

**PVDF-GRAPHENE CONDUCTIVE COMPOSITE MEMBRANE AND  
PVA-GRAPHENE CONDUCTIVE COMPOSITE MEMBRANE  
PREPARATION AND APPLICATION**

by

Lu Shi

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Applied Sciences in Civil Engineering

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## ABSTRACT

Graphene has a great potential to revolutionize many fields because of its perfect electrical conductivity. Therefore, it is considered a possible material for the preparation of conductive membrane. In this research, polyvinylidene fluoride (PVDF) and polyvinyl alcohol (PVA) were used together with graphene to create graphene based polymer composite conductive membrane. First, Boehm titration was used to determine the linkage of carboxyl groups on the surface of graphene sheet. Then pure PVDF membrane was trail-produced to investigate the best ratio of PVDF, plasticizer, and solvent. Results showed that PVDF/DMF weight ratio should not be higher than 0.15. In addition, the breaking stain and the contact angle increased with increasing plasticizer concentration; whereas the ultimate force that they could tolerate decreased.

The resistance of PVDF-graphene membrane was measured. Results showed that although the whole membrane became conductive, the resistance was not less than 8000 ohm.

PVA-graphene membrane was prepared. This membrane had much lower resistance than the PVDF-graphene membrane. However, PVA-graphene had a bad performance in perchlorate adsorption due to lack of inside area. Besides, it could not prevent membrane blocking in dead-end electrical filtration. Based on calculation, if charged particles were held into electric field, at least 118 V must be used in dead-end electrical filtration. But with a cross flow filtration equipment, only 1 to 2 V was needed. Further research should be taken about investigating physical properties of those conductive membranes and their applications.

## **Chapter 1**

### **INTRODUCTION**

Nearly 71% of our planet's surface is water of which only 3% is fresh water. Fresh water is stored in lakes, ponds, rivers, and streams, they serve countless essential functions for our environment and our life. Fresh water can maintain ecological balance, provide habitats for plants and animals, at the same time they are the critical part of life. As the development of our society, fresh water provides a myriad of daily uses such as cultivation, irrigation, wash, entertainment and hydropower. However, the increasing population and the pollutant of water enhance the serious situation of scarcity of water.<sup>1</sup>

There are many different ways to solve this serious situation, such as building reservoirs, implementing water diversion projects, and increasing water utilization rate. Moreover, enhancing water treatment technologies is the most essential target that environmental engineers aim their efforts at. Recently, membrane separation technology has gained considerable attention due to its high efficiency and low cost. Membrane separation technology is widely used in wastewater treatment, sea water desalination, food technology, and pharmaceutical

There are several advantages of membrane separation<sup>2</sup>

- Membrane can separate a wide range of particles, from 1 to  $10^7$  angstrom. Thus membrane separation technology can satisfy a large scale of separation processes.

- There is no phase change during membrane separation, which means energy requirement should be low. That is a major reason why membrane separation is safe and economical.
- Membrane separation is a simple, low maintenance, and low equipment operation cost process, which also makes it economical and wide spread use.
- Membrane can separate specific component in a high efficiency. It has high selectivity and since many organic and inorganic materials can be used in membrane preparation, this separation selectivity is easily to be controlled.
- Membrane can help extract specific component from a low concentration solution without large energy costs.

However, questions have arisen over how to increase the mechanical properties and decrease membrane pollution. To deal with this question, many studies about membrane modification have been processed.

### **1.1 Conductive Membrane Application**

Conductive polymer can be used in a variety of fields such as chemical sensors, artificial nerves, and organic solar cells<sup>3</sup>. Separation based on conductive membrane has been suggested since the last century. Conductive membrane can generate a magnetic barrier if current can flow in the membrane, and this can bring out separation. This membrane is different from ion-exchange membrane because there is no ion exchange during the whole process.<sup>4</sup>

Although polymer membranes are widely used, some problems still exist. Normal membrane lacks efficiency in charged particle separation, and cannot prevent

membrane blocking. But those problems will not plague conductive membranes. Moreover, by controlling the voltage, specific particles can be separated from suspension.

Conductive membrane based on some conductive polymer, such as polyacetylene, has been synthesized. However, those membranes are sensitive to oxygen and water<sup>4</sup>. In fact, many conductive polymers are considered potential materials for making conductive membrane, but those polymers cannot dissolve in common solvent, and they are hard to be stretched or molded<sup>3</sup>. Thus, to achieve desired properties, it is better to prepare a composite conductive membrane with multiple potential materials, which can provide the properties that we want.

## **1.2 Graphene: Electrical Property**

Because of the flexibility of carbon bonds, many different carbon-based structures have been developed. Graphene is one of those structures which have a 2-D allotrope of carbon. Recently, studies about graphene have expanded quickly since it has high thermal conductivity, mechanical strength and good electric property. Largely, this property comes from the half-filled  $\pi$  bond<sup>5</sup>. For one single carbon atom, it forms a trigonal structure with other three carbon atoms by  $\sigma$  bond, and the unaffected atom can covalently bond with other carbon atoms and form  $\pi$  bond. Those  $\pi$  bonds are flexible between carbon sheets. Then electrons can be transferred between those atoms. Obviously, this perfect electrical property comes from its highly symmetrical structure. Breaking this structure, such as adding function groups on the carbon sheets, may destroy this symmetrical structure and decrease the electrical property.

Since carbon is the only component of graphene, graphene is hydrophobic and stable. Thus graphene is hard to disperse in most of aqueous solutions. This makes

graphene not useful in any large scale industrial production. It is important to produce a stable graphene suspension in water or organic solvents before use.

### **1.3 PVDF Membrane: Mechanical Properties.**

PVDF is a highly non-reactive plastic material. It has high purity, strength and can resist strong acids, bases and high temperature. Those advantages put PVDF far ahead of other polymer as a membrane material. Besides, it has a relatively low melting point, which makes PVDF easy to use.

In the field of membrane separation, PVDF may be not hydrophobic enough compared to polypropylene (PP) and polytetrafluoroethylene (PTFE), but PVDF can easily dissolve in common organic solvents. Thus, it is still the best choice of membrane material. Besides, PVDF has thermodynamic compatibility and can mix with other polymers such as poly(methyl methacrylate) (PMMA), which is useful in preparing membrane with specific properties<sup>6</sup>.

### **1.4 PVA-graphene Membrane and PVDF-graphene Synthesis**

The key point to successfully prepare a conductive membrane is to assemble conductive materials, such as graphene, with materials that have desire properties. PVDF, as a popular membrane material, have many essential mechanical properties. Thus, mixing PVDF together with graphene should be a simple method to get conductive membrane.

Polyvinyl alcohol (PVA) is a water soluble polymer. With hydroxyl groups on the chain, it can react with other acid groups, and then it can be modified. De Lannoy and his group developed a PVA based composite material<sup>3</sup>. By reacting carboxylated

carbon nanotube with PVA, they successfully got a highly conducting polymer–multiwalled carbon nanotube composite membrane as shown in figure 1.1.

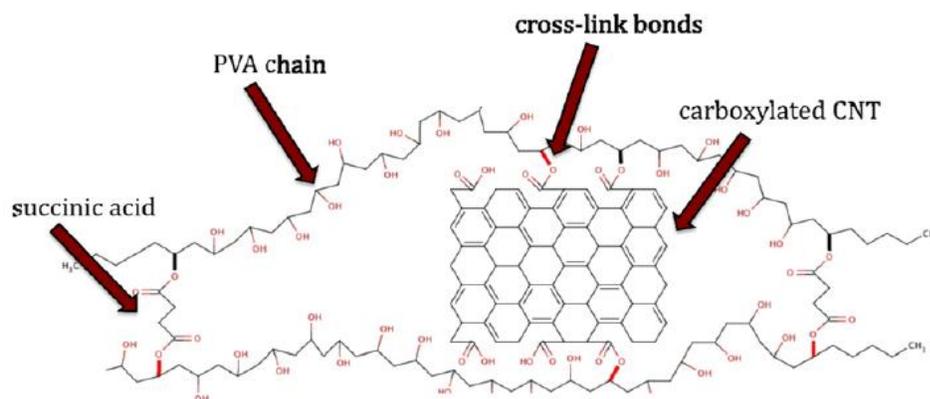


Figure 1.1 PVA can be linked by reacted with succinic acid. Besides, carboxyl groups on the carbon nanotube can react with hydroxyl group on the PVA chain. With these two reactions, carbon nanotube can be immobilized together with PVA chain<sup>3</sup>.

There are two carboxyl groups on succinic acid molecule and each of them can react with one hydroxyl group. With this reaction succinic acid can bond PVA chain together. Besides, carboxyl groups on carbon nanotube also can react with hydroxyl groups on PVA chain. Thus, with these two reactions, carbon nanotube can be immobilized with PVA chain. The whole material becomes conductive.

Theoretically, if there are some carboxyl groups on the surface of graphene, graphene, or called functionalized graphene, can be cross linked with PVA and build a PVA-graphene composite conductive membrane. And, based on the conductive theory of graphene, it is believed that if functional groups are linked with graphene, but not too much, this graphene can still be conductive.

## **1.5 Research Motivation**

In this research, graphene based membrane is prized in charged particle separation and toxic substance adsorption. Therefore, both PVDF and PVA were used to create conductive membranes. In those membranes, polymers offer mechanical properties and graphene provides conductive property. At first, Boehm titration was used to demonstrate that there were carboxyl groups in graphene and it can be linked with PVA chain. Physical properties such as mechanical strength and hydrophilicity were tested. As a major parameter of electrical conductivity, resistance was measured. Then prepared PVA-graphene was used as conductive separation membrane in dead-end filtration to separate  $\text{Al}_2\text{O}_3$ . As a conductive material, PVA-graphene membrane was also used as an electrode to adsorb perchlorate.

## Chapter 2

### CHEMICALS AND INSTRUMENTS

Polyvinylidene fluoride (PVDF), Tributyl O-acetylcitrate (TBAC), (n-octyl)trimethyl ammonium bromide, were bought from Sigma-Aldrich Inc. (St. Louis, MO, USA). A high reactivity carbon mixture contains graphene as its major content (larger than 70 wt%) was bought from Bionomic Technologies Inc. (Richmond Hill, ON, CA). Polyvinyl alcohol (PVA), SDS (sodium dodecyl sulfate), PEG 400 (polyethylene glycol), and HCl were bought from Fisher Scientific Inc. (Waltham, MA, USA). Dimethyl formamide (DMF), succinic acid, cetyl trimethyl ammonium bromide, aliquat 336, methyl tributyl ammonium chloride, benzyl dimethyl hexadecyl ammonium chloride, benzyl trimethyl ammonium bromide, tetra propyl ammonium chloride, tetra ethyl ammonium chloride hydrate, benzyl tributyl ammonium chloride, NaCl, NaClO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, NaOH were bought from Acros Organics Inc. (Fair Lawn, NJ, USA)

Tensile test was finished by Tytron™ 250 Microforce Testing System (MTS Systems Corporation, Monroe Township, NJ, USA). Sonication was finished by Model 505 Sonic Dismembrator (Fisher Scientific Inc. Waltham, MA, USA). Membrane was coated by K hand coater (RK Printcoat Instruments, Royston, Hertfordshire, UK). Ion concentration was measured by DX 500 system (Thermo Fisher Scientific Inc. Waltham, MA, USA). Perchlorate adsorption was measured by AFRDE4 Bipotentiostat three electrode system (PINE Research Instrumentation, Durham, NC, USA).

## Chapter 3

### GRAPHENE DISPERSION

Graphene has a strictly two-dimensional lamellar structure. Theoretically, there is no functional group on this structure and that is why pristine graphene is hydrophobic. In practical application, graphene is easy to form an irreversible aggregation via van der Waals interactions<sup>7</sup>, and aggregation makes graphene stay away from extensive usage. Graphene separation is really important because most of their properties are only reflected in the single sheets<sup>8</sup>. Graphene oxide (GO) was used to replace pure graphene because functional groups on the surface of GO make it easy to be separated into liquids. However, GO has a high resistance because of its broken symmetrical structure, therefore it cannot be used for the purpose of conduction. Some researchers try to reduce GO to graphene using different chemical reagents, e.g. hydrazine, dimethyl hydrazine, hydroquinone and NaBH<sub>4</sub><sup>9</sup>, but these methods are dangerous because of the toxicity. Besides, some chemicals with less perniciousness are baleful for delicate molecules<sup>10</sup>. Moreover, others tried to make graphene dispersion in high concentration by sonication. Umar Khan<sup>11</sup> tried to disperse graphene in liquid phase by a 460 h sonication. But this super long reaction time that may damage equipment which makes this application impractical. So techniques that can disperse pure graphene directly in water are still needed.

Surfactants are always amphiphilic organic compounds with high molecular weights; it can lower the surface tension (or interfacial tension) between graphene sheets. Obviously surfactants addition must be the first method that needed to be

developed in order to make a stable graphene suspension. In this part several different surfactants were used. The purpose was to find the most efficient surfactant:

cetyl trimethyl ammonium Bromide(MW 364.5),  
aliquat 336(MW 884),  
(n-octyl)trimethyl ammonium bromide(MW 252),  
methyl tributyl ammonium chloride(MW 404),  
benzyl dimethyl hexadecyl ammonium chloride(MW 396),  
benzyl trimethyl ammonium bromide(MW 230.14),  
tetra propyl ammonium chloride(MW 221.81),  
tetraethyl ammonium chloride hydrate(MW 165.7),  
benzyl tributyl ammonium chloride(MW 332)  
SDS (sodium dodecyl sulfate),  
PEG 400(Polyethylene glycol, MW 400).

### **3.1 Results and Discussion**

Nine samples were prepared and each contained 0.0003 g graphene powder, 3ml dimethyl formamide (DMF) and different kinds of surfactant. First the concentration of surfactant was 300 ppm (0.03 wt%), then the concentration was increased to 5000 ppm in order to rule out the possibility that the concentration of surfactants is too low to be efficient. Graphene was added into test tubes followed by 3ml DMF addition. Then different surfactant was added under the help of vortex mixer. Then those mixtures were sonicated for 5 hours and precipitate for 10 hours. Blank group, which also contained graphene and DMF without any surfactant was made.

Figure 3.1-3.5 show that PEG 400 was the best one among those nine different surfactants.

After mixing and sonicated for 10 hours, all of the solutions became black. But after sedimentation, most of the samples became clear. In the first eight samples, SDS was better than the others. Graphene particles remain suspended for 24 hours and then started to settle in the presence of SDS. Besides, the suspending graphene particle in the SDS group was visible. However, after adding PEG 400 to the graphene suspension, and apply sonication to it, the liquid became black and the color was stable for over 72 hours and then slowly started to settle. The suspended graphene particles in the PEG 400 group were small and invisible.

