

Research on the Helium Permeability of Graphene Oxide Membranes

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Abstract. In order to meet the sealing performance requirements, extra-high sensitive mass spectrometer leak detection method is developed. So the leak rate of $10^{-15}\text{Pa}\cdot\text{m}^3/\text{s}$ on the order of the standard leakage is demanded. Increasing the number of holes in the graphene on the artificial control, the leak rate of grapheme would be improved. Based on this idea, a certain defective graphene as a penetrating element, using in the ultra-sensitive leak detection can be made. In this paper the relationship among the permeability of helium and the pressure difference and the thickness of the GO membrane were studied. The permeation mechanism of GO membrane of the minimal leak rate was discussed, which provides a reference for the study of ultra-sensitive leak detection technology.

1. Introduction

The sealing performance is an important parameter to evaluate the quality of vacuum Components. With the continuous development of electronic technology, the size of vacuum electronic devices is getting smaller, life expectancy is longer, and reliability requirement is getting higher. Especially for long-life optical device, it is also crucial to maintain the internal gas composition constant for long periods of time. In order to meet the sealing performance requirements, extra-high sensitive mass spectrometer leak detection method is developed. The sensitivity of the leak detection method reached the order of $10^{-15}\text{Pa}\cdot\text{m}^3/\text{s}$, so the leak rate of $10^{-15}\text{Pa}\cdot\text{m}^3/\text{s}$ on the order of the standard leakage is demanded [1]. In vacuum technology, the leak rate of quartz infiltration helium standard leakage hole commonly used generally can only reach the order of $10^{-10}\text{Pa}\cdot\text{m}^3/\text{s}$. Lots of research work to carry out for a new standard leak, try to get the lower limit of $10^{-15}\text{Pa}\cdot\text{m}^3/\text{s}$ vacuum standard leaks in recent years. Hajime Yoshida using a stainless steel sintered filter with a pore size of less than $1\mu\text{m}$ as the standard leak, get the standard leak whose rate is $10^{-8}\text{Pa}\cdot\text{m}^3/\text{s} \sim 10^{-6}\text{Pa}\cdot\text{m}^3/\text{s}$ [2]. Yongheng Zhao used standard porosity of 70 nm porous alumina production to make the standard leak. The leakage rate of standard leak is $8.55 \times 10^{-9}\text{Pa}\cdot\text{m}^3/\text{s}$ [2].

Pure graphene, due to its perfect hexagonal structure, is not permeable to any gas molecule. Increasing the number of holes in the pure graphene on the artificial control, the leak rate of grapheme would be improved. Based on this idea, a certain defective graphene as a penetrating element, the ultra-sensitive leak detection standard leak can be made. The graphene oxide (GO) is a kind of separation membrane material with good engineering application prospect. Nair has studied the permeability of GO membrane with thickness of $1\mu\text{m}$. Hang Li has studied the gas permeability of GO membranes with thickness of $1.8\text{nm} \sim 180\text{nm}$. The results show that the permeability and the thickness of the membranes are exponentially related to the thickness and have good gas selectivity



[3-5]. Zhiping Xu uses molecular dynamics to simulate the process of passing gases through GO membranes [6].

Based on the previous research, this paper studies the relationship between the permeability and the pressure difference and the thickness of the GO membrane. The permeation mechanism of the minimal leakage rate GO membrane is discussed, that provides a reference for the study of ultra-sensitive leak detection technology.

2. Experiments

The modified Hummer method was used to prepare the graphene nanosilver dispersion, and the GO membrane was prepared by vacuum filtration. In this paper, a GO membrane with a thickness of $1.8\text{nm} \sim 2\mu\text{m}$ was obtained with a volume of $2.7\mu\text{l}$ to $3000\mu\text{l}$ and a 0.2% of the mass percent graphene solution. The based material of the GO membrane was made of an anodic alumina membrane (AAO) having a pore size of $0.2\mu\text{m}$ produced by Whatman Corporation, having an outer diameter of 2.5 cm and an effective alumina diameter of 2.0 cm. In order to prevent damage to GO on the seal in the test experiment, a layer of aluminum foil is covered on the GO and the final effective permeate area is about 1 cm in diameter. The actual situation is shown in figure 1.

