

Research Paper

## Effect of Graphene Oxide on the Characteristics of sPEEK-Chitosan Membranes for Direct Methanol Fuel Cells

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### Abstract

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Direct Methanol Fuel Cell (DMFC) can operate at low temperatures, but efficiency and performance are greatly influenced by the material. On the other hand, Sulfonated ketone polyether ethers (sPEEK) which have high thermal resistance, ductile, chemical resistance and high mechanical properties, can be combined with chitosan which has good proton conductivity properties. The sPEEK-Chitosan membrane is known to have good mechanical and thermal resistance, but its conductivity is low. The addition of graphene oxide as a filler material can increase the proton conductivity due to its properties. This research was conducted with a completely randomized design of 1 factor to investigate the characteristics of the sPEEK-Chitosan composite membrane as the dependent variable and the addition of graphene oxide solution to the variables 0, 1, 3, 6, and 9% w/w as independent variables. The test results show that the water uptake is in the range of 8.82-33.34%, the swelling degree is in the range of 5.55-20.75%, and the ion exchange capacity is 0.1875-0.2714 meq/g. With this good character, the sPEEK-chitosan membrane with the addition of graphene oxide is a promising candidate for DMFC applications.

**Keywords:** DMFC, Chitosan, sPEEK, Graphene Oxide

### Abstrak

Direct Methanol Fuel Cell (DMFC) dapat beroperasi pada suhu rendah, tetapi efisiensi dan kinerjanya sangat dipengaruhi oleh bahan. Di sisi lain, Sulfonated ketone polyether ethers (sPEEK) yang memiliki ketahanan termal tinggi, ulet, ketahanan kimia dan sifat mekanik yang tinggi, dapat dikombinasikan dengan chitosan yang memiliki sifat konduktivitas proton yang baik. Membran sPEEK-Chitosan diketahui memiliki ketahanan mekanik dan termal yang baik, tetapi konduktivitasnya rendah. Penambahan grafena oksida ini dilakukan dengan desain acak lengkap dari 1 faktor untuk menyelidiki karakteristik membran komposit sPEEK-Chitosan sebagai variabel dependen dan penambahan larutan graphene oxide ke variabel 0, 1, 3, 6, dan 9% w/w sebagai variabel independen. Hasil pengujian menunjukkan penyerapan air berada di kisaran 8,82-33,34%, swelling degree berada di kisaran 5,55-20,75%, dan kapasitas pertukaran ion 0,1875-0,2714 meq/g. Dengan karakter yang baik ini, membran sPEEK-Chitosan dengan penambahan grafena oksida adalah kandidat yang menjanjikan untuk aplikasi DMFC.

**Kata-kata kunci:** DMFC, Chitosan, sPEEK, Grafena oksida

## 1. Introduction

Methanol fuel cell or known as Direct Methanol Fuel Cell (DMFC) is a fuel cell with a polymer membrane and methanol that can

operate at low temperatures [1]. The main component of a fuel cell is the membrane. The most commonly used membrane is Nafion® because it has high proton conductivity, as well as



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good chemical and thermal stability. However, it has its disadvantages being high cost and methanol crossover resulting in decreased cell efficiency and performance [2].

Several membranes of hydrocarbons have been developed, including polyether sulfone, polyether ketone, and acrylonitrile butadiene styrene (ABS) [3]. Ketone polyether ethers have relatively high proton conductivity, good thermochemical properties and low cost [4]. sPEEK can be applied to fuel cells but must be modified with sulfonation to be hydrophilic. Some other efforts were made by modifying polymer membranes with natural polymers such as chitosan. The source of chitosan is chitin derived from crabs and shrimp [5]. Chitosan can be transformed as a membrane by dissolving it in organic acids, one of which is acetic acid [6].

Improving the chemical and mechanical properties can be done by adding filling materials such as carbon, silica, and graphene. One candidate stuffing material is graphene oxide [8]. Graphene oxide (GO) is a nanomaterial for nanocomposite and electronic applications because of its high conductivity and has unique mechanical strength and graphite structure [7]. Therefore, this study aims to determine the effect of adding graphene oxide on the sPEEK-chitosan membrane which includes water uptake, swelling degree, and ion exchange capacity.