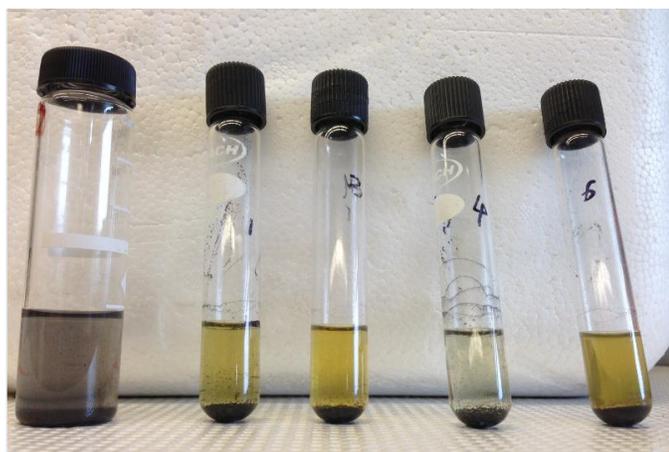


Figure 3.1 Graphene suspension with 300 ppm of surfactants after 5 hours of sonication and 10 hours of precipitation, from left to right: SDS(Sodium dodecyl sulfate), cetyltri methyl ammonium bromide ( $C_{19}H_{42}BrN$ ), (n-octyl) trimethyl ammonium bromide ( $C_{11}H_{26}BrN$ ), methyl tributyl ammonium chloride( $C_{13}H_{30}ClN$ ), benzyl trimethyl ammonium bromide( $C_{10}H_{18}FNO$ )

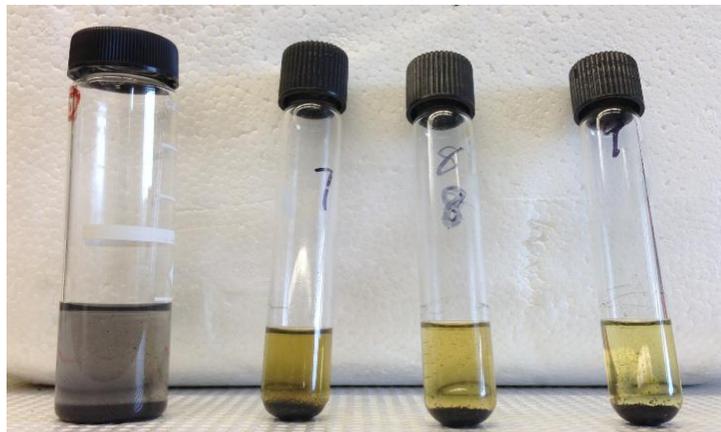


Figure 3.2 Graphene suspension with 300 ppm of surfactants after 5 hours of sonication and 10 hours of precipitation, from left to right: SDS(Sodium dodecyl sulfate), tetra propyl ammonium chloride ( $C_3H_7)_4NCl$ ), tetra ethyl ammonium chloride hydrate( $C_2H_5)_4NCl \cdot xH_2O$ ), benzyl tributyl ammonium chloride ( $C_6H_5CH_2N(Cl)(C_2H_5)_3$ )



Figure 3.3 Graphene suspension with 300 ppm of surfactants after 5 hours of sonication and 10 hours of precipitation, from left to right: SDS(Sodium dodecyl sulfate), blank.

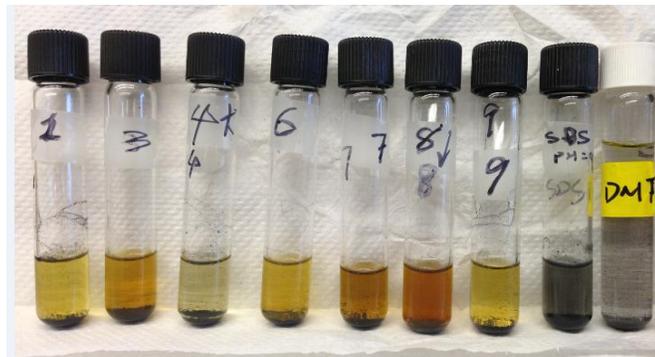


Figure 3.4 Graphene suspension with 5000 ppm of surfactants after 5 hours of sonication and 10 hours of precipitation, from left to right: cetyl trimethyl ammonium bromide ( $C_{19}H_{42}BrN$ ), (n-octyl)trimethyl ammonium bromide ( $C_{11}H_{26}BrN$ ), methyl ributyl ammonium chloride( $C_{13}H_{30}ClN$ ), benzyl trimethyl ammonium bromide( $C_{10}H_{18}FNO$ ). Tetrapropyl ammonium chloride ( $C_3H_7)_4NCl$ ), tetraethyl ammonium chloride hydrate( $C_2H_5)_4NCl \cdot xH_2O$ ),benzyl tributyl ammonium chloride ( $C_6H_5CH_2N(Cl)(C_2H_5)_3$ )

PEG400 was added as surfactant. Different amounts of surfactant may cause different effect as shown in figures 3.5.

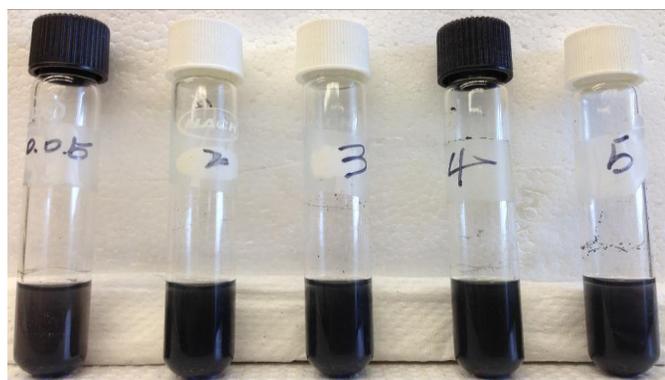


Figure 3.5 Graphene suspension with different amount of PEG 400 after 5 hours of sonication and 10 hours of precipitation. The amount of PEG 400 was (from left to right):0.05ml (19 wt%), 0.1ml (38 wt%), 0.15ml (57wt%) , 0.2ml (76 wt%), 0.25ml (95 wt%).

## Chapter 4

### BOEHM TITRATION

Boehm titration is a traditional technique to quantitatively determine acidic oxygen surface functional groups on the surface of carbon. Bases such as  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  can neutralize acid functional groups due to their different strength.  $\text{NaOH}$  is the strongest base and it can neutralize all of the acid functional groups, whereas  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  can neutralize some of the acid functional groups according to their acid strength.  $\text{Na}_2\text{CO}_3$  can react with carboxylic and lactonic groups.  $\text{NaHCO}_3$  can react with carboxylic acids functional groups. With the amount of base consumed, the functional groups can be identified and their content can be known<sup>12,13</sup>.

Instead of direct titrating samples, back titration was used in this research. The sample was let to react with known excess base for a long time and then the excess base was titrated to quantify the functional groups. Due to the small amount of functional groups and the tardiness of the acid-base reaction, it is barely impossible to quantify the functional groups by direct titration.

#### 4.1 Boehm Titration Procedure<sup>8,9</sup>

##### 4.1.1 NaOH Standard Solution and Calibration

110 g of  $\text{NaOH}$  powder was added to 100 ml of DI water, shook and let stand till clear. Take 2.7 ml supernatant and diluted to 1000 ml with DI water and shook well. 1 g phenolphthalein was added into 100 ml of ethanol (95%) as indicator. 0.36 g of potassium hydrogen phthalate was dried in oven under  $105^\circ\text{C}$  and diluted to 50 ml with DI water. Two drops of phenolphthalein indicator were added, then titrated by

NaOH standard solution until pink. Then the concentration of NaOH was calculated by equation 4.1:

$$C(\text{NaOH}) = \frac{m \times 1000}{(V_1 - V_2)M} \quad (4.1)$$

where  $m$  is the weight of potassium hydrogen phthalate (g),  $V_1$  is the volume of NaOH (ml).  $V_2$  is the volume of NaOH in blank (ml),  $M$  is the molecular weight of potassium hydrogen phthalate (g/mol), in this case  $M$  is 204.22 g/mol.

#### 4.1.2 HCl Standard Solution and Calibration

Bromocresol green-methyl red mixed indicator: 0.1 g of bromocresol green was added to 100 ml of ethanol (95%) as solution I, 0.1 g of methyl red was added to 100 ml of ethanol (95%) as solution II. Then mix 30 ml of solution I and 10 ml of solution II added.

$\text{Na}_2\text{CO}_3$  powder was dried in oven under 300 °C to constant weight, then added 0.1 g of  $\text{Na}_2\text{CO}_3$  to 50 ml DI water, which was added ten drops of bromocresol green-methyl red mixed indicator, titrated with HCl standard solution until dark red, boiled this mixture and continued to titrate until color became dark red. Blank was also needed. Concentration of HCl was calculated by the following equation:

$$C(\text{HCl}) = \frac{m \times 1000}{0.5 \times (V_1 - V_2)M} \quad (4.2)$$

where  $m$  is the weight of  $\text{Na}_2\text{CO}_3$  (g),  $V_1$  is the volume of HCl (L),  $V_2$  is the volume of HCl in blank (L),  $M$  is the molecular weight of  $\text{Na}_2\text{CO}_3$  (g/mol), in this case  $M$  is 106 mol/L.

#### 4.1.3 Na<sub>2</sub>CO<sub>3</sub> Standard Solution and Calibration

5.3 g of anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) was added to 1000 ml of DI water; shook well. 40 ml of anhydrous sodium carbonate solution with ten drops of bromocresol green-methyl red mixed indicator was titrated with HCl standard solution until dark red. Boiled and continued to titrate until color became dark red.

Concentration of sodium carbonate was calculated by the following equation:

$$C(\text{Na}_2\text{CO}_3) = \frac{V_1 \times C_1}{2V} \quad (4.3)$$

where V<sub>1</sub> is the volume of HCl standard solution (L), C<sub>1</sub> is the concentration of standard HCl solution (mol/L), V is the volume of Na<sub>2</sub>CO<sub>3</sub> (L).

#### 4.1.4 NaHCO<sub>3</sub> Standard Solution and Calibration

4.201 g of anhydrous sodium bicarbonate was added to 1000 ml DI of water; shook well, then took 40 ml of sodium bicarbonate solution, added 20 ml of DI water and 10 drops of bromocresol green-methyl red mixed indicator, titrated with HCl standard solution until dark red, boiled it and continue titrated until dark red.

Concentration of sodium bicarbonate was calculated by the following equation:

$$C(\text{NaHCO}_3) = \frac{V_1 \times C_1}{2V} \quad (4.4)$$

where V<sub>1</sub> is the volume of HCl standard solution (L), C<sub>1</sub> is the concentration of HCl standard solution (mol/L), V is the volume of NaHCO<sub>3</sub> (L).

#### 4.2 Boehm Titration and Calculation

In fact, physical processes during experiments may break the structure of carbon particles and affect their physical and chemical properties, which are not expected. Alicia<sup>13</sup> et al found that to make bases react with acid functional groups, shaking was the best method to agitate carbon samples compared with stirring and

sonication. After carbon samples were agitated by shaking, stirring and sonication for 24 hours, respectively, carbon particles presented different structures under microscope. Results showed that after shaking, the structure of carbon particles did not change much, whereas the structures of carbon particles after sonication and stirring were severely broken. Therefore, in this research graphene samples were shook before Boehm titration.

0.05 g of graphene was added to 50 ml each of NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and DI water, respectively. After shaking for 48 hours, samples were filtrated to get the supernatant. Then take 25 ml of supernatant, added 10 drops of bromocresol green-methyl red mixed indicator, titrated with HCl standard solution till the end point. Samples reacted with DI water were also titrated as blanks.

#### 4.2.1 Result and Discussion

Functional groups contained in unit mass of graphene were reacted with base, and the amounts of functional group were calculated by following equations:

$$n_{\text{NaOH}} = \left[ C_{\text{NaOH}} V_{\text{NaOH}} - C_{\text{HCl}} (V_{\text{HCl}} - \Delta V_1 - V_b) \right] / W \quad (4.5)$$

$$n_{\text{Na}_2\text{CO}_3} = \left[ 2C_{\text{Na}_2\text{CO}_3} V_{\text{Na}_2\text{CO}_3} - C_{\text{HCl}} (V_{\text{HCl}} - \Delta V_2 - V_b) \right] / 2W \quad (4.6)$$

$$n_{\text{NaHCO}_3} = \left[ 2C_{\text{NaHCO}_3} V_{\text{NaHCO}_3} - C_{\text{HCl}} (V_{\text{HCl}} - \Delta V_3 - V_b) \right] / W \quad (4.7)$$

where  $n_{\text{NaOH}}$  is the amount of functional group that reacted with NaOH(mol),  $n_{\text{Na}_2\text{CO}_3}$  is the amount of functional group, which reacted with Na<sub>2</sub>CO<sub>3</sub>(mol).  $n_{\text{NaHCO}_3}$  is the amount of functional group, which reacted with NaHCO<sub>3</sub>(mol).  $V_b$  is the volume of HCl, which was used to titrate the blanks (ml),  $V_{\text{HCl}}$  is the volume of HCl that was used in titration (L),  $C_i$  is the concentration of standard solution (mol/L),  $W$  is the

weight of graphene samples (g),  $\Delta V_i$  is the volume of correction for theoretical end point of indicator to the titration end point (L),  $V_i$  is the volume of base that was titrated by HCl standard solution, in this research it is 25 ml.

In above equations,  $\Delta V_i$  can be calculated by equation 4.8-4.10.

$$\Delta V_1 = (V_{\text{NaOH}} + V_{\text{HCl}})([H^+] - [H^+]_{\text{NaOH}}) / C_{\text{HCl}} \quad (4.8)$$

$$\Delta V_2 = (2V_{\text{Na}_2\text{CO}_3} + V_{\text{HCl}})([H^+] - [H^+]_{\text{Na}_2\text{CO}_3}) / C_{\text{HCl}} \quad (4.9)$$

$$\Delta V_3 = (V_{\text{NaHCO}_3} + V_{\text{HCl}})([H^+] - [H^+]_{\text{NaHCO}_3}) / C_{\text{HCl}} \quad (4.10)$$

where  $[H]^+$  is the proton concentration at color change point,  $[H]^+_i$  is the proton concentration at the theoretical end point of titration.

Based on the above equations, carboxyl groups, weak acid groups and phenolic hydroxyl groups can be qualified.

$$n_{\text{RCOOH}} = n_{\text{NaHCO}_3} \quad (4.11)$$

$$n_{\text{RCOOCOR}'} = n_{\text{Na}_2\text{CO}_3} - n_{\text{NaHCO}_3} \quad (4.12)$$

$$n_{\text{ROH}} = n_{\text{NaOH}} - n_{\text{Na}_2\text{CO}_3} \quad (4.13)$$

After calibration, real concentration of standard solutions were listed in table 4.1

Table 4.1 Concentration of standard solution

Ingredients	Theoretical concentration (mol/L)	Real concentration (mol/L)
HCl	0.05	0.0494
NaOH	0.05	0.0498
Na <sub>2</sub> CO <sub>3</sub>	0.05	0.0499
NaHCO <sub>3</sub>	0.05	0.0494

Samples were shook for 48 hours and filtered. Supernatant was titrated twice to take calculate value.