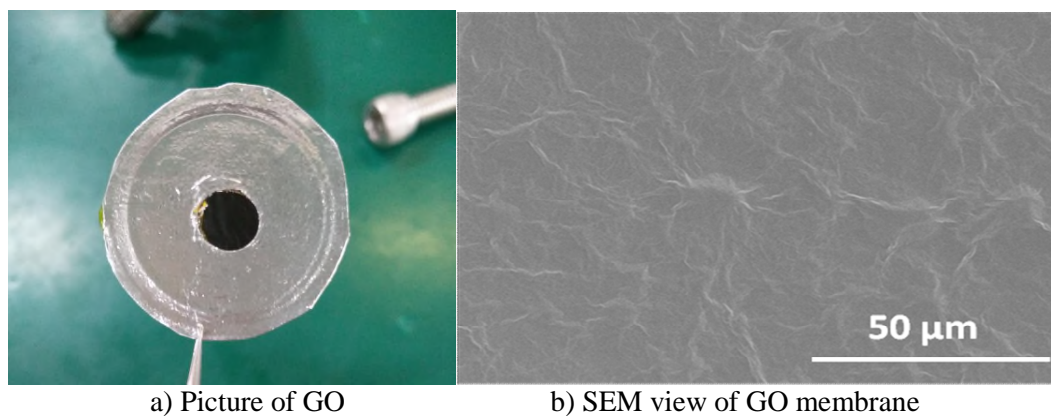
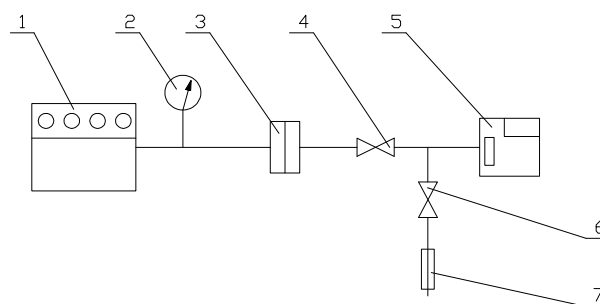


Figure 1. Picture of GO membrane.

The principle of helium permeability measurement of GO membrane by helium mass spectrometer leak detector is shown in figure 2. The inflatable console provides high-purity helium gas to the upstream of the GO membrane, and the helium flow through the membrane downstream of the GO membrane is leaked by the helium mass spectrometer. The calibration of the helium mass spectrometer leak detection system is carried out using standard leaks to avoid errors in the signal drift of the helium mass spectrometer leak detector. Based on this system, the effects of pressure difference on both sides of the membrane and the effect of membrane thickness on the infiltration rate of GO were carried out.



1-Inflatable console, 2-pressure gauge, 3-membrane permeation module, 4-leak detecting valve, 5-helium mass spectrometer leak detector, 6-calibration valve, 7-standard leak

Figure 2. Schematic diagram of helium permeability test system.

3. Experimental results and analysis

3.1 Relationship between the infiltration helium rate and the pressure difference on both sides of the membrane

Using the experimental methods shown in figure 2, the relationship between the infiltration rate of the GO membrane and the pressure difference on both sides of the film was tested. The top view of the GO membrane to be measured is shown in figure 1(b). During the experiment, the pressure downstream of the membrane has been kept below 10Pa, and the upstream pressure of the membrane has changed in the range of 100kPa (absolute pressure) and 500kPa (absolute pressure). The helium permeation rate of 11 kinds of thickness of the membranes in the range of 200nm ~ 2μm was measured, that is shown in figure 3. The experimental results show that the flow conductance of GO membranes with thickness of 2μm reached $10^{-13} \text{ m}^3/\text{s}$. For a variety of GO membranes, the helium permeability is proportional to the pressure difference between the two sides of the film. That is to say, as the pressure difference on both sides of the film changed, the flow conductance of the film remains stable. The experimental results show that the flow of helium in the membrane is molecular flowing in the pressure range of 100 kPa ~ 500 kPa for the GO membrane with thickness of 200 nm ~ 2μm.

