

그래핀옥사이드 멤브레인의 기체 및 이온 투과 특성

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Intrinsic Permeation Properties of Graphene Oxide Membranes for Gas and Ion Separations

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요 약: 그래핀옥사이드는 우수한 물리적 특성 및 가공성으로 멤브레인 소재로 각광받고 있다. 특히, 이론적 예측과 실험적인 접근을 통해 그래핀옥사이드의 원자 수준의 얇은 두께, 뛰어난 기계적 강도, 높은 수준의 내화학적, 기공 생성이 가능한 2차원 구조 또는 기체 확산 유로 생성이 가능한 적층구조 등 멤브레인 소재로서 매우 유리한 특성들을 보유하고 있음이 밝혀졌다. 또한 그래핀옥사이드에서의 분자 투과 거동은 적층된 그래핀옥사이드 사이의 채널 크기에 따라 영향을 받는다는 것이 발견되었다. 그 후, 이러한 특성을 응용하여 그래핀옥사이드를 멤브레인 소재로 활용하기 위해 많은 연구가 집중적으로 진행되고 있다. 본 총설에서는 그래핀옥사이드의 고유 특성을 기반으로 멤브레인 분야로의 응용 가능성에 대하여 논하고자 한다.

Abstract: Graphene oxide (GO) has been considered as a promising membrane material, because of its easy processability and distinct properties, including controllable pore size distribution and diffusion channels. Particularly, the feasibility has been proposed a number of simulation results and proof-of-concept experimental approaches towards GO membranes. That is, GO already shows many outstanding intrinsic properties suitable for promising membrane platforms, such as the minimum membrane thickness and the ability to generate nanopores in the two-dimensional lattices or to create slit-like nanochannels between adjacent sheets. This review will be addressed the important experimental development in GO-based membranes for gas and ion separations, emphasizing on intrinsic transport phenomena, and critical issues for practical applications.

Keywords: membrane, graphene oxide, gas separation, ion transport

1. Introduction

Since the research on graphene oxide (GO) conducted by R. S. Ruoff et al. in 2007[1], studies on GO have significantly increased in scientific communities, including materials science, physics, and chemistry. Generally, GO has an amphiphilic structure with isolated graphitic sp^2 carbons and amorphous carbons, which are decorated with various oxygen functional groups either at the edge or on the basal plane (Fig.

1)[2]. Because of its distinctive structural configuration, GO has unique material properties, including pH-sensitive amphiphilicity, a mesomorphic ordered state in an aqueous solution, fast proton conductivity under humidified conditions, high affinity for certain gases and vapors, and gas barrier behaviors in polymer composite systems[3-8].

However, there are various controversial topics on GO. For instance, the chemical properties of GO are the most complex; therefore, it is difficult to identify

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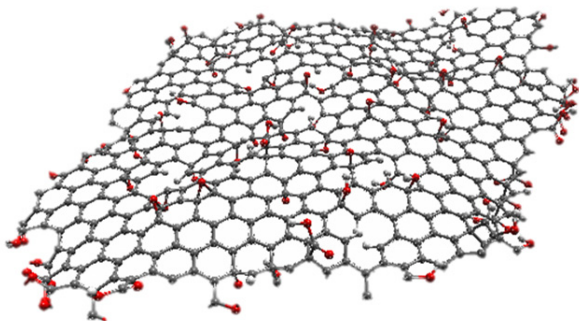


Fig. 1. Illustration of GO chemical structure.

its original chemical and physical structures[2]. Therefore, a clear understanding and an exact reaction mechanism for chemical modifications are elusive[2]. Although the exact chemical structure is elusive, owing to the intensive studies on the chemistry of GO, various guidelines for incorporating the desired heteroatoms including nitrogen, boron, metals, and metal oxides as well as to functionalize useful species such as polymers and organic groups have been suggested[2, 9,10]. However, owing to the heterogeneous nature of GO, controlling reactions involving specific types of functional groups precisely while preserving others is a challenge.