Volume of correction for theoretical end point of indicator to the titration end point can be calculated by equation 4.14-4.16.

$$\begin{aligned}\Delta V_1 &= \frac{(V_{\text{NaOH}} + V_{\text{HCl}})([\text{H}^+] - [\text{H}^+]_{\text{NaOH}})}{C_{\text{HCl}}} \\ &= (0.025 + 0.0221)(10^{-5.1} - 10^{-7}) / 0.0494 \\ &= 7.48 \times 10^{-6} \text{ L}\end{aligned}\quad (4.14)$$

$$\begin{aligned}\Delta V_2 &= \frac{(2V_{\text{Na}_2\text{CO}_3} + V_{\text{HCl}})([\text{H}^+] - [\text{H}^+]_{\text{Na}_2\text{CO}_3})}{C_{\text{HCl}}} \\ &= (0.025 \times 2 + 45.1)(10^{-5.1} - 10^{-7}) / 0.0494 \\ &= 1.51 \times 10^{-5} \text{ L}\end{aligned}\quad (4.15)$$

$$\begin{aligned}\Delta V_3 &= \frac{(V_{\text{NaHCO}_3} + V_{\text{HCl}})([\text{H}^+] - [\text{H}^+]_{\text{NaHCO}_3})}{C_{\text{HCl}}} \\ &= (0.025 + 0.02365)(10^{-5.1} - 10^{-7}) / 0.0494 \\ &= 7.72 \times 10^{-6} \text{ L}\end{aligned}\quad (4.16)$$

Based on equation 4.14-4.16, those correction values can be ignored because they are too small. Therefore, the amount of functional group, which reacted with the base can be calculated by following equations.

$$\begin{aligned}n(\text{NaOH}) &= [c(\text{NaOH})V(\text{NaOH}) - c(\text{HCl})(V_{\text{HCl}} - \Delta V_1 - V_b)]/W \\ &= [0.0498 \times 0.025 - 0.0494 \times (0.022 - 0.0234)] / 0.05 \\ &= 0.0263 \text{ (mol/g)}\end{aligned}\quad (4.17)$$

$$\begin{aligned}
n(\text{Na}_2\text{CO}_3) &= [2c(\text{Na}_2\text{CO}_3)V(\text{Na}_2\text{CO}_3) - c(\text{HCl})(V_{\text{HCl}} - \Delta V_2 - V_b)]/2W \\
&= [2 \times 0.0499 \times 0.025 - 0.0494(0.0451 - 0.0482)]/2 \times 0.05 \\
&= 0.0264 \text{ (mol/g)}
\end{aligned} \tag{4.18}$$

$$\begin{aligned}
n(\text{NaHCO}_3) &= [c(\text{NaHCO}_3)V(\text{NaHCO}_3) - c(\text{HCl})(V_{\text{HCl}} - \Delta V_3 - V_b)]/W \\
&= [(0.0494 \times 0.025 - 0.0494(0.02365 - 0.02465)]/0.05 \\
&= 0.0257 \text{ (mol/g)}
\end{aligned} \tag{4.19}$$

NaOH is the strongest base and it can neutralize all of the acid functional groups, whereas  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  can neutralize some of the acid functional groups according to their strength.  $\text{Na}_2\text{CO}_3$  can react with carboxylic and lactonic groups.  $\text{NaHCO}_3$  can react with carboxylic acids functional groups. Thus, according to equation 4.11, 4.12, 4.13:

$$n_{\text{RCOOH}} = n_{\text{NaHCO}_3} = 0.0257 \text{ mol/g} \tag{4.20}$$

$$n_{\text{RCOOCOR}'} = n_{\text{Na}_2\text{CO}_3} - n_{\text{NaHCO}_3} = 0.007 \text{ mol/g} \tag{4.21}$$

$$n_{\text{ROH}} = n_{\text{NaOH}} - n_{\text{Na}_2\text{CO}_3} = -0.001 \text{ mol/g} \tag{4.22}$$

The amount of ROH is close to 0, which means there is almost no hydroxyl group. This graphene sample has been partially oxidized and most of functional groups on the surface are carboxylic groups, which amount is larger than lactonic groups.

In fact mechanical cleavage of graphite is a straight way to get graphene but it is an uneconomical method. More common way to get graphene is chemical reduction. Graphene oxide can be dispersed in aqueous solution easily and graphene oxide can be converted to graphene. However, this method will not get pure graphene because some functional groups such as carboxyl acid group are hard to be removed because of its

double bond. Thus, after this Boehm titration, a large amount of carboxyl acid groups were found.

## **Chapter 5**

### **PVDF MEMBRANE**

PVDF is one of the famous materials in microfiltration (MF) and ultrafiltration (UF) membranes preparation. It has hydrophobic nature and good chemical resistance that can resistant to many corrosive compounds.

PVDF membrane was used as reverse osmosis membrane and was prepared by immersion precipitation by Loeb and Sourirajan since 1962<sup>14</sup>. Nowadays this process is still widely used to prepare PVDF membrane and other asymmetrical membranes. PVDF membrane can be prepared by both liquid-liquid demixing and crystallization. To acquire a PVDF membrane, coagulation bath can be an essential element for membrane structure. If soft coagulation bath is used, L-L demixing process would be slow and crystallization may dominate this coagulation process and form a particulate symmetric structure<sup>15</sup>. If a harsh coagulation bath, such as water, is used, L-L demixing takes place and asymmetric membrane is formed. During this process, L-L demixing builds a cellular structure and crystallization then followed to builds particulate morphology as what happens in soft coagulation phase. Besides, since L-L demixing happens rapidly, the surface of asymmetric membrane becomes dense nonporous.<sup>15</sup>

Asymmetric membrane is widely used, especially as a reverse osmosis membrane<sup>16</sup>. Beside, water is cheap and accessible, so we chose water as coagulation bath in this research.

Tributyl O-acetylitate( TBAC) is a friendly plasticizer. It is widely used in food industry, medical plastics, and aqueous pharmaceutical coatings. It is also competitive with other plasticizers in PVDF preparation<sup>17</sup>. Thus, in this research TBAC was used as a plasticizer to modify physical properties of conductive membrane.

### **5.1 PVDF Membrane Preparation**

PVDF powder was slowly added into dimethyl formamide (DMF) and stirred constantly. After the mixture became clear, plasticizer was added drop by drop. Stir was needed.

The whole mixture was then defoamed by standing for 3 hours, then the polymer solution was casted on a glass plate with thickness being controlled to 300  $\mu\text{m}$ . After pre-evaporation in the air for 10 min, the glass plate was immersed in DI water for 10 hours. PVDF membrane would be detached from the glass plate and moved out from the DI water coagulation bath. The membrane was washed in DI water and dried in the air for further use. The whole process can be expressed by figure 5.1.

The weight ratio of PVDF powder and DMF and the amount of plasticizer need to be decided. First different amount of PVDF powder was added to reach specific ratio. PVDF/DMF weight ratio equals to 0.05, 0.1 and 0.15 were chosen, and the weight ratio of TBAC/PVDF was from 0.1 to 0.7. The corresponding amount of materials used was showed in table 5.1 and table 5.2.

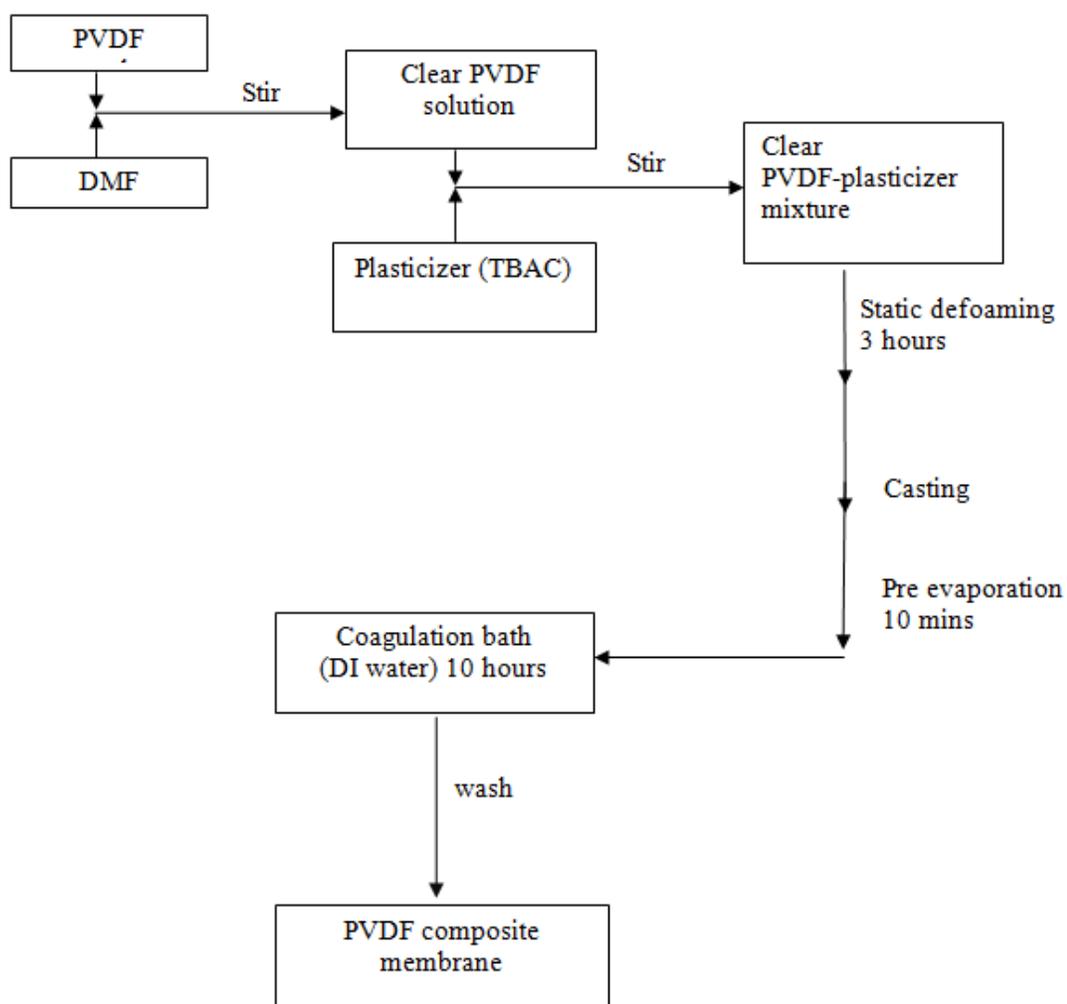


Figure 5.1 Process of PVDF membrane preparation<sup>21</sup>

Table 5.1 The amount of PVDF and DMF added in samples which have different PVDF/DMF weight ratio

PVDF/DMF(g/g)	PVDF (g)	DMF(g)
<b>0.05</b>	4.72	94.4
<b>0.1</b>	9.44	94.4
<b>0.15</b>	14.16	94.4

Table 5.2 The amount of TBAC added in samples which has different PVDF/DMF weight ratio

TBAC/PVDF(g/g) PVDF/DMF(g/g)	TBAC/PVDF(g/g)					
	0.2	0.3	0.4	0.5	0.6	0.7
0.05	–	–	–	–	–	–
0.1	1.89 (g)	2.83 (g)	3.77 (g)	4.72 (g)	5.66 (g)	6.61 (g)
0.15	2.83 (g)	4.25 (g)	5.66 (g)	7.08 (g)	8.50 (g)	9.91 (g)

## 5.2 Tensile Test and Contact Angle

Tensile test is a fundamental method to test the mechanical properties of materials. In tensile test, samples were under a controlled tension until failure. This test can predict how different type of force will affect materials. Also, ultimate tensile strength and maximum elongation can be measured<sup>18</sup>. In this test, each sample was cut to 0.7 cm×2 cm. All tests were conducted under 20°C and 60% relative humidity. The deformation rate was 120% per minute. Samples were fixed according to the following figures.

Contact angle was measured by reading the value directly through eyepiece. Membrane was cut into small pieces and the size is 10 cm ×10 cm. Then membrane was fixed on the glass plates and make sure that the membrane surface is smooth and dry. Put the sample in front of scene and align membrane surface with horizontal line by looking inside of the eyepiece. Slowly drop a drop of water on the surface, adjust scene like figure 5.3 shows and read the angle. Test 8 times for each piece and calculate average contact angle.

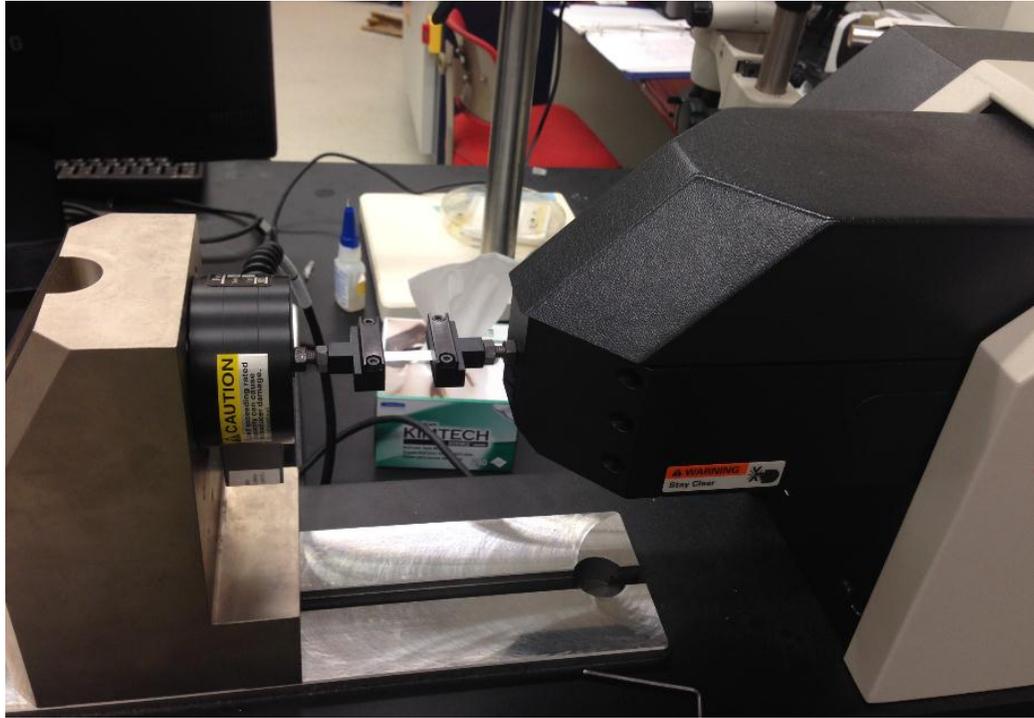


Figure 5.2 Instrument for tensile test and sample installation

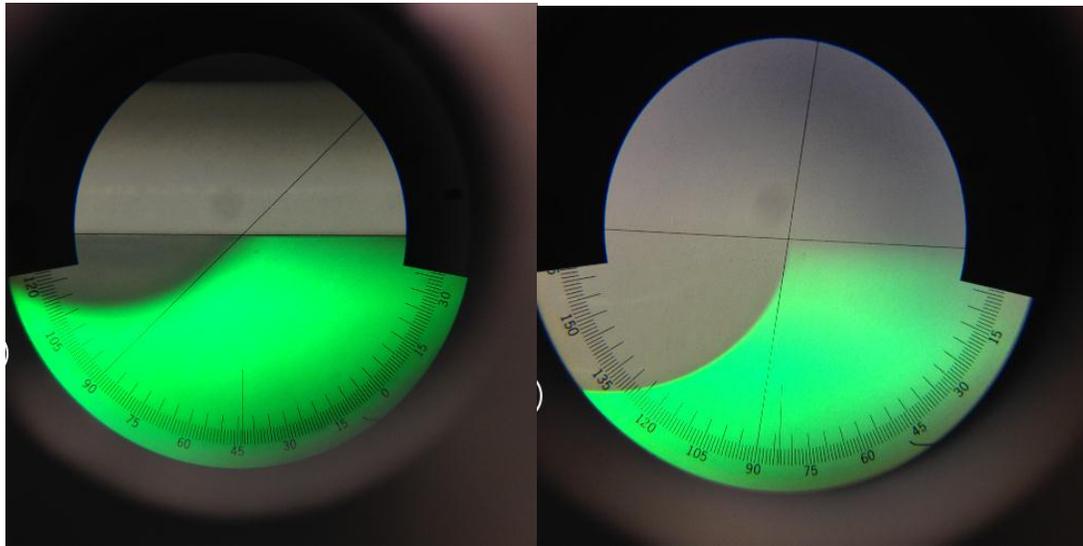


Figure 5.3 Contact angle measurement, the left panel is at small contact angle (of  $43^\circ$ ), the right panel is when the contact angle is large (at  $90^\circ$ ).

### 5.3 Results and Discussion

When the PVDF/DMF weight ratio is lower than 0.1, such as 0.05, the whole mixture was dilute and after mixed with graphene powder, graphene would precipitate. If coated on glass plate, graphene would flocculate during pre-evaporation and could not form a homogeneous membrane. After immersed in coagulation bath and take out, the aggregated graphene particle would tear the membrane and the whole membrane was fell into pieces.

When PVDF/DMF reached to 0.1, thin membrane was formed but when a plasticizer was added, the whole membrane became crispy and cannot be taken out of water. The higher percentage of plasticizer was added, the more crispy membrane was. Results were shown in figure 5.4.

As figure 5.5 shows, when TBAC/PVDF weight ratio was lower than 0.6, smooth, strong and intact membranes were formed. But when this ratio reached to 0.7, membrane became extremely soft and semi-transparent. With an intuitionistic view, as the weight ratio of TBAC/PVDF increased, membrane became softer, has higher malleability and lower strength.