## 2. Materials and Method

The materials used were polyether ether ketone imported from China, chitosan shrimp and graphite from local stores, sulfuric acid, acetic acid and dimethyl formamide from Merck. The study was conducted at the Laboratory of Chemical Engineering, Universitas Muhammadiyah Surakarta, Indonesia. The study used a completely randomized design of 1 factor with graphene oxide content as an independent variable.

### 2.1. Polyether ether ketone sulfonation

Polyether ether ketone was sulfonated with sulfuric acid at 60°C for 4 hours. The solution was terminated by pouring the solution into ice water. The white deposit was then washed with distilled water until the water pH reached 7. The sPEEK was then dried to remove water.

### 2.2. Synthesis of graphene oxide

A total of 3 grams of  $\text{NaNO}_3$  and 140 mL of sulfuric acid were given an ice bath in a glass beaker. The solution was stirred to a temperature below 20°C to avoid spontaneous reactions. Then, 3 grams of graphite and 15 grams of  $\text{KMnO}_4$  were added slowly and stirred for 2 hours. The beaker was kept at room temperature for 24 hours so that oxidation occurred. Next, the solution was added with 100 mL of distilled water and stirred for 1 hour and added 10 mL  $\text{H}_2\text{O}_2$ . The solution was then washed with 1 M HCl and distilled water until it reached a neutral pH. Finally, graphene oxide was heated at 80°C for 6 hours.

### 2.3. Preparation of sPEEK-chitosan membranes

The membrane was prepared by making sPEEK solution and chitosan solution. As much as 2 grams of sPEEK was dissolved in 100 mL dimethyl formamide and 1 gram of chitosan in 100 mL of 2% acetic acid. The sPEEK solution and the chitosan solution to make the membrane used a ratio (20:80) % wt. The ratio of graphene oxide was added to the solution with variations (0, 1, 3, 6 and 9) % wt and stirred with ultrasonic for 30 minutes at 50°C. Then, the solution was poured into a glass plate mold. The solution was heated at 60°C for 24 hours. Finally, the membrane was irradiated with ultraviolet light for 24 hours.

### 2.4. TGA analysis

Thermogravimetric analysis was applied to test the thermal properties and thermal degradation processes. TGA tests were carried out using Setaram LabSys Evo Model S60/58998 instrument by heating the membrane sample up to a temperature of 800°C with a heating rate of 10°C/min under the nitrogen atmosphere.

### 2.5. Water uptake analysis

Water uptake was measured based on the difference in wet and dry weight. The membrane was dried and then weighed to obtain a dry weight ( $w_{dry}$ ). The wet weight ( $w_{wet}$ ) was acquired by soaking the membrane in distilled water for 48 hours.

### 2.6. Swelling degree analysis

The swelling degree was calculated by measuring the length of the membrane before soaking ( $L_{dry}$ ) and after soaking ( $L_{wet}$ ). Then, the

membrane was immersed in distilled water for 48 hours.

### 2.7. Ion exchange capacity analysis

Ion Exchange Capacity (IEC) was measured using the titration method. The dry membrane was immersed in NaCl solution at room temperature for 48 hours. The solution was then titrated with 0.01 N NaOH solution using the phenolphthalein indicator.

## 3. Results and Discussion

In the present article, the effect of adding graphene oxide to the sPEEK-chitosan membrane is as reported. The resulting membrane has a thickness of around 60-65  $\mu\text{m}$ .

### 3.1. TGA

Thermal properties are one of the important parameters for proton exchange membranes. Composite sPEEK-chitosan membranes were investigated by thermogravimetric analysis (TGA). The resulting data from TGA can be used for determining the appropriate temperatures for MEA preparation without thermal degradation. In such cases, the membranes were estimated to be stable enough at different temperatures in the polarization test. Figure 1 shows the TGA results representing the pattern of thermal degradation rate, onset temperatures and maximum weight loss rate. The membranes' weight losses had occurred in three main steps.