Another unique characteristic of the GO-related scientific field that is the center of debate is the difference between bulk and ultrathin (i.e., under 5 layers) properties[11,12]. Additionally, this characteristic has fascinated those who consider the engineering of material features using the physical and chemical changes such as structural tuning and surface modification. For instance, the freestanding GO film (which has bulk properties) blocks the penetration of small-sized mole-

cules[13], whereas the few-layered GO composite system (which has ultrathin properties) exhibits permeable and selective transport behaviors to allow the diffusion of specific molecules such as H_2 , CO_2 , and water[11, 14,15]. These disjunctions originate from the different physicochemical properties such as diffusion path length and sorption ability[11,15,16]. Therefore, discovering a way to control the intrinsic features suitable for desired applications selectively would be the best route for the GO-based nanotechnologies[17-20].

The aim of this review presents the aspects of GO-related studies, which are important for understanding the characteristics of GO involving the disconnection between bulk and few-layered properties for environmental applications such as purification of air and liquids. Here, we discuss only the selective literature that directly contributes to the topics. These topics include configurations of GO depending on synthetic routes, molecular transport behaviors through micron and nanometric thick GO films[2,11,12,15]. Generally, this review is based on our experimental studies.

2. Synthetic Methods and Diverse Structures

GO synthesis has a long history[21], and oxidation is an essential step for the synthesis of GO. Thus, oxidants are key reagents for the formation of GO, that is, they determine the chemical configuration of GO[2, 9,22,23]. Therefore, oxidants are used for the development of GO synthesis. Based on the research trends, it comprises four generations around important aspects (Fig. 2).

The first phase is the discovery and synthesis of oxi-

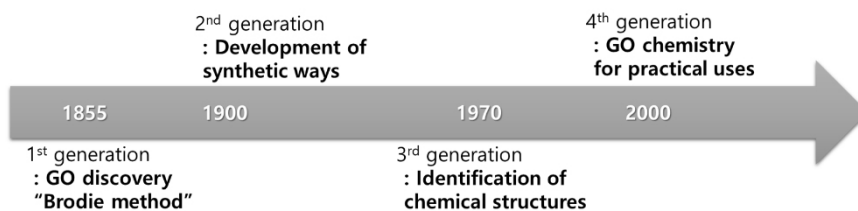


Fig. 2. Major points on graphene oxide research.

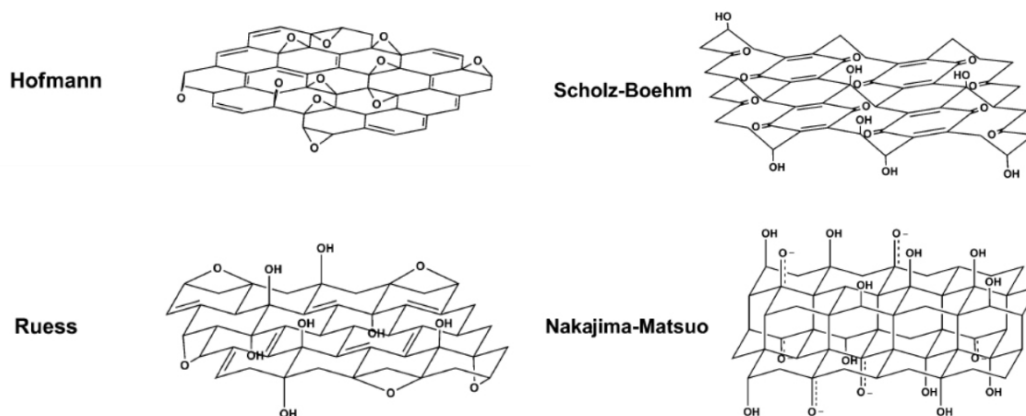


Fig. 3. Summary of several older structural models of GO. Reproduced from [29] with permission of ACS.

ductive graphitic carbon[21]. In 1855, Brodie wrote a short note that described the oxidation of graphite[24]. Afterwards, Brodie method was introduced, it involved the formation of GO with a detailed explanation of its composition and chemical properties[21]. B. C. Brodie first introduced a method for the oxidation of graphite[21,24]. However, he did not recognize his first finding of a new carbon allotrope because his research objective was not to prepare a new carbon analog. His discovery received significant attention in 1870 when Bertheot proclaimed Brodie's method for preparing GO as a method for distinguishing between different forms of graphitic carbon[25,26].