Results of tensile test were shown in figure 5.6. With the increasing amount of TBAC, their tensile strength was decreased. When the weight ratio of TBAC/PVDF was 0.2, the maximum elongation was 8 mm, since the initial length is 2mm, the breaking strain was 400%, and when the amount of TBAC was higher but TBAC/PVDF weight ratio was still lower than 0.6, the strain remained the same but the ultimate force that the membrane could tolerate was decreased from 1.65 to 1.3 N. When the TBAC/PVDF weight ratio reached to 0.6, tensile strength was obviously decreased. Ultimate force was decreased to 1 N and the breaking strain was increased to 675%.

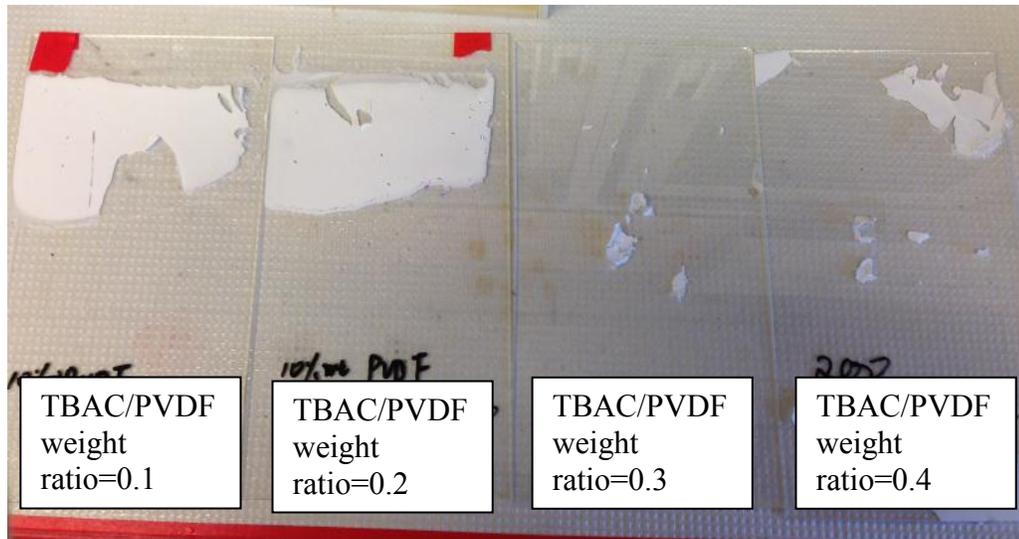


Figure 5.4 When PVDF/DMF weight ratio was 0.1. Membranes cannot be formed with different amount of plasticizer.

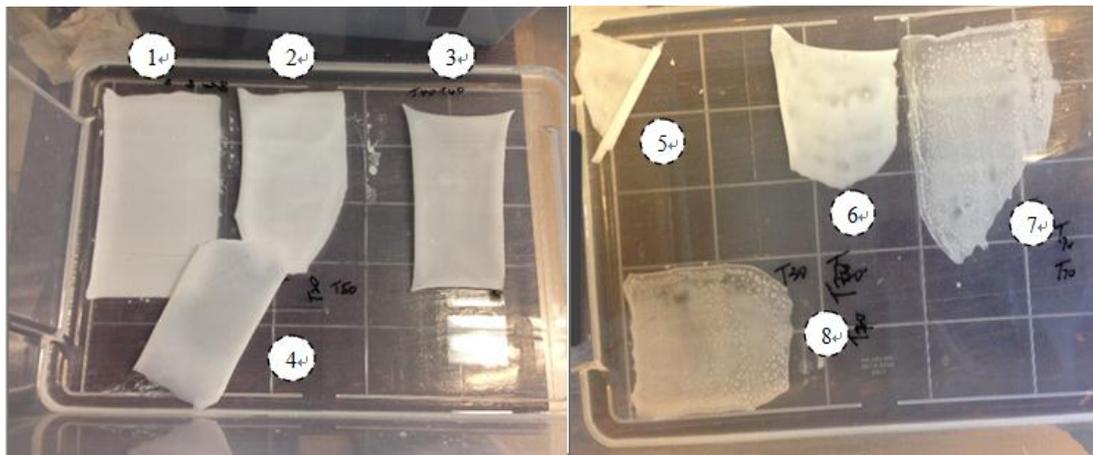


Figure 5.5 When the PVDF/DMF ratio was 0.15, a homogeneous and strong membrane could form. As the plasticizer was added, membrane would become soft and the transparency changed slightly. When the ratio was 0.7, the whole membrane would become semi-transparent. PVDF membrane with different TBAC/PVDF weight ratio: ① TBAC/PVDF = 0.6 ② TBAC/PVDF = 0.5, ③ TBAC/PVDF = 0.4, ④ TBAC/PVDF = 0.2 ⑤ ⑥ TBAC/PVDF = 0.3 ⑦ TBAC/PVDF = 0.7

This result is similar with Sothornvit's research<sup>19</sup> and shown in figure 5.7 and figure 5.8. Dibutyl phthalate (DBP) was added as plasticizer when they prepared hard elastic PVDF fibers. Their strain rate was 120%/min, which was the same on the present work. The breaking strain of PVDF fibers increased when the DBP content increased, whereas the breaking force decreased with DBP content. Sothornvit also measure the cyclic loading on PVDF fibers with different DBP amount. In this experiment, the PVDF fiber was drawn to 50% elongation first and then back to the original length and this process repeated for five times. When the amount of DBP was zero, the elastic recovery of PVDF fibers was about 85%. With DBP amount increased, the initial modulus and stress were decreased.

Marius Murariu et al<sup>20</sup> also used TBAC as a plasticizer and test how it will affect mechanical strength of polylactide. Results showed that when the concentration of TBAC was 10%, tensile strength at break was 35 Mpa, and breaking strain was 8%. When concentration of TBAC increased to 15%, tensile strength at break was also 35 Mpa but breaking strain increased to 221%. At last when the concentration of TBAC increased to 20%, the tensile strength at break was 30 Mpa and the breaking strain is 317%. This tendency was similar with the present study.

Plasticizer can increase the plasticity of plastic materials and increase their practicability. Pure PVDF membrane is crispy and almost has no ductility, but high content of plasticizer makes the membrane excessively soft and has a low tensile strength. Based on the above results, the percentage of plasticizer should be no more than 20%. This result is similar with those of Sothornvit et al<sup>19</sup>, who indicated that the content of DBP should be 5%.

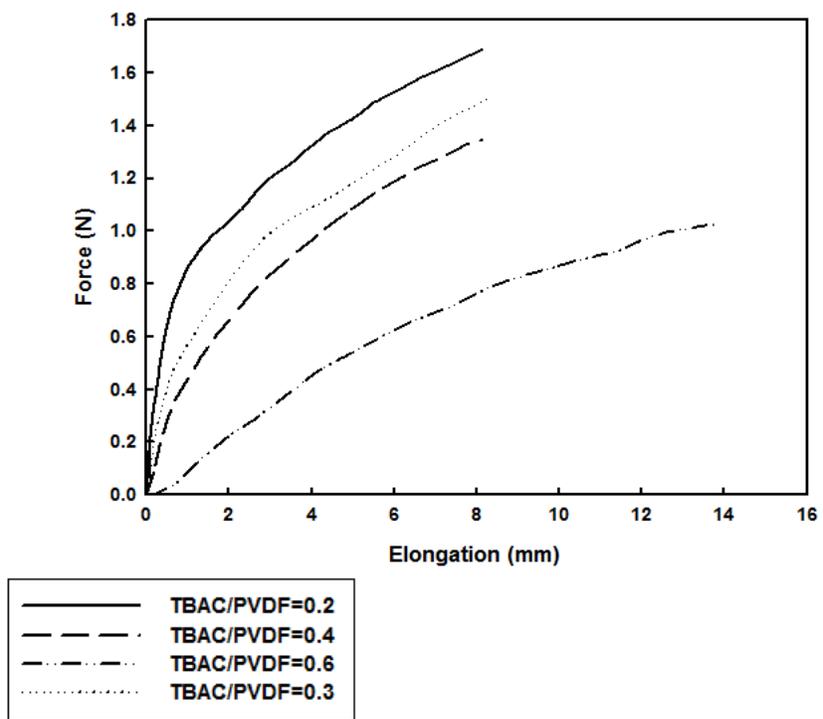


Figure 5.6 Results of tensile test.

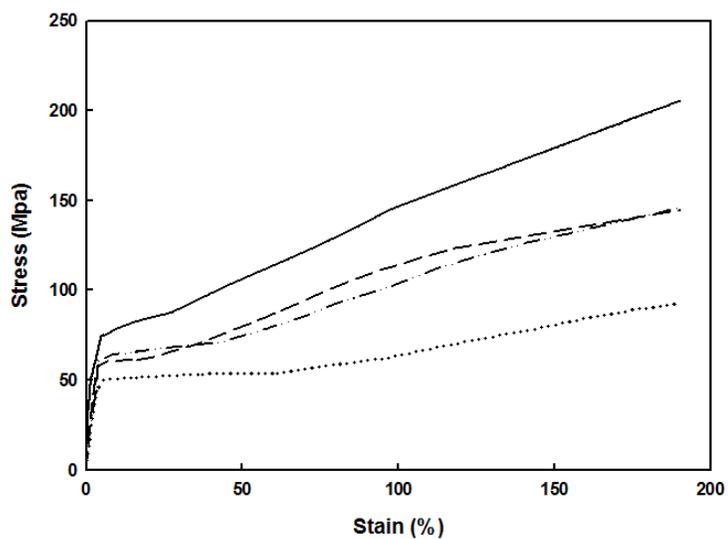


Figure 5.7 Tensile test of PVDF fibers with DBP concentrations of (a)0, (b)2, (c)5, (d) 10 wt%<sup>19</sup>

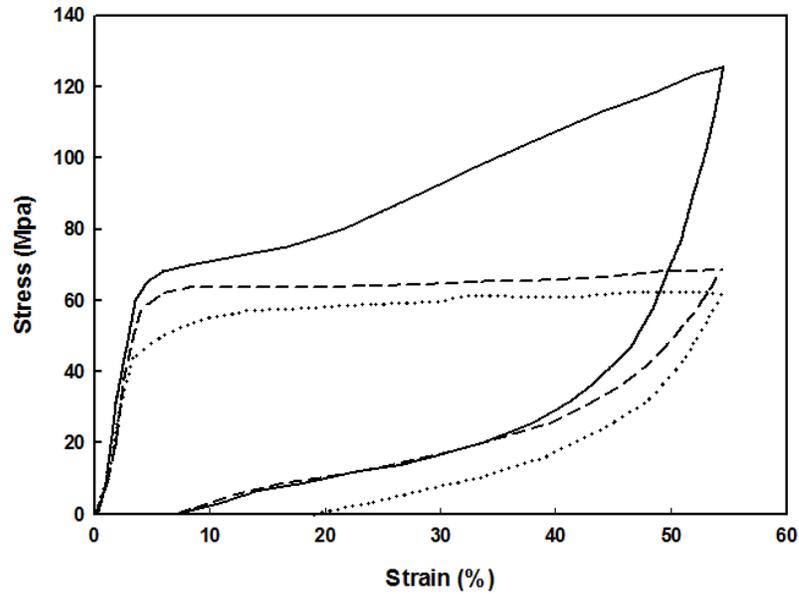


Figure 5.8 Cyclic loading to 50% extension of PVDF fibers with DBP concentration of (s)0,(b)5, (c)10 wt%. (rate=120%/min)<sup>19</sup>

Contact angle is increased when plasticizer amount increase. Results were shown in table 5.3 and figure 5.9. When the weight ratio of TBAC and PVDF was 0.2, average contact angle was 50.5°, when the ratio increased to 0.6, the contact angle increased to 76.30°. TBAC is hydrophobic, so more TBAC plasticizer added will increase the hydrophobicity of PVDF membrane.

This inference could be verified by Nugraha et al<sup>21</sup>, who used glycerol (GLY), ethylene glycol (EG), poly (ethylene glycol) (PEG), and propylene glycol (PG) as plasticizer and hoped to change the mechanical and surface properties of chitosan films. Pure chitosan films were hydrophobic and adding hydrophilic plasticizer could increase hydrophilia of the whole membrane. Results showed that contact angles were around 80° when no plasticizers were added. After that contact angles were decreased

with the increasing plasticizer concentration. When the amount of plasticizer was 40%, the contact angles were around 45°.

Bharathi Bai J. Basu et al<sup>22</sup> tried to prepare superhydrophobic PVDF membrane by adding hydrophobic modified fumed silica (HMFS). HMFS was a hydrophobic additive for PVDF membrane preparation. Results showed that when the concentration of HMFS was 33.3%, water contact angle of the whole membrane was 95°, and when the concentration of HMFS increased to 71.4%, the contact angle was 168°. Contact angle was increased with the HMFS concentration increasing.

Therefore, the properties of additive can affect the whole membrane obviously. If a hydrophobic plasticizer is added, the whole membrane will become more hydrophobic than before. On the contrary, if a hydrophilic plasticizer is added, the whole membrane will become more hydrophilic.

TBAC is a safe and common used plasticizer. However, it is not a solvent of PVDF powder. Thus, after TBAC was added, invisible micelle will be formed and this micelle will roughen the membrane surface. But after increasing the amount of TBAC, a mass of micelle gather together and the membrane surface became smooth. Wenzel reported the relationship between surface roughness and contact angle in 1949<sup>23</sup>. In his research:

$$\cos\theta^* = r\cos\theta \quad (5.1)$$

$$r = \frac{\text{actual surface}}{\text{geometric surface}} \quad (5.2)$$

where  $\theta^*$  is the real contact angle,  $\theta$  is the theoretical contact angle--the contact angle when surface is perfect smooth,  $r$  is roughness factor, which is the ratio of the area of actual surface to the shadow area,  $r = 1$  for perfect smooth surface.

For a hydrophilic surface which real contact angle ( $\theta^*$ ) is always lower than  $90^\circ$ , when the surface gets roughness,  $r$  becomes bigger, the value of  $\cos\theta^*$  becomes bigger. Thus, real contact angle becomes smaller. But for a hydrophobic surface, when  $r$  becomes bigger, the value of  $\cos\theta^*$  become bigger, and real contact angle becomes bigger.

This inference matches the result comes from Lin et al<sup>25</sup> . They added propylene glycol (PG) into PVDF membrane and measured contact angle. When PG concentration was increased from 26% to 34%, contact angle increased from  $150^\circ$  to  $165^\circ$ . However, if PG was increased to 38%, contact angle decreased to  $140^\circ$ . That was because a mass of micelle smooth membrane surface and decrease  $r$  value, then decrease contact angle. Besides, PG was a hydrophilic material, which could increase the hydrophilia of the whole membrane. That is why the final contact angle was even smaller than the original one.

But in the present research, as a hydrophilic membrane whose contact angle was lower than  $90^\circ$ , contact angle should be decreased with the increasing plasticizer amount. However, when the weight ratio of TBAC/PVDF was increased from 0.2 to 0.6, contact angle was increased from  $50.5^\circ$  to  $76^\circ$ . That may because slightly increasing the plasticizer concentration will roughen the membrane surface and decrease contact angle. However, too much plasticizer may smooth the membrane, decrease  $r$  value and then increase contact angle. Besides, too much hydrophobic plasticizer added also can increase the hydrophobicity of membrane. To prove this inference, further exploration may be needed.