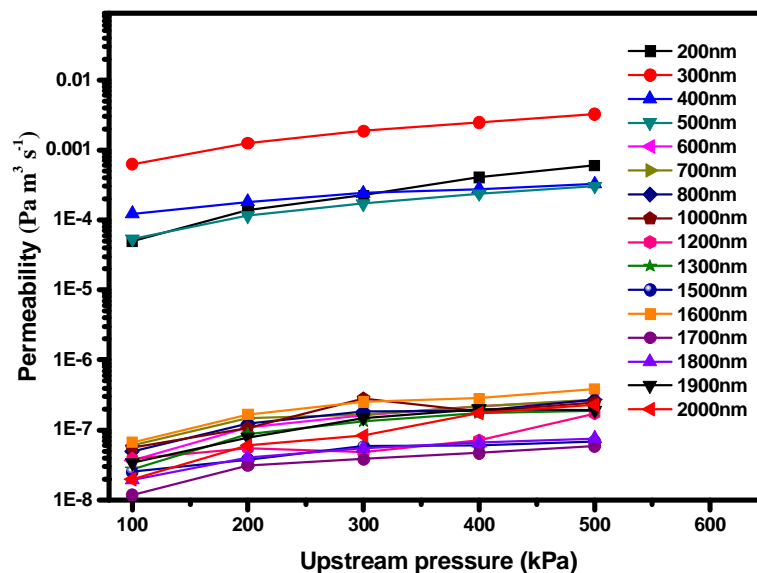


Figure 3. Relationship between flow conductance of GO membrane and pressure.

All experiments in this paper were carried out at room temperature of 20 °C, and the free path of any gas molecule at 20°C was calculated by the following equation (1) [7].

$$\bar{\lambda} = \frac{9.108 \times 10^{-22}}{p\sigma^2} \quad (1)$$

where, $\bar{\lambda}$ - mean free-path of gaseous molecules, m; p -gas pressure, Pa; σ^2 -gas molecular diameter, m.

From the above formula can be obtained, helium molecular at a pressure of 1atm molecular average free path is 192nm at 20 °C. The GO membrane is made of monolithic layer GO sheets. The gas molecules pass through the gap among monomolecular layers. The GO membrane samples used in this paper are measured by XRD, and the interlayer spacing can be calculated by the equation 2 [7].

$$2d\sin\theta = n\lambda \quad (2)$$

where, λ -wavelength, nm; d - the interlayer spacing, nm; θ -angle. And the interlayer spacing is 0.88nm, as shown in figure 4. The average molecular free range of helium is much larger than that of the GO, and the helium flow through the GO membrane always keeps the molecular flow state. As a result, the flow conductance of a thin membrane remains constant for helium under different pressure differences. In the case of constant temperature, the mean free path of a gas is inversely proportional to the pressure. It is calculated that the mean free path of the molecule is 1.92nm when the helium pressure reaches 10MPa at 20 °C. It can be deduced that for the GO membrane, the permeation of helium in the film can be maintained in the molecular flow state when the upstream pressure of the film is in the range of 0-10MPa.

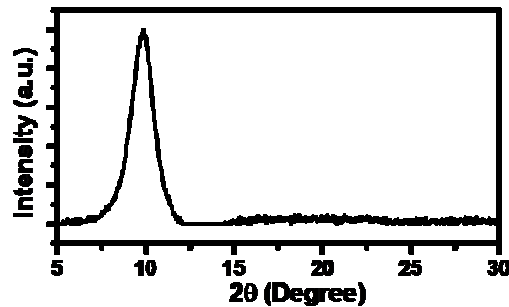


Figure 4. Interlayer spacing of the GO samples was tested by XRD.

3.2 Relationship between helium permeability and membrane thickness

As for the above experimental data, the relationship between the helium permeability and the thickness of the GO membrane can be obtained, and the thicknesses of the GO membrane were measured by SEM method. The cutaway view is shown in figure 5. Under the pressure difference of 100kPa ~ 500kPa, the relationship between the helium permeability and the thickness of the membrane is shown in figure 6. The results of more than 100 times experiments shown that, when the pressure on both sides of GO membrane remains unchanged, the permeability of the helium is exponentially related to the thickness of the membranes, which is consistent with the results reported in Reference [7]. In the vacuum leak detection technology, based on the characteristics of the relationship between the permeability and the thickness of the GO membrane, the change of the leak rate can be achieved by the small change of the thickness, so that the wide range permeability of standard leakage could be obtained.