Subsequently, various scientists have tried to develop new synthetic recipes under relatively mild conditions [27-29] and identify the chemical structures of the synthetic GO[30-34]. In particular, in 1898, Staudenmaier proposed a convenient and less dangerous preparation protocol for complementing the various existing methods [35]. This is known the "Staudenmaier method," which is used in the mixing of concentrated nitric acid and sulfuric acid instead of the strong oxidants (i.e., fuming nitric acid, concentrated sulfuric acid, and potassium chlorate) in the Brodie method. Finally, Hummers and Offeman established the most mild method for introducing permanganate as an oxidant and conducting a low reaction temperature between 20 to 35 °C for the formation of GO[29]; however, their method (Hummers method) contains various impurities, including sulfur.

Therefore, a purification step is necessary in the Hummers method. As different reagents are used for the formation of GO, the individual chemical composition is observed in various synthesized materials[2,33]. Generally, the degree of oxidation in GO followed the order Brodie > Staudenmaier > Hummers.

The second phase involved the construction and proposal of the chemical structures of GO by adopting spectroscopy methods, including powder X-ray diffraction (XRD)[36]. During this phase, Hofmann and Ruess proposed several chemical structures (Fig. 3) [33], and most structural models are based on regular lattices consisting of discrete repeated units[37]. For instance, Hofmann suggested a GO composition composed of epoxy groups either in the basal plane or at the edge[38]. Ruess suggested the GO structure to replace epoxy groups with hydroxyl groups on the basal plane and to alter the basal plane structure to a sp^3 hybridized system in comparison with the Hofmann model[39]. In 1969, Scholz and Boehm suggested a different model that eliminates the epoxide and ether groups and incorporates a regular quinoidal form[40]. Nakajima and Matsuo reported the most distinctive structure forming a double graphite intercalation compound in decoration with various oxygen groups[30]. This is because the chemical structure was obtained through a target study (i.e., a stepwise mechanism for its formation via three of the more common oxidation protocols). Therefore, we believe that this approach began

the third phase in the study of GO.

The third phase focused on the identification of detailed GO structures along with cutting edge techniques, including magic angle spinning nuclear magnetic resonance on ^{13}C [41]. Mermoux, who led this study, tried to find the best fitting model based on his data[41]. However, solving the chemical identity of GO is still a challenge. This is because the GO structures are strongly dependent on the type of synthetic protocol used[2,10]. Therefore, various studies are conducting investigations to solve this challenge.

The last stage focused on the findings and modifications suitable for industrial applications. In particular, the discovery of graphene by Gein and Novoselov enhanced the reduction chemistry of GO[42]. This is because the reduction ability of GO was regarded as an economical method for obtaining graphene layers[2, 10]. While implementing this concept, various researchers have looked at GO as a promising alternative to the current important commercial materials[43]. As a result, many exciting applications have been envisioned and demonstrated[43]. In particular, we will focus on GO in environmental applications such as absorption of CO_2 , separation of ions.

3. Gas Transport Features

Membrane-based gas separation is an active research area in material science, along with its rapid growth in significance within industrial fields[44-47]. Currently, because of their distinctive features such as easy scalability, processability, and feasibility in practical applications, polymers occupy 90% of the market for membrane materials[44,45]. However, polymeric membranes have a definite trade-off with respect to the desired properties of permeability and selectivity for the required gas component[48]. To solve this problem, various approaches such as molecular structure engineering and addition of materials containing silica, zeolites, and carbons into a polymer have been investigated[49-51].

Recent has been paid significant attention to advanced membrane materials specifically for carbon-based

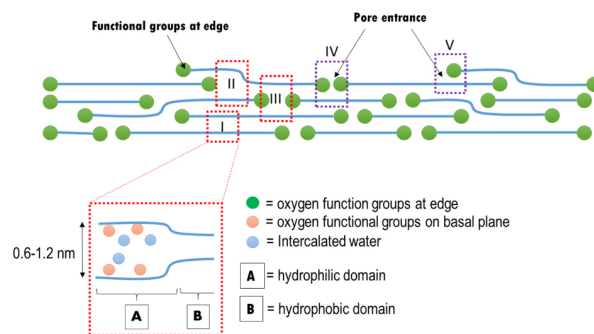


Fig. 4. Simplified GO membrane structure to be considered for molecular separation. Reproduced from [58] with permission of Willey.