Table 5.3 Results of contact angle (°)

TBAC/PVDF	Contact angle (°)								Average(°)	Standard deviation
0.2	44	50	49	41	66	50	57	47	50.50	7.84
0.3	61	68	51	62	52	60	60	49	57.88	6.53
0.4	66	59	57	62	50	59	58	60	58.88	4.60
0.5	74	79	58	66	77	83	68	73	72.25	8.00
0.6	82	79	73	67	73	77	80	80	76.30	5.01

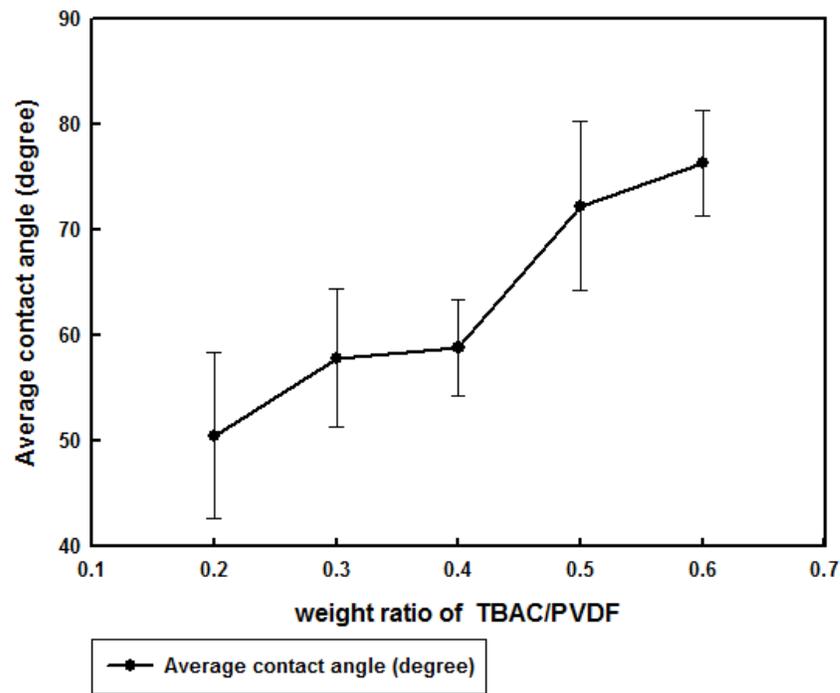


Figure 5.9 Curve of average contact angle change.

## Chapter 6

### PVDF-GRAPHENE MEMBRANE

#### 6.1 PVDF-graphene Membrane Preparation and Conductivity Measurement

The most intuitive and simple method to make a conductive PVDF membrane is mixing graphene powder together with PVDF. Graphene powder was added into DMF and was sonicated for 10 hours. Certain amount of PVDF powder was added and the mixture was stirred for 30 min, then let it stand for 3 hours to defoam. After that the mixture was cast on a glass plate with 300 $\mu$ m thickness. After pre-evaporation in the air, the glass plate was immersed into DI water for 10 hours. PVDF-graphene membrane would detach from the glass plate and could be moved out of DI water coagulation bath. The membrane was washed by flowing DI water and was dried in the air for further use. The whole process can be expressed by figure 6.1.

Non-woven fabric and plastic mesh were used as backbones of PVDF membrane. Previous research have proved that a low concentration of PVDF could not provide enough membrane strength, but obviously, since PVDF itself is not a conductive material, low amount of PVDF may decrease membrane conductivity. Besides, graphene additive can predictably decrease the membrane strength by its huge particle size. That means, theoretically, decreasing PVDF/graphene ratio can increase the electrical conductivity and weaken the membranes. As a consequence, a backbone may solve this problem. In this case, the backbone usage provides a possibility to form a thin membrane with low resistance and high membrane strength.

In this research, as table 6.1 shows, samples were divided into three different groups: PVDF membrane without backbone, membrane with plastic mesh backbone,

membrane with fabric backbone. In each group, three membranes were made, for PVDF-graphene membrane without backbone group, the weight ratio of PVDF and DMF is 0.15. For the membrane with backbone, the weight ratio of PVDF and DMF is 0.05. The weight ratio of graphene and PVDF was 0.05, 0.1, and 0.15, respectively.

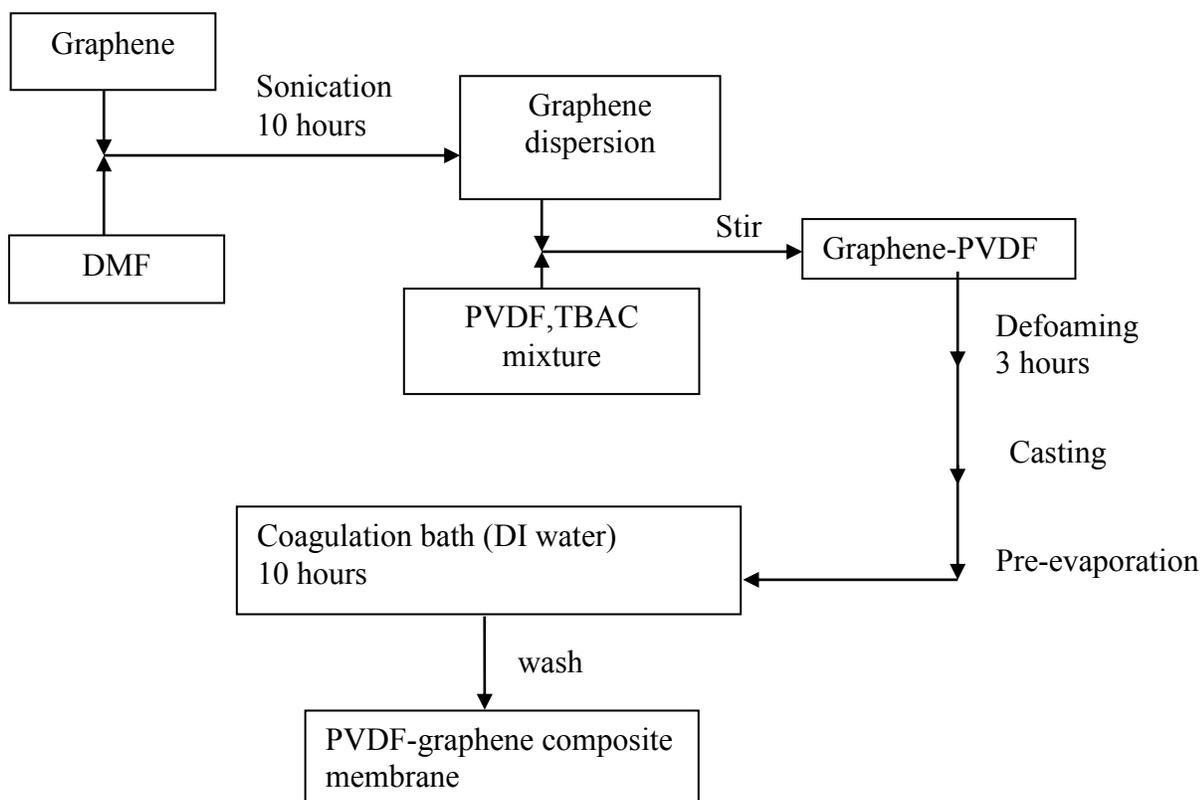


Figure 6.1 Process to prepare PVDF-graphene composite membrane

Table 6.1 PVDF/DMF ratio and graphene/PVDF ratio change in three different groups: membrane without backbone, membrane with plastic mesh backbone, membrane with fabric as backbone.

	No backbone	Plastic mesh	Fabric
<b>PVDF/DMF (weight ratio)</b>	0.05	0.15	0.15
<b>Graphene/PVDF(weight ratio)</b>	0.05,0.1,0.2	0.05,0.1,0.2	0.05,0.1,0.2

The electrical conductivity was measured by multimeter–voltage detector. First PVDF-graphene membrane was cut into 7 cm ×7 cm square. Multimeter-voltage detector was placed at three different places along this square. Each time the distance between anode and cathod was 2 cm. The resistance could be read from screen and the distance could be used to calculate resistivity of the membranes by the following equation:

$$\rho = R \frac{A}{l} \quad (6.1)$$

where  $\rho$  is electrical resistivity ( $\Omega \cdot m$ ),  $l$  is distance between two electrode (cm). In this research  $l$  is 2 cm.  $A$  is the cross section area ( $cm^2$ ).  $R$  is the resistance read from multimeter–voltage detector ( $\Omega$ )

Electrical conductivity is the inverse of electrical resistivity:

$$\sigma = \frac{1}{\rho} \quad (6.2)$$

## 6.2 Results and Discussion

Results were shown in the following tables. Practices proved that when graphene /PVDF weight ratio was higher than 0.2, membranes became crispy and could not be moved out of DI water. When the graphene/PVDF weight ratio was 0.05, the resistance was much higher than the other graphene/PVDF weight ratios. In 0.05 groups, membranes with plastic mash as backbone had the highest resistance than others, followed by PVDF-graphene membrane without backbone.

Table 6.2 Resistances with different graphene/PVDF weight ratio in different groups.

	<b>No backbone (KΩ)</b>	<b>Non-woven fabric (KΩ)</b>	<b>Plastic mash (MΩ)</b>
<b>Graphene/PVDF( weight ratio) 0.05</b>	46	17.5	530
<b>Graphene/PVDF ( weight ratio) 0.1</b>	24	12.2	5
<b>Graphene /PVDF ( weight ratio) 0.2</b>	20	8	1.25

Electrical conductivity can be calculated. In this research, distance between two electrodes was 2 cm, thickness of membrane was 300 μm (0.03cm), length of membrane was 7 cm. For example, when graphene/PVDF ratio was 0.05 and in pure PVDF-graphene membrane, resistance was 46000 Ω, according to equation 6.3 and 6.4, the electrical conductivity was  $2.07 \times 10^{-4}$  s/cm.

$$\rho = R \frac{A}{l} = 46000 \times \frac{7 \times 0.03}{2} = 4830 \Omega \cdot \text{cm} \quad (6.3)$$

$$\sigma = \frac{1}{\rho} = \frac{1}{4830} = 2.070 \times 10^{-4} \text{ s/cm} \quad (6.4)$$

Table 6.3 Electrical conductivity of membranes in different groups.

	<b>No backbone (s/cm)</b>	<b>Non-woven Fabric (s/cm)</b>	<b>Plastic mash (s/cm)</b>
<b>Graphene/PVDF 5%</b>	$2.070 \times 10^{-4}$	$5.44 \times 10^{-4}$	$1.800 \times 10^{-8}$
<b>Graphene/PVDF 10%</b>	$3.968 \times 10^{-4}$	$7.81 \times 10^{-4}$	$1.9 \times 10^{-6}$
<b>Graphene /PVDF 20%</b>	$4.761 \times 10^{-4}$	$1.19 \times 10^{-3}$	$7.62 \times 10^{-6}$

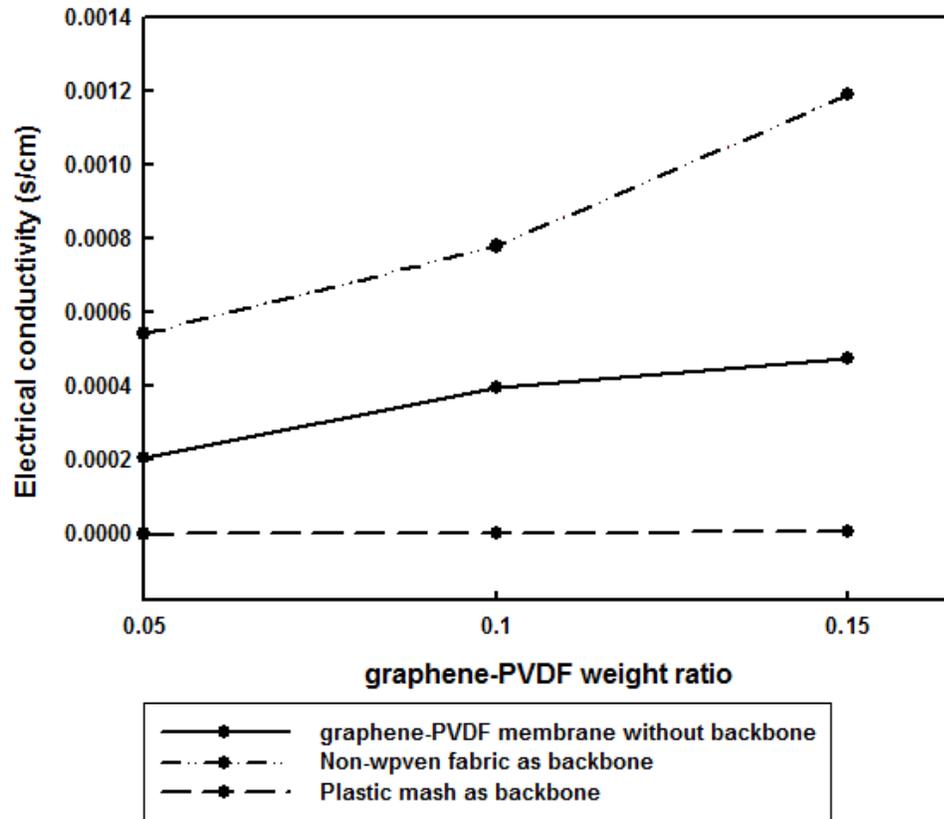


Figure 6.2 Electrical conductivity of membranes in different groups.

As table 6.2 showed, when graphene/PVDF weight ratio was increased from 0.05 to 0.1, electrical conductivity was increased obviously. But when the graphene/PVDF weight ratio was increased to 0.2, electrical conductivity did not change much. In fact, both PVDF particles and backbone materials were non-conductive. When preparing a homogeneous PVDF-graphene mixture, PVDF particles and graphene particles interspersed with each other. Graphene particles, which were considered as a major role to provide electric conductivity, were crowded with non-conductive materials. Since it was hard to form perfect current path, resistance was high.

Theoretically, growing graphene concentration can decrease resistance. In this research, electrical conductivity was increased with the growing graphene concentration. When graphene concentration was low, graphene particle was surrounded by PVDF particles and there was almost no current path. So no matter which backbone was used, the resistance was high. After graphene concentration was increased, membrane with non-woven fabric as backbone had a perfect PVDF-graphene coating on the top of the fabric, thus it could form better current path than that of membrane with plastic mesh as backbone. PVDF-graphene membrane without backbone had the similar situation. In contrast, PVDF-graphene membrane with plastic mesh as backbone did not have enough current paths, because huge plastic fiber stumble the current and break the completeness of the membrane.

Compare backboneed PVDF-graphene membrane with the one without backbone, they have similar resistance. The one that has backbone is more solid, but it has no malleability and looks like a piece of paper. But the one without backbone has lower strength and better malleability than backboneed membrane.

In summary, plastic mesh is not a good backbone material because plastic fiber will block current path. PVDF-graphene membrane without backbone and membrane with non-woven fiber have lower resistance. But doubtless, membrane with backbone has high strength. Therefore, if a thinner and stronger membrane is needed, non-woven fiber will be a good material as membrane backbone.

If graphene/PVDF increased to 0.25, PVDF membrane became crispy. Besides, that breaking structure was harm to resistance decreasing.

Those results are similar with Ansari's research<sup>26</sup>. The results were shown in figure 6.3. They used PVDF, exfoliated graphene (EG) and functionalized graphene

sheet (FGS) to prepare a composite membrane. Similar method was used to prepare PVDF-graphene membrane and measure electrical conductivity. Results showed that when graphene concentration was zero, electrical conductivity was really small. When graphene concentration was increased to 6%, electrical conductivity was  $1 \times 10^{-6}$  s/cm, and when graphene concentration was 14%, electrical conductivity was 0.01 s/cm. Those results showed a great growing of electrical conductivity with the increasing graphene weight percentage.

However, although the increasing amount of graphene could decrease resistance and increase electrical conductivity, researches have proved that the resistance of PVDF-graphene was not low enough to be a perfect conductive membrane. Thus, in order to get a low resistance composite membrane, other polymer materials must be developed.