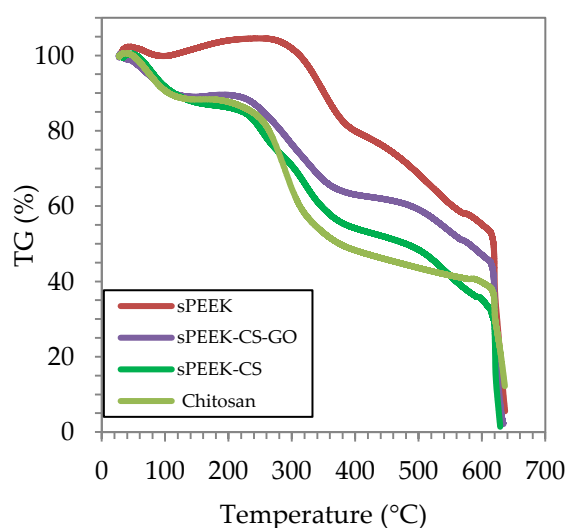


Figure 1. TGA curves of pure sPEEK, chitosan, and composite sPEEK-Chitosan membranes.

The first step was attributed to the vaporization of absorbed water and residual casting solvent at a temperature around 100°C. The second one was at a temperature 250-400°C which corresponded to the decomposition of the sulfonic acid group in the membrane structures. The third step, showed by the sharp curve decline, was at a temperature of around 600°C which might correspond to the decomposition of the polymeric backbone of membranes. From the results, it is observed that composite membranes of sPEEK-CS and sPEEK-CS-GO have higher weight loss than sPEEK membrane, but they have more thermal stability than pure chitosan membrane.

### 3.2. Water uptake

Water uptake is an important parameter in the membrane. Water uptake shows the ability of the membrane to absorb water. Water uptake has a relationship with ion conductivity and membrane stability. Figure 2 shows the relationship between graphene oxide content and water uptake.

sPEEK-chitosan membranes with prepared graphene oxide material decrease the membrane's ability to store water. The tendency for a decrease is from 33.34% to 22.22% in the membrane. Previous research showed the ability of the sPEEK-GO membrane to store water from 29% to 39% [7]. Other studies show that the water uptake of graphene oxide PVA-chitosan membranes is 26.275% [9].

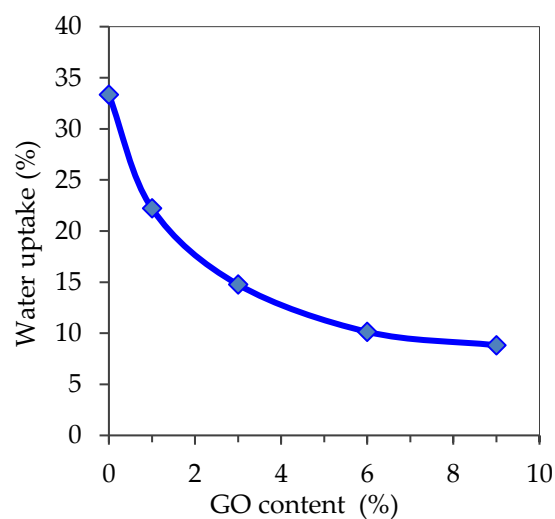


Figure 2. Relationship of water uptake with graphene oxide content

### 3.3. Swelling degree

Swelling Degree is a parameter of size change in polymers that can affect membrane performance [8]. The mechanical properties of membranes affect membranes in membrane elasticity and stability. Figure 3 shows the relationship between swelling degree and graphene oxide content.

sPEEK-chitosan membrane with stuffed graphene oxide produced a decrease in swelling degree from 20.75% to 12.75%. This indicates an increase in the mechanical ability of the membrane due to an increase in the amount of graphene oxide in the membrane. Previous studies have shown swelling ranges of sPEEK membranes between 7.9% -17.7% [10]. Swelling values indicate the membrane's ability to adsorb solvents which can change the pore structure of the membrane. In addition, the swelling degree can represent the flexibility and strength of the membrane [7].