nanomaterials, such as fullerenes[52], carbon nanotubes (CNT)[53,54], graphene[55,56], and GO[13]. A significant amount of effort has also focused on tailoring nanocarbon-based membranes to obtain outstanding gas separation performance[57]. In particular, GO has been regarded the most promising candidate for gas separation membranes because of its distinct properties such as single-atom thicknesses, potential for mass production, ease of scalability, and processability in solution[58]. Good dispersion ability in various types of solvents such as water and polar organic solvents facilitates the preparation of pristine GO films and composite GO layers on substrates through various methods[59]. For gas separation, studies on preparation of a thin film composite system have been mainly concentrated, because a short diffusion pathway is generally preferred to avoid barrier character of two-dimensional (2D) materials and improve gas diffusion rate. Furthermore, the prepared GO films form lamellar structures, and the interlayer spacing between the stacked GO sheets is between 0.6 and 1.2 nm, which can be controlled by the amount of intercalated water and the degree of oxidation[60]. Owing to the complex chemistry of the GO film, it is difficult to estimate or calculate the intrinsic permeation properties of any gases going through the GO membranes (Fig. 4). Notably, it is a key to control the interlayer spacing as well as the film thickness of the GO film for practical use as a membrane material.

The ultrathin GO coated on a porous substrate ex-

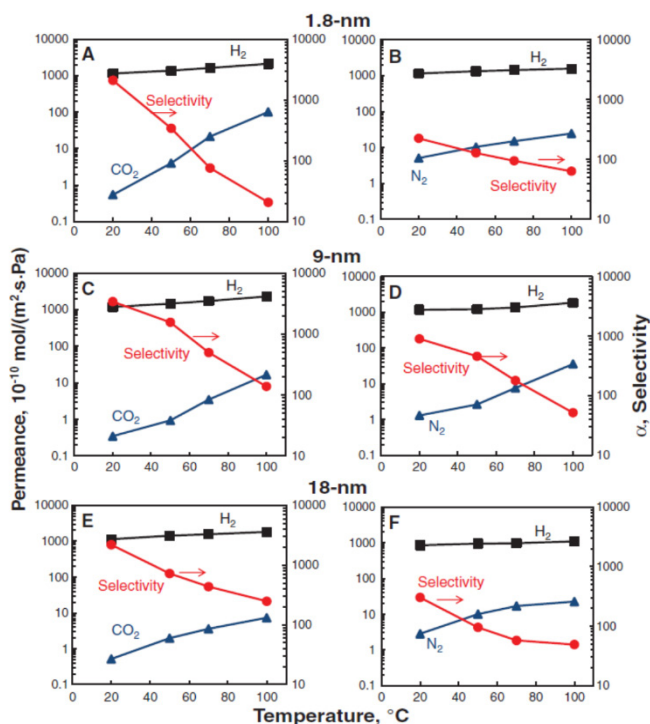


Fig. 5. 50:50 H_2/CO_2 and H_2/N_2 gas mixture separations and comparison with literature data. (A) and (B) show separation results for a 1.8-nm-thick GO membrane, (C) and (D) for 9-nm membrane, and (E) and (F) for an 18-nm membrane. Reproduced from [57] with permission of AAA Science.