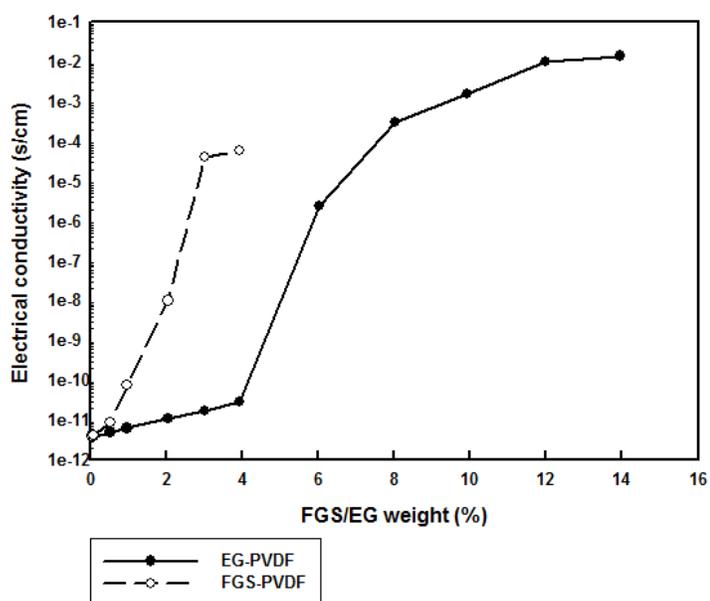


Figure 6.3 Electrical conductivity of FGS and EG/PVDF nanocomposites<sup>26</sup>.

## Chapter 7

### PVA-GRAPHENE MEMBRANE

Previous experience proves that although membranes can be made by simply mixing PVDF powder together with graphene, the resistance is really high. Thus, grafting is an effective method to modify non-conductive polymer materials. By grafting conductive functional groups on polymer chains, the whole electrical properties of membrane will be changed. However, PVDF is a long chain polymer which does not have any effective position that can be used for grafting. Therefore, polyvinyl alcohol (PVA) should be used as a backbone polymer to prepare a conductive membrane.

De Lannoy<sup>3</sup> prepared PVA-multiwalled carbon nanotube nanocomposite membrane. Multiwalled carbon can be functionalized by carboxyl groups. With the reaction between carboxyl and hydroxyl, PVA can be modified by carboxyl multiwalled carbon and becomes conductive.

Previous experiments proved that the graphene sample was not pure and large amount of carboxyl existed. Since carboxylic multiwalled carbon that De Lannoy et al used could be linked with PVA. It is believed that this carboxylic graphene can be used to prepare PVA based conductive membrane.

#### 7.1 PVA-graphene Membrane Preparation

Based on De Lannoy's research<sup>3</sup>, 0.05 g of graphene powder was dispersed in 5 ml of DI water for 1wt% and sonicated for 30 min under 140 w. 1 g of PVA was added in 100 ml DI water, heated and stirred for 6 hours under 90°C, and then cooled down to room temperature. 10 ml of PVA solution was mixed with desired amount of

graphene suspension. For example, if 10 ml 10wt% of PVA-graphene solution was needed, 1 ml 1% of graphene suspension could be added to 10ml 1% of PVA solution. Thus the ratio of graphene to PVA was 0.1. This PVA-graphene mixture was put in ice bath and then sonicated by a microtip sonicator under 70 w in intervals of 3 seconds on and 3 seconds off in order to prevent the mixture from foaming. 15 ml 0.1% of succinic acid was added to cross link with PVA chain. At the same time, enough HCl was added to the mixture, making sure the concentration was 2 mol. In this process, HCl was a catalyst to the cross link reaction. Stirred the whole mixture for 1 hour, then the mixture was added to the top of a cellulose nitrate support membrane which was in a vacuum filtration flask. Open the vacuum to force filtrate this mixture until excess liquid went through the membrane and the graphene remained on the top of cellulose membrane. The cellulose nitrate membrane was moved out of filtration flask, put on a glass plate and placed in a 100oC oven for 20 minutes. Then the membrane was moved out of the oven, cooled down to room temperature and soaked into DI water overnight for further use. The process was shown in figure 7.1.

Resistance was measured by multimeter–voltage detector. Multimeter-voltage detector was placed at three different places along the two long straight lines on the membrane, which were shown in figure 7.2. Each time the distance between anode and cathode was 2 cm. Electrical conductivity was calculated by equation 6.1 and 6.2. Since the PVA membrane was round, for an easier calculation, we approximated the area that current passed through was a square.

The thickness of membrane was estimated by optical microscope. Membrane was cut into 2 mm ×2 mm square, fixed under objective lens vertically. Then the thickness of PVA-graphene coating could be read from eyepiece.

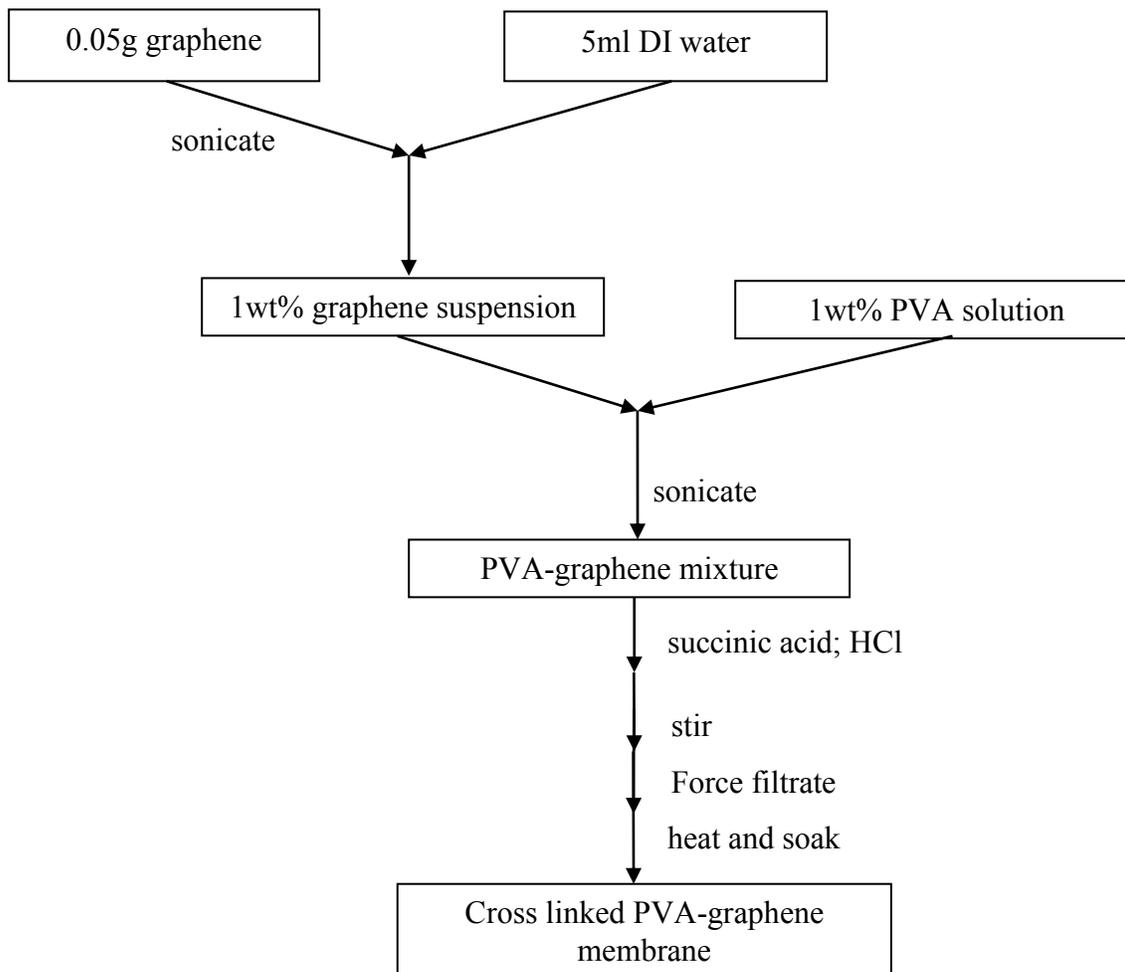


Figure 7.1 Process to prepare PVA-graphene membrane

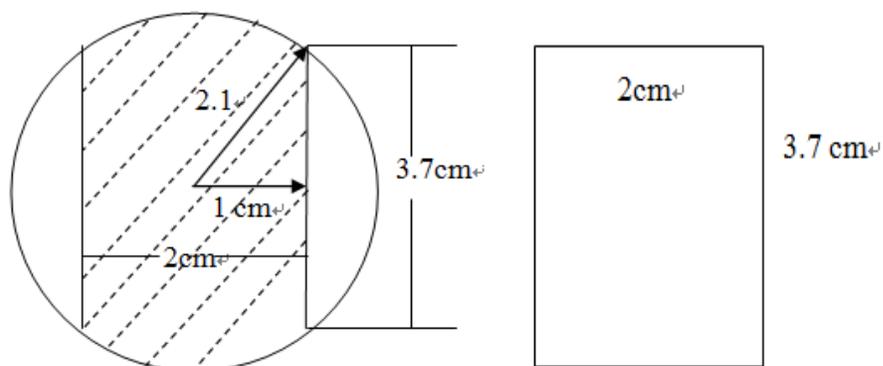


Figure 7.2 The left figure was the PVA-graphene membrane, the shaded area is the area that current passed through. This area was considered as a square, and the size the same with the right figure showed.

## 7.2 Perchlorate Adsorption in Three-electrode System

Three-electrode system was used to adsorb perchlorate. PVA-graphene membrane was used as anode and platinum wire was used as cathode. NaCl was used to maintain ionic strength.

0.029 g of NaCl and 0.02558 g of NaClO<sub>4</sub> was added into 1000 ml of DI water. Thus, the concentration of NaCl was 500 ppm and the concentration of NaClO<sub>4</sub> was 200 ppm. Membrane was fixed on a plastic mesh, dipped halfway into the solution and connected with anode input port with wire. Kept reference electrode attached to the membrane. Platinum cathode was soaked into solution at the side of membrane and the distance between cathode and membrane was 1 cm. Stirring was needed during the whole process. Voltage between cathode and reference electrode was 1 V. The system was shown in figure 7.3.

Took samples every 30 min, diluted 20 times and measured the concentration of ClO<sub>4</sub><sup>-</sup> by ion chromatography (IC). pH was measured by pH meter, simultaneously.

Standard line was needed before testing the perchlorate concentration. Known concentrations of  $\text{NaClO}_4$  were prepared from 0.5 ppm to 16 ppm in intervals of 2 ppm. Test each of them with IC and draw a standard line between peak area and concentration.

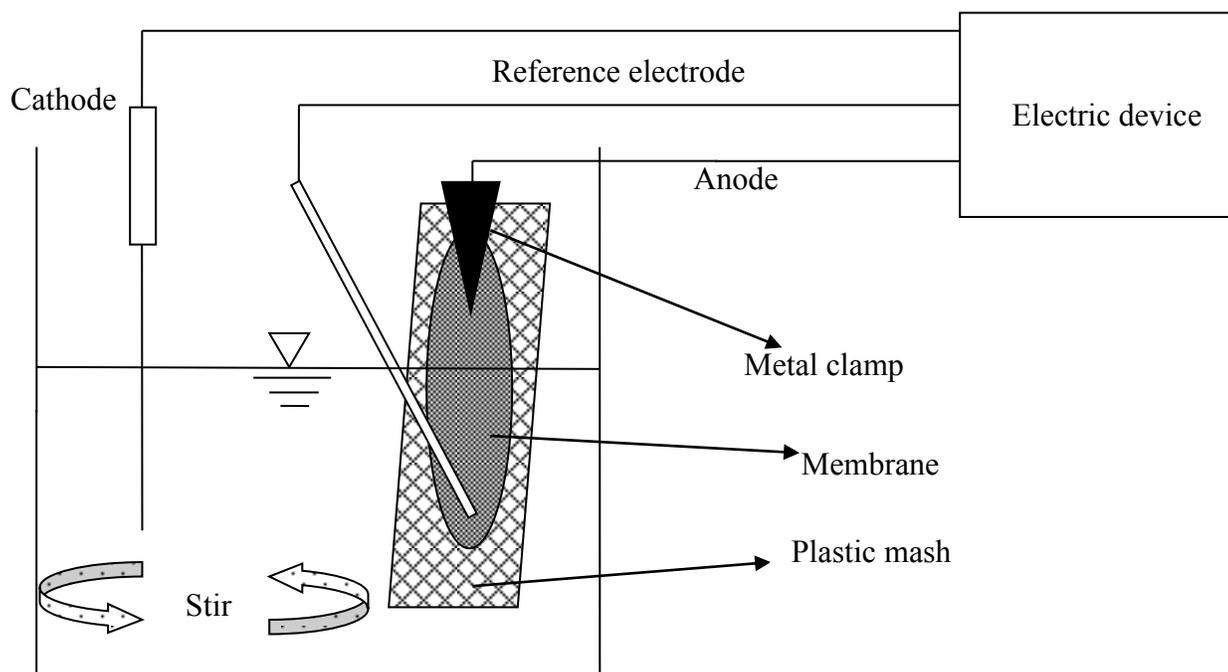


Figure 7.3 Instrument of perchlorate adsorption in three-electrode system

### 7.3 Charged Particle Adsorption in Dead-end Filtration

In dead-end filtration, all the solution passed through the membrane and the particles large than the pore size could be stopped on the top of its surface. However, as filtration was processed, more and more particles accumulated on the surface, some smaller particles even could block the pores. That means captured particles started to build up a “sedimentation cake” which could decrease filtration efficiency. Most of the time, this “sediment cake” was hard to be washed away, and membrane blocking was

irreversible. Thus, membrane pollution would be the first problem that needed to be solved in order to process an economical filtration.

Theoretically, if charged particles, such as  $\text{Al}_2\text{O}_3$ , can be held in electrical field during filtration process, it may alleviate membrane blocking. A straight way to hold  $\text{Al}_2\text{O}_3$  particles is adding an electric field in dead-end filtration process.

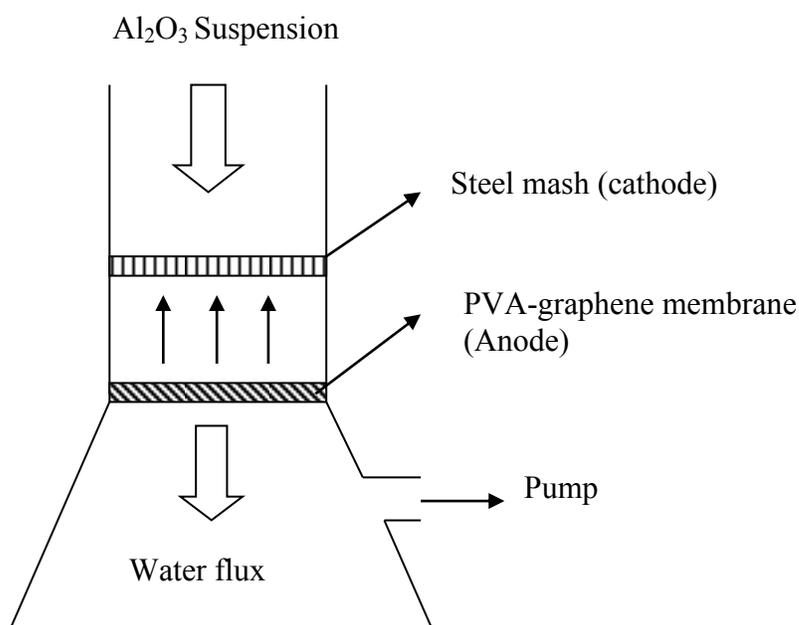


Figure 7.4 Add electric field in dead-end filtration

As figure 7.4 shows. Stick PVA-graphene membrane with wire by waterproof glue and held it in a glass vacuum filtration flask. This membrane would work as an anode. A steel mesh covered on the top of the membrane which was used as cathode, the distance between them was 5 mm. Turned on the power and an upward electrical field was formed.  $\text{Al}_2\text{O}_3$  solution was added from the top of flask. Water flux that went through the membrane was measured. As blank control, pure water fluxes passed

through cellulose nitrate membrane and PVA-graphene membrane were measured, respectively.

