text{BTC})_2$ additives on the performance of PVDF membranes for water flux improvement*, Desalination and Water Treatment, 57 (2016) 17637-17645.
- [297] D.-D. Zu, L. Lu, X.-Q. Liu, D.-Y. Zhang, L.-B. Sun, *Improving hydrothermal stability and catalytic activity of metal-organic frameworks by graphite oxide incorporation*, The Journal of Physical Chemistry C, 118 (2014) 19910-19917.
- [298] J. Ma, D. Ping, X. Dong, *Recent developments of graphene oxide-based membranes: A review*, Membranes, 7 (2017) 52.
- [299] G. Kresse, J. Hafner, *Ab initio molecular dynamics for liquid metals*, Physical Review B, 47 (1993) 558.
- [300] G. Kresse, J. Hafner, *Ab initio molecular dynamics for open-shell transition metals*, Physical Review B, 48 (1993) 13115.
- [301] P.E. Blöchl, *Projector augmented-wave method*, Physical Review B, 50 (1994) 17953.
- [302] J.P. Perdew, K. Burke, M. Ernzerhof, *Generalized gradient approximation made simple*, Physical Review Letters, 77 (1996) 3865.
- [303] M.V. Parkes, H. Demir, S.L. Teich-McGoldrick, D.S. Sholl, J.A. Greathouse, M.D. Allendorf, *Molecular dynamics simulation of framework flexibility effects on noble gas diffusion in HKUST-1 and ZIF-8*, Microporous and Mesoporous Materials, 194 (2014) 190-199.
- [304] M.C. Kim, G.S. Hwang, R.S. Ruoff, *Epoxide reduction with hydrazine on graphene: A first principles study*, The Journal of Chemical Physics, 131 (2009) 064704.
- [305] C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *The Cambridge Structural Database*, Acta Crystallographica Section B, B72 (2016), 171-179. DOI: 10.1107/S2052520616003954.
- [306] G.-T. Bae, B. Dellinger, R.W. Hall, *Density functional calculation of the structure and electronic properties of Cu_nO_n ($n = 1-8$) clusters*, The Journal of Physical Chemistry A, 115 (2011) 2087-2095.
- [307] L. Zhao, Q. Yang, Q. Ma, C. Zhong, J. Mi, D. Liu, *A force field for dynamic Cu-BTC metal-organic framework*, Journal of Molecular Modeling, 17 (2011) 227-234.
- [308] S.L. Mayo, B.D. Olafson, W.A. Goddard, *DREIDING: A generic force field for molecular simulations*, The Journal of Physical Chemistry, 94 (1990) 8897-8909.

- [309] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard, W.M. Skiff, *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations*, Journal of the American Chemical Society, 114 (1992) 10024-10035.
- [310] D. Stauffer, N. Dragneva, W. Floriano, R. Mawhinney, G. Fanchini, S. French, O. Rubel, *An atomic charge model for graphene oxide for exploring its bioadhesive properties in explicit water*, The Journal of Chemical Physics, 141 (2014) 044705.
- [311] Q. Yang, C. Zhong, *Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks*, The Journal of Physical Chemistry B, 110 (2006) 17776-17783.
- [312] J.P.G. Villaluenga, P. Godino, M. Khayet, B. Seoane, J.I. Mengual, *Pervaporation of alcohols and methyl tert-butyl ether through a dense poly(2,6-dimethyl-1,4-phenylene oxide) membrane*, Industrial & Engineering Chemistry Research, 43 (2004) 2548-2555.
- [313] Y. Yu, J. Fan, A. Esfandiar, Y. Zhu, H. Wu, F. Wang, *Charge asymmetry effect in ion transport through angstrom-scale channels*, The Journal of Physical Chemistry C, 123 (2019) 1462-1469.
- [314] J. Xiao, Y. Zhu, S. Huddleston, P. Li, B. Xiao, O.K. Farha, G.A. Ameer, *Copper metal-organic framework nanoparticles stabilized with folic acid improve wound healing in diabetes*, ACS Nano, 12 (2018) 1023-1032.
- [315] N. Wei, C. Lv, Z. Xu, *Wetting of graphene oxide: A molecular dynamics study*, Langmuir, 30 (2014) 3572-3578.
- [316] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, *Characterization of metal-organic frameworks by water adsorption*, Microporous and Mesoporous Materials, 120 (2009) 325-330.
- [317] J.B. DeCoste, G.W. Peterson, B.J. Schindler, K.L. Killops, M.A. Browe, J.J. Mahle, *The effect of water adsorption on the structure of the carboxylate containing metal-organic frameworks Cu-BTC, Mg-MOF-74, and UiO-66*, Journal of Materials Chemistry A, 1 (2013) 11922-11932.
- [318] Y. long Xue, C.H. Lau, B. Cao, P. Li, *Elucidating the impact of polymer crosslinking and fixed carrier on enhanced water transport during desalination using pervaporation membranes*, Journal of Membrane Science, 575 (2019) 135-146.
- [319] X. Feng, R.Y. Huang, *Estimation of activation energy for permeation in pervaporation processes*, Journal of Membrane Science, 118 (1996) 127-131.
- [320] D.R. Lide, *CRC handbook of chemistry and physics*, CRC Boca Raton (2012).
- [321] R. Jiraratananon, A. Chanachai, R. Huang, D. Uttapap, *Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes: I. Effect of operating conditions*, Journal of Membrane Science, 195 (2002) 143-151.

- [322] A. Okhulkov, Y.N. Demianets, Y.E. Gorbaty, *X-ray scattering in liquid water at pressures of up to 7.7 kbar: Test of a fluctuation model*, The Journal of Chemical Physics, 100 (1994) 1578-1588.
- [323] B. Hribar, N.T. Southall, V. Vlachy, K.A. Dill, *How ions affect the structure of water*, Journal of the American Chemical Society, 124 (2002) 12302-12311.
- [324] S. Zheng, Q. Tu, J.J. Urban, S. Li, B. Mi, *Swelling of graphene oxide membranes in aqueous solution: Characterization of interlayer spacing and insight into water transport mechanisms*, ACS Nano, 11 (2017) 6440-6450.