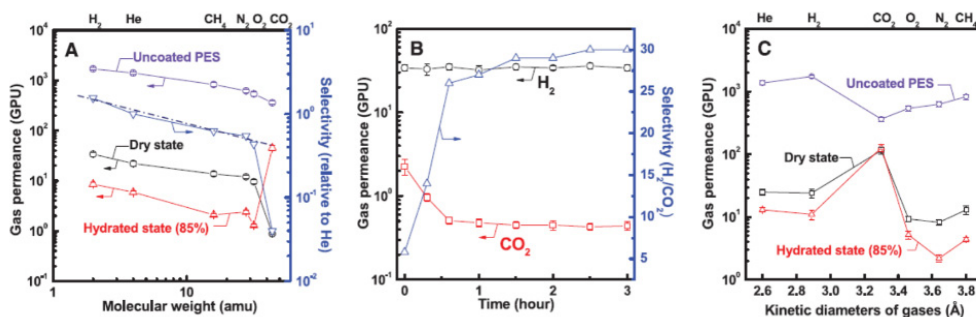


Fig. 6. Gas transport behavior through ultrathin GO membranes. (A) Gas permeances of GO membranes as a function of molecular weight (method one; dashed line represents the ideal Knudsen selectivity) under dry and humidified conditions. amu, atomic mass unit. (B) H_2 and CO_2 permeances and H_2/CO_2 selectivity of method one GO membranes as a function of permeation time. (C) Gas permeances of GO membranes as a function of kinetic diameter (method two) under dry and humidified conditions. Reproduced from [11] with permission of AAA Science.

hibits outstanding selective gas transport behaviors[11, 14,57]. For example, an ultrathin GO (1.8 nm thick) membrane on an anodized aluminum oxide (AAO) supported and measured its gas permeability[57]. This group experimentally demonstrated that gas permeation through the GO film is dependent on the effective

thickness of the GO film[57]. Moreover, the GO film that reduces the thickness at a nanometer level exhibits an ultrapermeable H_2 -selective character with reasonable separation factors (H_2/CO_2) (Fig. 5)[57].

More interesting study on ultrathin GO composite system has been reported to show the different gas

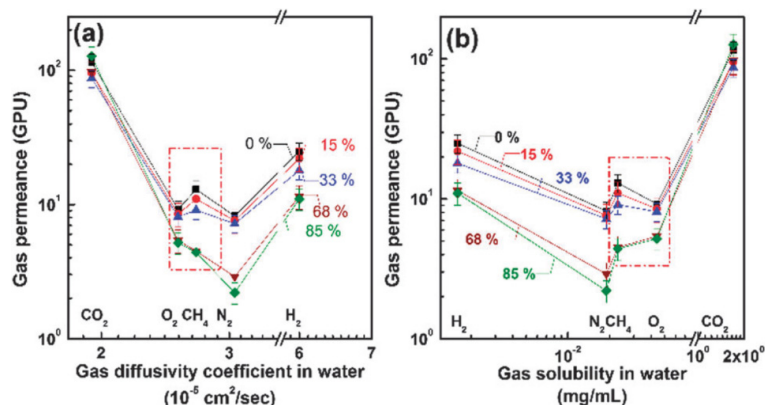


Fig. 7. Gas permeances of ultrathin GO membranes as a function of gas diffusivity coefficient (a) and gas solubility (b) in water at 25 °C. Gas permeance order of such GO membranes strongly depends on the RH levels of feed pressure. Reproduced from [14] with permission of RSC.

transport behaviors (Fig. 6)[11]. The few-layered GO-coated porous polymeric membranes exhibit totally different CO₂ transport behavior[11]. In other words, the few-layered GO membranes exhibit facilitated or retarded CO₂ diffusion features, depending on the stacking manners, which gives rise to different diffusion path sizes[11]. To control the stacking manner, the GO layers (<10 nm) were coated on the porous polymeric membranes in two different ways: (1) static spin coating and (2) dynamic spin casting[11]. The thin GO membranes prepared via static spin coating exhibits the Knudsen transport, which shows nanoporous membranes[11]. The selectivity shows the Knudsen selectivity with increasing coating cycles, indicating that the nanopores formed between the GO sheets are difficult to form selective gas diffusion channels by reapplying the coating method[11]. On the other hand, the GO membranes prepared via dynamic spin casting showed high CO₂ selective transport behavior following the solution-diffusion model in polymers with ultrahigh free-volume[61].

Furthermore, these GO membranes maintain outstanding CO₂ separation characteristics even under humidified conditions[11,14]. This can be attributed to both the water- and CO₂-philic features of GO, and the high CO₂ solubility coefficient in water (Fig. 7)[14, 16]. Thus, this synergistic effect can contribute to the achieving of stable CO₂/N₂ and CO₂/CH₄ selectivities

under humidified conditions[14]. The hydrophilic GO can be the stable existing water vapors inside the GO layers. Such intercalated water molecules increase the CO₂ solubility term, thus leading to a high CO₂ permeation rate[14]. In general, when exposed to water vapor, the commercial polymeric membranes for separating CO₂ significantly lose their CO₂ separation ability. This is because the condensation of water vapor blocks the thermodynamic pores in the polymeric membranes[14]. Therefore, these outstanding CO₂ separation properties can envision the GO membranes as next-generation membrane materials for CO₂ capture.