First pure cellulose nitrate was used to test water flux without voltage. The volume of water passed through the membrane in first, second and third 10 seconds were measured. Then changed to PVA-graphene membrane and did the same test. Finally added 3 V between cathode and anode, and test the volume of water passed through PVA-graphene membrane.

#### 7.4 Results and Discussion

Figure 7.5 is what PVA-graphene membrane looks like. The left shows the result that the graphene suspension was simply force filtrated. After dried in oven, graphene powder fell off from cellulose nitrate membrane easily. The right one is successful cross linked PVA-graphene membrane. The whole membrane was smooth and graphene was hard to be removed.



Figure 7.5 PVA-graphene membrane. The left one shows graphene suspension was simply force filtrated, the right one is successful linked PVA-graphene composite membrane.

#### 7.4.1 Thickness and Resistance

When the weight ratio of graphene to PVA was 0.01, the thickness of PVA-graphene coating was  $7 \times 10^{-5}$  m. When this ratio increased to 0.1, thickness was around  $7 \times 10^{-6}$  m. When the ratio was 0.8, thickness was  $1 \times 10^{-3}$  m. As figure 7.6 shows, the thin, gray and rough coating on the left side is PVA-graphene coating. The thick and black part on the right side is cellulose nitrate membrane support. The roughness of PVA-graphene coating may be because unreacted graphene accumulate on the surface of cellulose membrane. The roughness impedes reading exact membrane thickness through eyepieces. Thus, all of the above thickness value is just a rough number in order to estimate the electrical conductivity PVA-graphene of membrane.

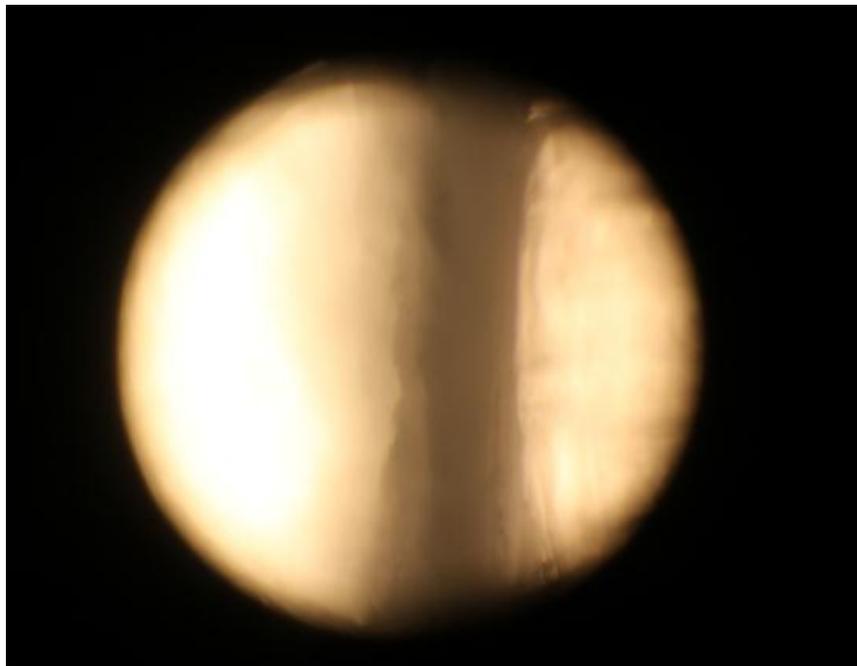


Figure 7.6 PVA-graphene membrane under electron microscope

The graphene/PVA weight ratio was from 0.1 to 0.8. Resistances were shown in table 7.1. Resistance was decreased from 772  $\Omega$  to 10  $\Omega$  with the increasing amount of graphene.

When the graphene-PVA ratio was 0.01, the average resistance was 772  $\Omega$ , but when this ratio was increased to 0.8, the average resistance was 10  $\Omega$ . Based on the relationship between resistance and electric conductivity, when the resistance was 772  $\Omega$ , electrical conductivity could be calculated by equation 7.1 and 7.2.

$$\rho = R \frac{A}{l} = 772 \times \frac{3.7 \times 0.00007}{2} = 0.1 \Omega \cdot \text{m} \quad (7.1)$$

$$\sigma = \frac{1}{\rho} = \frac{1}{0.1} = 10 \text{ s/m} \quad (7.2)$$

Table 7.1 Average resistance in different graphene PVA weight ratio

<b>Graphene concentration (graphene/PVA weight ratio)</b>	<b>Average resistance (<math>\Omega</math>)</b>
<b>0.01</b>	772
<b>0.1</b>	550
<b>0.2</b>	274
<b>0.3</b>	188
<b>0.4</b>	142
<b>0.5</b>	95
<b>0.6</b>	33
<b>0.7</b>	25
<b>0.8</b>	10
<b>Pure graphene</b>	2

The calculated electrical conductivity was shown in table 7.2. When graphene/PVA ratio was 0.01, the electrical conductivity was around 10 s/m, but when the ratio was increased to 0.8, the electrical conductivity was only i 54.05s/m. De Lannoy et al also measured electric conductivity. They found that when graphene/PVA weight ratio was 0.01, the electrical conductivity was around 150 s/m. But when the ratio was increased to 20, the electrical resistance was increased obviously to 3597 s/m. This value is much higher than the present result.

During the PVA-graphene membrane preparation process, graphene was hard to disperse in DI water. As a result, it was hard to react with succinic acid completely. In fact, after filtration, some unreacted graphene was still remained on the surface of membrane. They could contribute to electrical conductivity. However, this unreacted graphene would greatly increase the thickness of PVA-graphene and built many tiny cavities inside of the PVA-graphene coating. Those cavities could decrease electrical conductivity. Besides, based on equation 7.1 and 7.2, electrical conductivity was inversely proportional to cross section area, which means it was inversely proportional to thickness. Therefore, the thicker the membrane was, the lower electrical conductivity it had. In De Lannoy's research, the functionalized carbon nanotube that they used was easy to be dispersed in DI water. Thus succinic acid could react with the carbon nanotube completely, and the membrane they got was much thinner than those of the present research. Those thin membranes could have a better electrical property than the PVA-graphene membranes.

Table 7.2 Electrical conductivity in different graphene-PVA weight ratio

<b>Graphene/PVA</b>	<b>Thickness(m)</b>	<b>Electric conductivity(s/m)</b>
<b>0.01</b>	$7 \times 10^{-5}$	10.00
<b>0.1</b>	$8 \times 10^{-4}$	10.92
<b>0.8</b>	$7 \times 10^{-3}$	54.05

#### 7.4.2 Perchlorate Adsorption in Three-electrode System

Standard line was made and the results were shown in table7.3. Plotted  $\text{NaClO}_4$  concentration versus peak area and standard line could be calculated.

Based on figure 7.7, standard equation for  $\text{NaClO}_4$  is

$$y = 364458x \quad (7.3)$$

where y is peak area, x is  $\text{NaClO}_4$  concentration (ppm).

Table 7.3 Peak area tested by ion chromatography in different  $\text{NaClO}_4$  concentration

<b><math>\text{NaClO}_4</math> concentration(ppm)</b>	<b>Peak area</b>
<b>2</b>	621,519
<b>4</b>	1,330,797
<b>6</b>	2,064,616
<b>8</b>	2,835,184
<b>10</b>	3,562,090
<b>12</b>	4,366,755
<b>14</b>	5,181,595
<b>16</b>	5,949,856

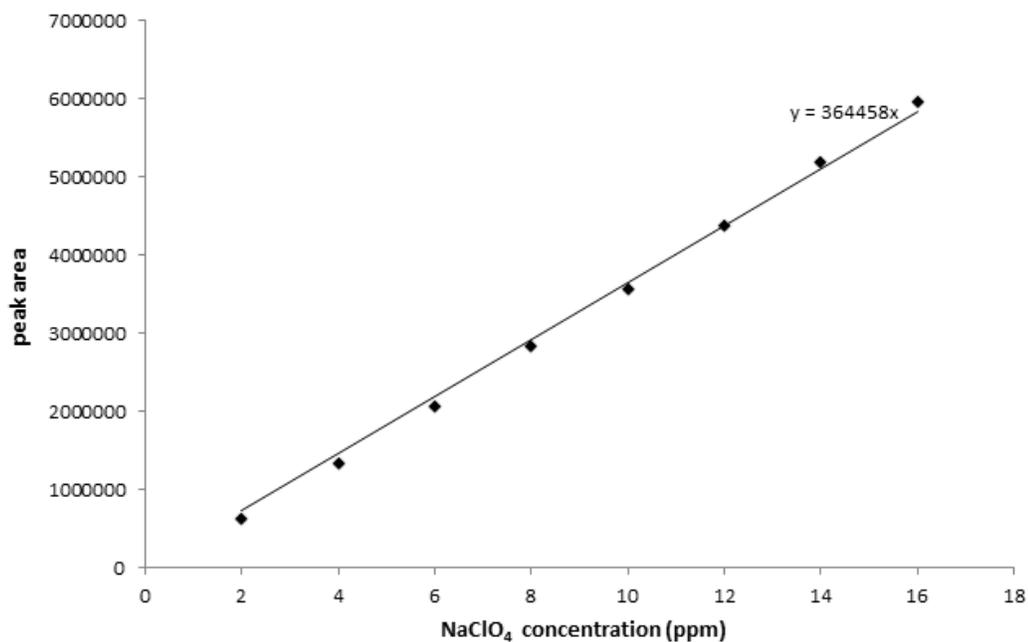


Figure 7.7 Standard line of NaClO<sub>4</sub> concentration

Based on the standard equation, NaClO<sub>4</sub> concentration of samples can be calculated, which are shown in table 7.4 and table 7.5.

Table 7.4 When graphene/PVA ratio is 0.2, NaClO<sub>4</sub> concentration in different time. Initial and final pH was included

Time	Concentration (ppm)	pH
0	512.40	7.81
30	509.82	-
60	500.37	-
90	498.13	-
120	513.97	7.42

Table 7.5 When graphene/PVA ratio is 0.8, NaClO<sub>4</sub> concentration in different time. Initial and final pH was included

<b>Time</b>	<b>Concentration(ppm)</b>	<b>pH</b>
<b>0</b>	500.82	7.54
<b>30</b>	495.00	-
<b>60</b>	491.41	-
<b>90</b>	501.55	-
<b>120</b>	514.8	7.71

Based on the above results, perchlorate did not decrease in first two hours. Simultaneously, pH did not change. During 30 to 60 minutes, perchlorate concentration was decreased slightly, but after 60 minutes, it was increased again. That may be because first perchlorate was adsorbed on the surface of membrane, but they were desorbed soon and back to the solution. Unreacted graphene have built many tiny cavities inside of this membrane, however, it was not enough to hold perchlorate and prevent them from desorption. Besides, although PVA-graphene membrane had much lower resistance than PVDF-graphene membrane, they were still not low enough to act as a good anode.

#### **7.4.3 Charged Particle Adsorption in Dead-end Electrical Filtration or Cross-flow Electrical filtration**

In the present research, PVA-graphene membrane had two different parts. Membrane structure was shown in figure 7.8. PVA-graphene coating, which had a loose spongy structure and huge pore size, was coated on the top. This coating only provided conductivity property, but its own pore size must be much bigger than cellulose nitrate membrane. On the bottom was cellulose nitrate support membrane. It was non-conductive and only provided known pore size. This support membrane

predominately resisted particles. Thus, the pore size of the whole membrane was almost the pore size of cellulose nitrate membrane.

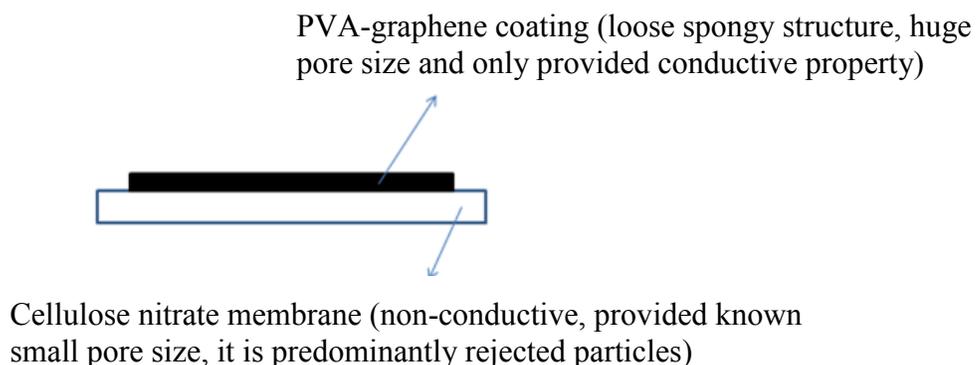


Figure 7.8 PVA-graphene membrane.

Results of water flux test were shown in figure 7.9-7.12. In the first 10 seconds, 14 ml of DI water passed through pure cellulose nitrate membrane, and in the second 10 seconds and third 10 seconds, water flux did not change much. After changing pure cellulose nitrate membrane to PVA-graphene membrane, 12 ml of DI water passed through during the first 10 seconds. During the second 10 seconds 13 ml of DI water passed through the membrane and during the third 10 seconds 11 ml of DI water passed through. Overall, there was no significant water flux change. In fact, if two membranes with similar pore size overlap each other, water flux passed through the two overlapped membranes will be much smaller than just passing through a single membrane. But if the pore size of one membrane is much larger than the other one, water flux will not change much. Thus, this experimental phenomenon proved that the pore size of PVA-graphene coating had a huge pore size and it will not affect water

flux much, the pore size of the whole membrane was similar with the cellulose nitrate membrane, which was  $0.2\ \mu\text{m}$  in the present research.

In figure 7.11 and 7.12, when there was no voltage, 8 ml of DI water passed through the membrane in the first 10 seconds and it was decreased quickly to 3 ml in the fifth 10 seconds. However, when 3 V was added, water flux was still decreased quickly. It seems that electrical field could not hold particles.