### 3.4. Ion exchange capacity

Ion exchange capacity is the consideration of the number of moles of  $\text{SO}_3^-$  per gram of polymer. The ion exchange capacity of the membrane is important for the conductivity of protons in methanol fuel cells. Figure 4 shows the relationship between graphene oxide content and sPEEK-chitosan membrane ion exchange capacity and graphene oxide stuffing.

The ion exchange capacity indicates the number of ionic groups in the polymer matrix. This test shows proton transfer so that it can be connected with proton conductivity. Graphene oxide has acidic properties which result in an increased ability to transfer ions in the membrane. In Figure 3, it can be observed that the ion exchange capacity increases with the addition of graphene oxide from 0.5625 meq/g to 0.8142 meq/g. Prior research showed the greatest ion exchange capacity in 5% graphene oxide was 1.11 meq/g [7]. The results show that the ion exchange capacity increases with the addition of graphene oxide. The change being the physical properties of graphene oxide which easily conducts ions (conductors).

## 4. Conclusion

From the research results obtained the value of water uptake, swelling degree and ion exchange capacity on the sPEEK-chitosan membrane is influenced by the content of graphene oxide. Increasing graphene oxide decreases the value of water uptake and swelling degree but increases the value of the ion exchange capacity of the membrane. From the research results, sPEEK-chitosan membrane with the addition of graphene oxide is a good potential for methanol fuel cell applications.

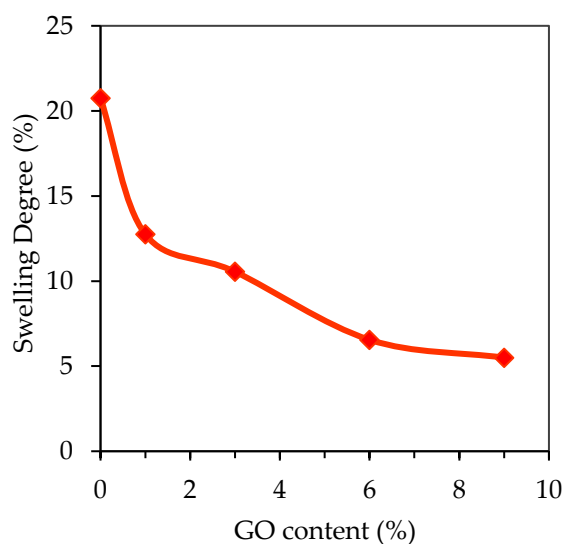


Figure 3. Relationship between swelling degree and graphene oxide content

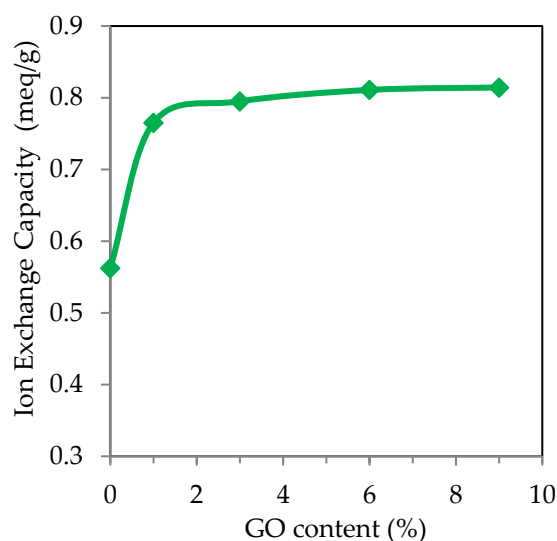


Figure 4. Relationship of ion exchange capacity with graphene oxide

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#### Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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#### Availability of data and materials

All data are available from the authors.

#### Competing interests

The authors declare no competing interest.

#### Additional information

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