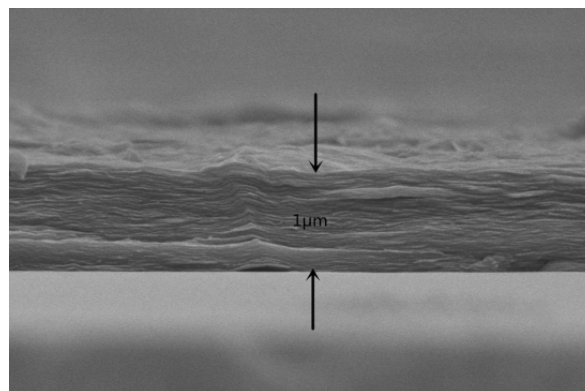
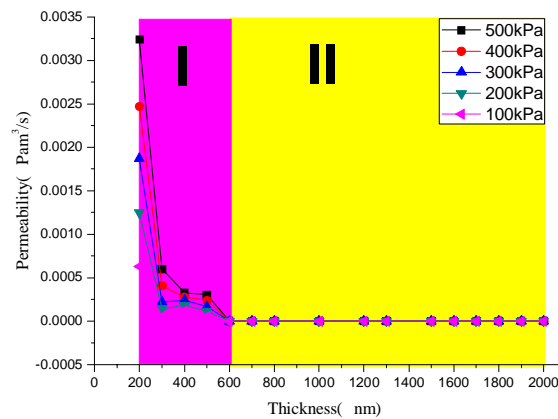
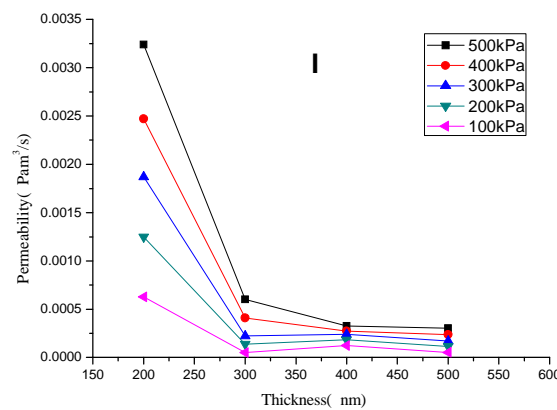


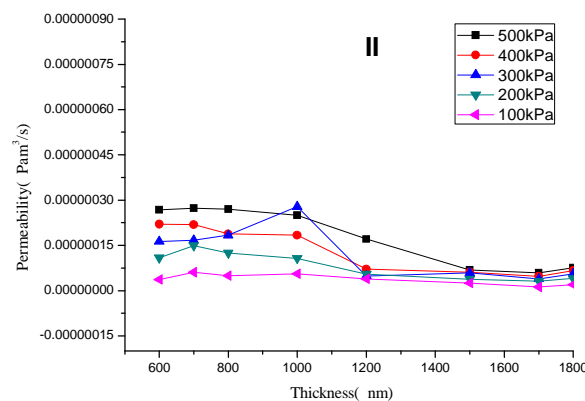
Figure 5. The sectional view of 1μm thickness GO membrane.



(a) Relationship between helium permeability and thickness of GO membranes



(b) The helium permeability of 200nm-500nm of GO membranes



(c) The helium permeability of 200nm-500nm of GO membranes

Figure 6. Relationship between helium permeability and thickness of GO membranes.

4. Conclusion

In this paper, an improved Hummer method was used to prepare GO membranes with various thicknesses, which range from 200nm to 2 μ m. The relationship between the permeation rate and the pressure difference and thickness were studied. When the upstream pressure of GO membranes is lower than 500kPa, the permeation process of helium in the membranes belongs to the molecular flow state, and the permeability of the membranes to helium varies exponentially with the thickness. The

permeability of the helium is exponentially related to the thickness of the membranes. These characteristics provide a suggestion that GO membranes could be used to prepare Permeable helium-type standard leak with a small leak rate or a large leak rate.

Reference

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Acknowledgements

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