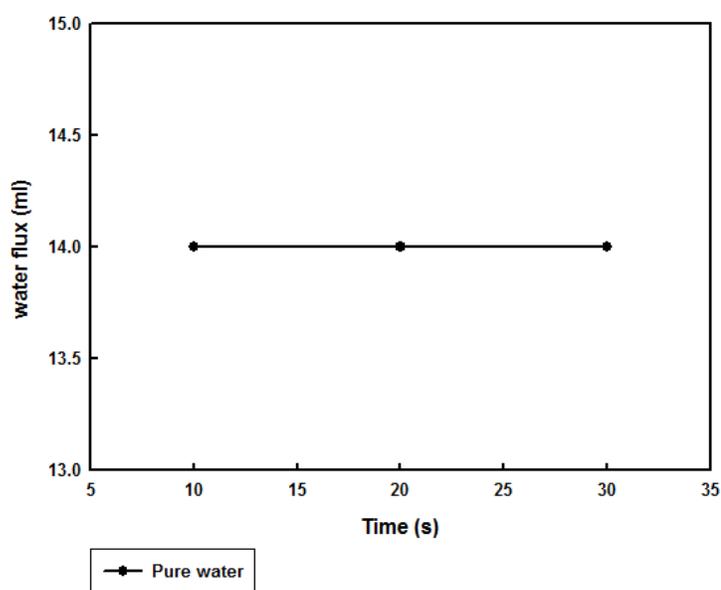


Figure 7.9 Water flux using pure cellulose nitrate membrane

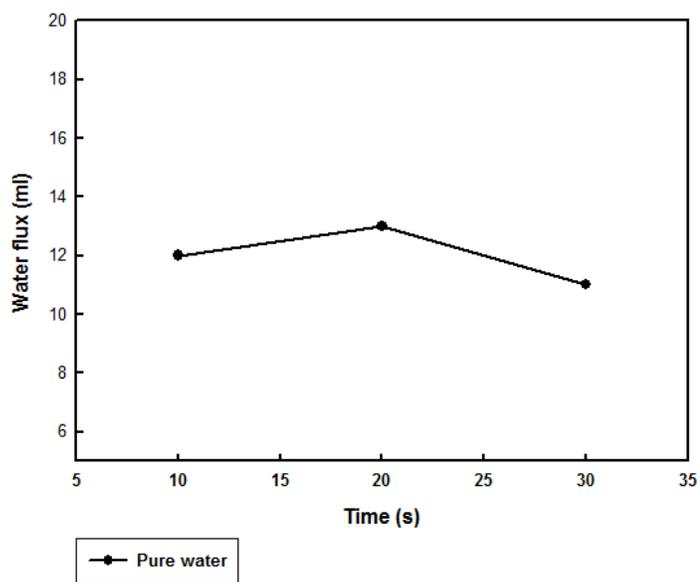


Figure 7.10 Water flux using PVA-graphene membrane

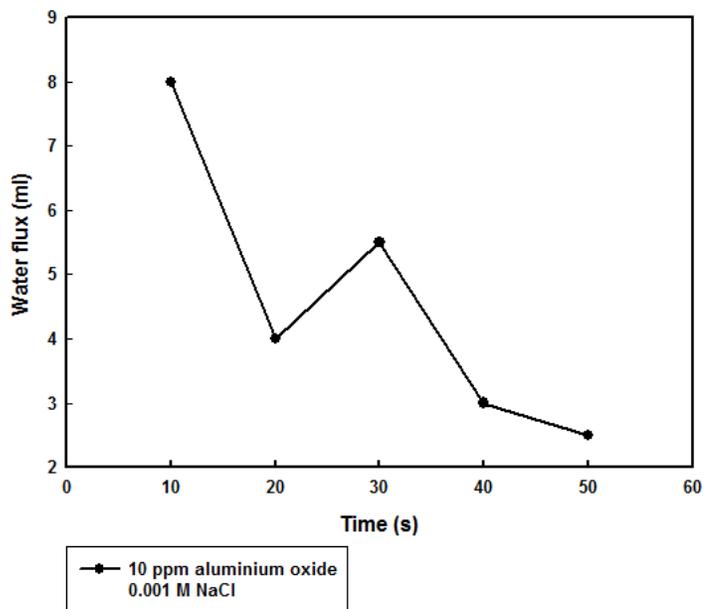


Figure 7.11 Water flux using 100 ppm of  $\text{Al}_2\text{O}_3$  suspension and no voltage

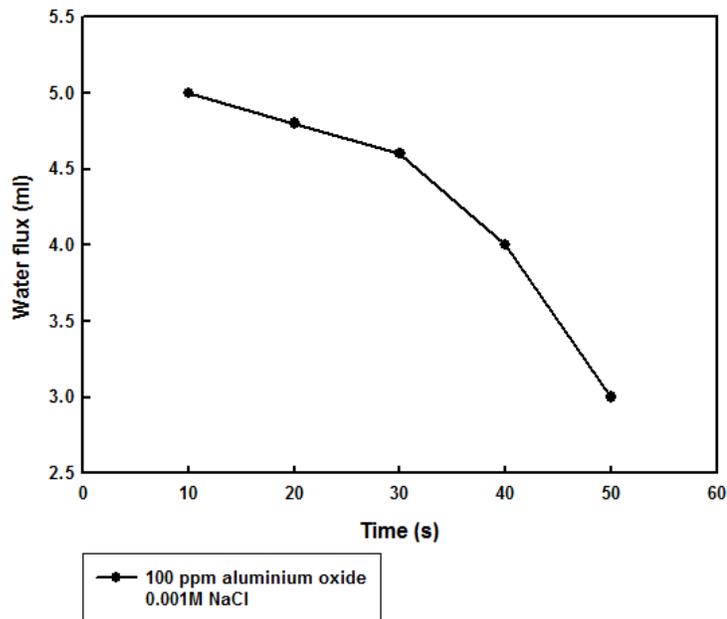


Figure 7.12 Water flux using 100 ppm of  $\text{Al}_2\text{O}_3$  suspension and 3 V

It was easy to imagine that the pump built a big pressure gradient between the two sides of the membrane. So the electrical force must be big enough to resist this pressure gradient. That means a big enough voltage must be added. Force balance of particles was shown in figure 7.13.  $F_e$  is the force comes from electric field.  $F_d$  is the drive force comes from water resistance. Since the particle is really small, the gravity can be ignored. Equation 7.4-7.8 can be used to calculate the needed voltage.

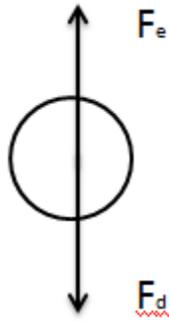


Figure 7.13 Force balance of particles in dead-end filtration

$$F_d = 3\pi\mu dv \quad \text{Stoke's law} \quad (7.4)$$

$$F_e = Eq \quad (7.5)$$

$$E = \frac{U}{D} \quad (7.6)$$

$$\zeta = \frac{q}{4\pi\epsilon r^2} \quad \text{Coulomb's law} \quad (7.7)$$

$$q = 4\pi r^2 \zeta \quad (7.8)$$

where  $\mu$  is the viscosity, in this research  $\mu$  is  $0.001 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ .  $d$  is the diameter of  $\text{Al}_2\text{O}_3$  particle. In this research  $d$  is  $200 \times 10^{-9} \text{ m}$ .  $E$  is the electric field.  $Q$  is the surface charge.  $v$  is the velocity.  $D$  is the distance between two electrodes. In this research  $D$  is  $0.005 \text{ m}$ .  $\epsilon$  is the permittivity of free space. It is  $6.95 \times 10^{-10} \text{ C/V}\cdot\text{m}$ .  $\zeta$  is the zeta potential, it is  $0.05 \text{ V}$ <sup>27</sup>

Since  $\text{Al}_2\text{O}_3$  was positive charged, if it could be hold by electrical held, the electrical field force must be equal to drive force. Suppose that the electrical field was homogeneous, electrophoresis was happened. Thus, stoke's law could be used. Based on equation 7.4 and 7.5, when  $F_e$  equal to  $F_d$ :

$$\frac{uq}{d} = 3\pi\mu dv \quad (7.9)$$

Then based on equation 7.6, 7.7, and 7.8

$$\begin{aligned} U &= \frac{3\pi\mu dvD}{q} = \frac{3\pi\mu dvD}{4\pi\epsilon r^2\zeta} \\ &= \frac{3 \times 3.14 \times 0.001 \text{kg} / \text{ms} \times 200 \times 10^{-9} \times 0.001 \text{m} / \text{s} \times 0.005 \text{m}}{4 \times 3.14 \times 6.95 \times 10^{-10} \text{C} / \text{Vm} \times (200 \times 10^{-9})^2 \times 0.05 \text{V}} \\ &= 118.7 \text{ V} \end{aligned} \quad (7.10)$$

Those calculations indicated that 118.7 V was needed in order to hold  $\text{Al}_2\text{O}_3$  particles. This value was much larger than 3V. Besides, for this instrument, 118.7 V is too high. This high voltage required high powerful generator and could cause short circuit, which was very dangers. In this case, this high voltage was not practical.

Another possible electrical filtration method is cross-flow filtration which was used by De Lannoy et al<sup>28</sup>. This cell had a platinum mesh electrode located on the top as cathode. Membrane was located on the bottom, 5mm below the platinum electrode. Pressured solution was feed horizontally between the anode and cathode. Then the feed solution was separated by membrane. Permeated steam went through the membrane and was collected. Retentate steam was passed through the reaction zone and was recycled to the feed steam. The cross-flow section worked as figure 7.14 showed.

Thus, according to figure 7.14, pressured  $\text{Al}_2\text{O}_3$  suspension was feed from left side and particles tend to be held by steel mash. Motion trail was shown on the lower picture in figure 7.14. The velocity of particles could be separated into three different parts, upward velocity ( $V_e$ ) which was afforded by electric field, downward velocity ( $V_d$ ) which was afforded by pressure, and horizontal velocity ( $V_h$ ). The critical

condition was when a particle came from left lower edge, and  $V_d$  was equal to  $V_e$ , particles would pass through the reaction zone directly, and membrane block could be prevented.

According to electrophoresis equation  $V_e$  can be calculated.

$$\frac{V_e}{E} = \frac{\varepsilon\zeta}{\mu} \quad \text{Electrophoresis} \quad (7.11)$$

$$V_e = \frac{\varepsilon\zeta E}{\mu} = \frac{\varepsilon\zeta U}{\mu D} \quad (7.12)$$

When particle tend to pass through the membrane pore, it could be considered that particle moved in a tube, as lower figure showed in figure 7.4. Thus Poiseuille's equation could be used. According to Poiseuille's equation,

$$V_d = \frac{\Delta P r^2}{8\mu L} \quad \text{Poiseuille's equation} \quad (7.13)$$

where  $L$  is the thickness,  $\Delta P$  is the transmembrane pressure,  $\varepsilon$  is the permittivity of free space, which is  $6.95 \times 10^{-10} \text{ C/V}\cdot\text{m}$ .,  $r$  is the radius of pore ( $100 \times 10^{-9} \text{ m}$ ).

As figure 7.14 shows, when  $V_d$  is equal to  $V_e$ , particles could pass through reaction zone directly, that was critical condition.

$$V_e = V_d \quad (7.14)$$

$$\frac{\varepsilon\zeta U}{\mu D} = \frac{\Delta P r^2}{8\mu L} \quad (7.15)$$

$$U = \frac{\Delta P r^2 D}{8L\varepsilon\zeta} \quad (7.16)$$

From the equation 7.14-7.16, the voltage that we needed can be calculated.

The only unknown parameter is pressure drop between the two sides of the membrane.

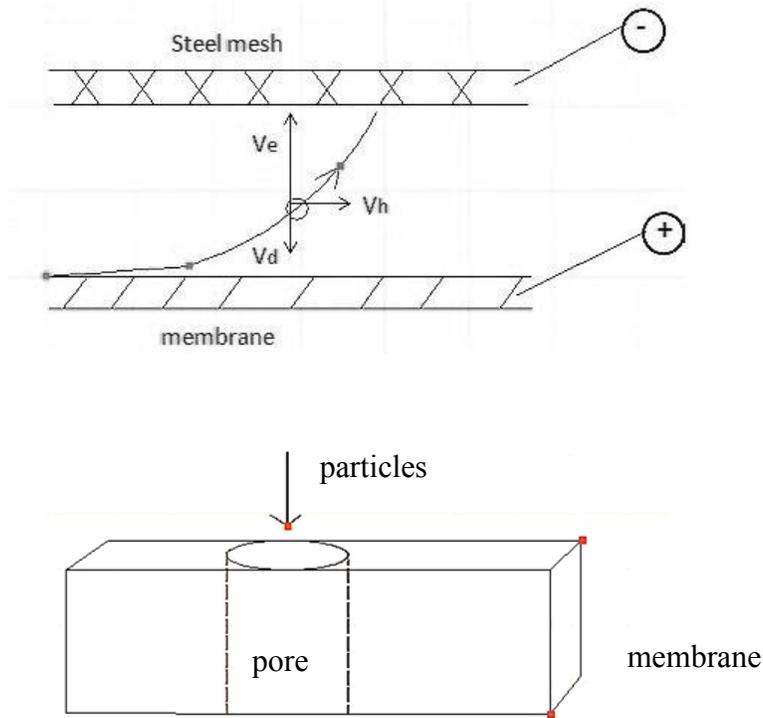


Figure 7.14 Cross flow filtration. The lower picture is how particles pass through membrane pore.

Suppose this pressure is 1000 kpa, which is a possible condition in cross-flow filtration, according to equation 7.16.

$$\begin{aligned}
 U &= \frac{\Delta P r^2 D}{8 L \varepsilon \zeta} \\
 &= \frac{1000 \text{pa} \times (100 \times 10^{-9})^2 \times 0.005}{8 \times 140 \times 10^{-6} \text{m} \times 6.95 \times 10^{-10} \text{C} / \text{V} \cdot \text{m} \times 0.05 \text{V}} \\
 &= 1.28 \text{V}
 \end{aligned} \tag{7.17}$$

This value is small and practicable. The only pressure that prompt membrane block was transmembrane pressure generated by pressure flow and that was much smaller than the pressure generated by pump. Thus, the needed voltage was decreased a lot.

## **Chapter 8**

### **CONCLUSION**

Graphene is a new material which has many unique properties, but it is hard to disperse in most of aqueous solutions. This makes graphene can hardly be used in any large scale industrial production. Therefore, it is important to produce a stable graphene suspension in water or organic solvents. The first issue to solve this problem is to prevent graphene sheets from aggregation. Thus, adding surfactant must be a simple method. In this research nine different surfactants were used and found that PEG 400 was the best one among them. The whole mixture could be stable for over 72 hours. Besides, SDS could keep graphene suspension stable for 24 hours. Other surfactants did not work well in keeping graphene suspension stable.

Boehm titration was used and found that most of the functional groups in graphene samples were carboxylic acid functional groups, followed by lactonic groups. There was almost no hydroxyl group. In fact, in industrial production, a common way to produce graphene is chemical reduction. Graphene oxide can be dispersed in aqueous easily and converted to graphene. However, this method will not generate pure graphene since some functional groups such as carboxyl acid group is hard to be reduced because of its double bond. That is why after this Boehm titration, large amount of carboxyl acid groups were found.

The weight ratio of PVDF/DMF could affect the thickness and mechanical strength of the membrane. When the ratio was lower than 0.1, it was hard to form a

whole membrane. But if this ratio was higher than 0.15, the mixture was too thick to be stirred. Thus, 0.15 should be a better weight ratio to prepare PVDF membrane.

TBAC was used as a plasticizer, when the weight ratio of TBAC/PVDF was lower than 0.6, a smooth and strong membrane was formed. But when this ratio was increased to 0.7, membrane became transparent and mechanical strength decreased a lot. Results of tensile testing showed that when the amount of TBAC was increased, the tensile strength was decreased. Simultaneously, the break strain was increased.

Contact angle was increased with the increasing TBAC percentage. According to previous researches, as a hydrophilic membrane, if water drop contacts directly with a rough surface, the contact angle will be smaller than a smooth surface. That means slightly increase plasticizer concentration will roughen the membrane surface and decrease contact angle. However, too much plasticizer may smooth the membrane, then increase contact angle. In this research, the contact angle increasing may because of the large amount of plasticizer and its hydrophilia. Further researches are needed to investigate the changing rule of contact angle.

PVDF-graphene resistance can be affected by backbone materials, but overall, it does not have a good electrical property. The weight ratio of graphene/PVDF cannot be higher than 0.2, because too much graphene particles will break membrane structure and the whole membrane will become crispy. Plastic mesh is not a good backbone material, because plastic fiber will block current path. PVDF-graphene membrane without backbone and membrane with non-woven fiber backbone has similar resistance. But doubtless, membrane with backbone is thin and has high mechanical strength. Therefore, if a thinner and stronger membrane is needed, non-woven fiber will be a good material as membrane backbone.

PVA-graphene composite membrane has much lower resistance and higher electrical conductivity than PVDF-graphene membrane. Its resistance can be as low as 10 ohm. However, it is supposed to be lower, but unreacted graphene accumulated on the surface of membrane and decreased membrane electrical property by built tiny cavity.

PVA-graphene composite membrane is not good as an electrode in perchlorate adsorption. Because it does not have enough inner space to adsorb perchlorate and prevent it from desorption. Besides, the resistance is still not low enough.

In dead-end filtration, a high voltage must be needed to stop membrane pollutant. In order to hold  $\text{Al}_2\text{O}_3$  particles in electric field, at least 118.7 V is needed, but this may cause short circuit, which is very dangers. Moreover, this high voltage is not practical.

If cross flow section is used, only 1.28 V is needed, which becomes more safe and economic.

In summary, as two different electrical conductive membranes, PVDF-graphene membrane and PVA-graphene membrane have a huge great application potential in particle separation. As a common used filtration method, cross flow filtration by PVA-graphene membrane should be a further research content. Therefore, more experiences should be taken to study their physical and electrical properties.

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