4. Ion Separation Properties

Because of the hydrophilic nature of GO, an ion transport through the GO-based films has been more extensively studied than other applications, including gas separation. Various researchers are actively investigating from fundamental studies to applied research[13,15,62-64]. Several permeation systems such as a simple two-chamber diffusion cell, a high-pressure cell, and specially designed equipment were employed to determine the intrinsic GO properties for ion separations[15]. As a result, it was revealed that GO membranes have wide potential for water purification and ion sieving, as compared with the commercial polymeric membranes[15]. Although the transport mecha-

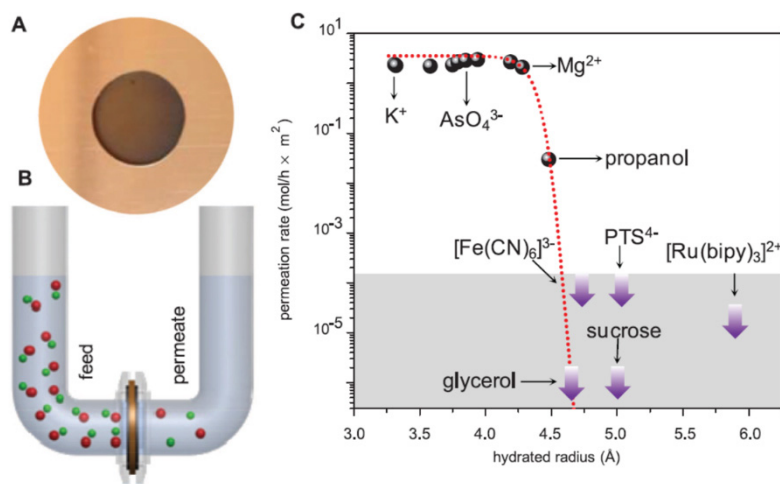


Fig. 8. Ion permeation through GO laminates. (A) Photograph of a GO membrane covering a 1-cm opening in a copper foil. (B) Schematic of the experimental setup. A U-shaped tube 2.5 cm in diameter is divided by the GO membrane into two compartments referred to as feed and permeate. Each is filled to a typical level of ~ 20 cm. Magnetic stirring is used so as to ensure no concentration gradients. (C) Sieving through the atomic-scale mesh. The shown permeation rates are normalized per 1 M feed solution and measured by using 5-mm-thick membranes. Reproduced from [15] with permission of AAA Science.

nism is still unknown, a promising performance is mainly attributed to the distinctive structural properties of the GO membranes such as atomic-level thickness, controllable diffusion channel size, and abundant oxygen group[58]. In this section, we briefly present the overall research on ion transport through the lamellar GO films.

A first report on ultrapermeable water vapor diffusion demonstrated that the micron-thick GO films can permeate water vapor while blocking others, including various organic solvents and even small-sized gas molecules like helium[15]. This discovery contradicts the traditional concept that it is difficult to pass through the lamellar structure in molecules such as helium[13]. Thus, this initiated to extensively study the transport phenomena of water and ion transport through GO films, including thin composite membranes.

According to the abovementioned research, a permeation rate of various liquids including water and organic solvents through the freestanding GO films was measured using a simple diffusion cell[15]. It was established that liquid water diffused through the GO films, whereas no permeation of other liquids was ob-

served via chemical analysis[15]. Furthermore, a conductivity meter coupled with a total carbon analyzer can characterize the permeability of hydrated ions with different salts[15]. Ions with relatively small sizes, such as potassium ions, can rapidly pass through the GO films[60]. On the other hand, large-sized ions and organic molecules could not penetrate the same films (Fig. 8)[60]. These data support the fact that a liquid water molecule and hydrated ions of small size penetrate the interlayer gaps created by the stacked GO sheets[60]. In addition, the physical channel size between the GO sheets is approximately 4.5 Å, to calculate based on the hydrated size of the penetrated ions (i.e., K⁺ (3.3 Å) and Mg²⁺ (4.4 Å) can be diffused but larger molecules do not.)[15].

These studies indicate that GO can be a promising candidate as a new membrane material. However, the size-sieving transport mechanism of the GO films is still unclear. This is because the proposed mechanism is too simplified to ignore the complicated structure of the GO membranes (Fig. 4). The detailed transport study of the GO films has established that the intrinsic water permeability coefficient is measured in the range

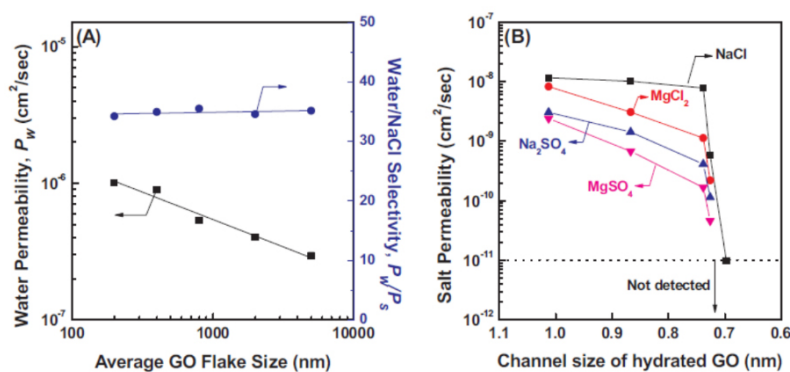


Fig. 9. (A) The effect of GO flake size on the water permeability of GO membranes. (B) The effect of interlayer spacing on the salt permeabilities of GO layers. The channel size was simply calculated by subtracting GO thickness (0.34 nm) from the interlayer spacing. Reproduced from [60] with permission of Elsevier.

of 3.0×10^{-7} to 1.0×10^{-6} cm²/s, which strongly depends on the physical and chemical properties of GO, such as the flake size and oxidation level (Fig. 9)[60]. This permeability of the GO film is similar to that of a commercial polyamide membrane for desalination [65]. Moreover, the GO membrane exhibits a lower diffusion coefficient than the common polyamide-based membranes, whereas the water partition coefficient of the GO films is higher than that of hydrophilic polymers[60]. This indicates that the water transport mechanism of the GO films looks likely to follow the solution-diffusion mechanism rather than the size-sieving mechanism.

Notably, it is true that the GO membrane exhibits outstanding ion separation ability, which is suitable for nanofiltration (NF) applications that allow the penetration of small-sized ions and blocking unwanted large molecules. The GO thin-film composite shows higher water flux ranging from 8 to 27.61 L·m⁻²·h⁻¹ when proper engineering size of the interlayer spaces and the effective film thickness is reduced[60]. Considering that the flux of the conventional NF membranes is approximately 2.0 L·m⁻²·h⁻¹[63], the GO membranes exhibit higher water flux with reasonable rejections, which can reduce the energy consumption for desalination process. Thus, the GO thin-film composite system has been considered the most promising candidate for NF applications.

5. Conclusions

GO has several advantages over conventional materials in industrial applications. However, new platforms require further development owing to the need for precise criteria to compete with the conventional materials such as polymers metal alloys for membrane. Understanding the intrinsic properties of GO is suitable for its applications. This is because GO shows entirely different behaviors between bulk and ultrathin (i.e., under 5 layers) properties. This unique feature provides an opportunity for exploring GO-based engineering. Notably, because of its 2D platform, ease of thin-film formation, and scalability, GO is the most unique material among various nanomaterials. However, various important issues need to be addressed before the chemistry of GO and the modified GO become practical. The first is the chemical and physical stability owing to the metastable nature of GO and the modified GO. Second, owing to their nanoscale structure, it is necessary to discover a suitable substrate with good affinity for GO and the modified GO. These questions range from a complete systematic study of a GO-based structure to a more fundamental understanding of the structure and consequently a processing pathway. Therefore, we need to establish a unique tunable structure of GO and the modified GO that gives them an edge in various application fields.

Acknowledgments

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