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Synthesis of Acrylonitrile Butadiene Styrene Membrane with Sulfonated Reduced Graphene Oxide and Cerium Filler

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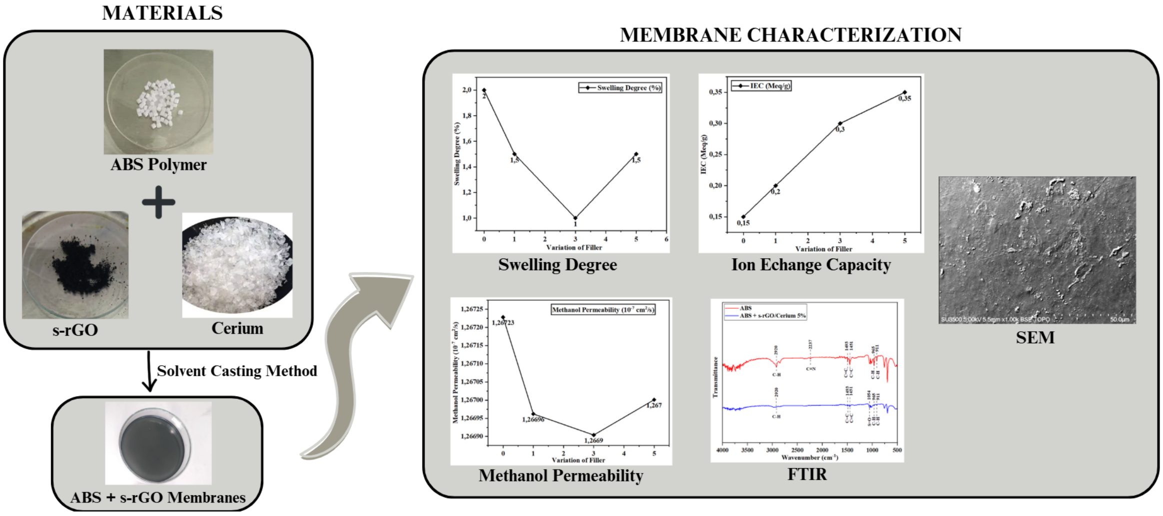
GRAPHICAL ABSTRACT



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ABSTRACT

The study investigates the use of acrylonitrile butadiene styrene (ABS) polymer modified by sulfonated reduced graphene oxide (s-rGO) and cerium (Ce) as an alternative membrane to Nafion for Direct Methanol Fuel Cell (DMFC) applications. Pure ABS membranes and ABS membranes with s-rGO/Ce fillers were synthesized and characterized, with sulfonation at 60 °C using filler concentrations of 1%, 3%, and 5% v/v. The addition of fillers aimed to enhance ion exchange capacity (IEC), water absorption, and reduce methanol permeability. The membrane with 5% filler content showed optimal performance, with an IEC of 0.35 meq/g, a swelling degree of 1.5%, and controlled methanol permeability of 1.2670×10^{-7} cm²/s. FTIR analysis confirmed the presence of sulfonate groups (S=O) at 1054 cm⁻¹, indicating successful sulfonation. SEM analysis revealed that the filler was well-dispersed and formed more defined pores without compromising the structural integrity of the ABS matrix. This study demonstrates the potential of s-rGO/Ce-modified ABS membranes as a viable alternative to Nafion membranes in DMFC applications.

1. INTRODUCTION

Fuel cell technology is currently being explored as one of the high-efficiency energy conversion systems. A fuel cell is an electrochemical reaction that converts chemical energy into electrical energy [1]. The main advantages of fuel cells are their ability to operate at high efficiency levels (around 50–70%) and to produce no greenhouse gas emissions [2]. Fuel cells can be classified based on the characteristics of their electrolytes and operating temperatures, including Solid Oxide Fuel Cells (SOFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Proton Exchange Membrane Fuel Cells (PEMFC) [3]. Among these, PEMFC is considered the most effective type due to its ease of operation using a polymer electrolyte membrane, corrosion resistance, high energy conversion efficiency (above 50%), environmental friendliness with zero emissions, relatively fast start-up, and ability to operate at low temperatures [4].

Direct Methanol Fuel Cell (DMFC) is a type of Proton Exchange Membrane Fuel Cell (PEMFC) that uses liquid methanol as a fuel and operates at room temperature with relatively high power output, making it suitable for use in vehicles, power plants, medical devices, and portable electronic equipment. In a DMFC, methanol is oxidized at the anode to produce protons, electrons, and carbon dioxide. The protons migrate through the proton-conducting membrane to the cathode, which reacts with oxygen and electrons to complete the electrochemical reaction. A commonly used membrane in this process is Nafion, due to its high proton conductivity [5]. However, this membrane has disadvantages, such as high methanol leakage, the price is still relatively expensive, and it is easy to degrade at temperatures above 100°C, which makes its performance decrease [6]. Further research is needed to find alternative membranes that have good mechanical capabilities, can prevent methanol transfer, and have the ability to exchange ions and protons.

Several hydrocarbon-based membranes have been developed as alternatives to Nafion, including Acrylonitrile Butadiene Styrene (ABS). ABS is a strong and durable polymer with good thermal and mechanical stability. In addition to being more cost-effective than Nafion, ABS also possesses chemical stability, making it a promising candidate for Direct Methanol Fuel Cells (DMFC) application. However, to be effectively used in DMFC, ABS requires further modification to enhance its proton conductivity, reduce methanol permeability, and improve water uptake capacity [7].

The performance of ABS based membranes can be enhanced through modification with sulfonated reduced graphene oxide (s-rGO) and cerium (Ce). S-rGO contributes to increasing ion exchange capacity (IEC) and enhancing chemical stability [8], while cerium improves the membrane's mechanical properties and oxidation resistance [9]. This combination of fillers is expected to improve the ion exchange capacity, reduce methanol permeability, and stabilize water uptake, thereby optimizing membrane performance for application in DMFC [5].

This article discusses the synthesis and characterization of pure ABS membranes and ABS membranes modified with s-rGO/Ce fillers, emphasizing their swelling degree, ion exchange capacity, and methanol permeability. Furthermore, the membranes' functional groups, surface morphology, and elemental composition will be analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

2. EXPERIMENTAL METHODS

2.1. Material

Reduced graphene oxide (rGO), acrylonitrile butadiene styrene (ABS, Polylac®), cerium(III) nitrate [$Ce(NO_3)_3$, pro analysis grade], dimethylformamide (DMF, ACS grade), sulfuric acid (98%), isopropyl alcohol, methanol, sodium hydroxide (NaOH), sodium chloride (NaCl), and distilled water were used. All chemicals were obtained from Merck unless otherwise specified.

2.2. Preparation of ABS Solution

The ABS polymer was dried in an oven at 50 °C for 30 minutes to remove contaminants and reduce moisture content. After that, 1.5 grams of ABS polymer was dissolved in 50 mL of dimethylformamide (DMF) and stirred using a magnetic stirrer for 2 hours at room temperature.

2.3. SrGO and Cerium Filler Manufacturing

Sulfonation was carried out with a reflux device, where 0.1 gram of rGO was reacted in 50 mL of concentrated sulfuric acid (98%) at 60 °C for 2 hours while stirring with a magnetic stirrer. After the reaction, the mixture was poured into ice water to stop the process. The precipitate formed was filtered with filter paper and neutralized using distilled water to reach a neutral pH, then dried in an oven at 60 °C for 12 hours. 0.05 grams of s-rGO was mixed with 0.05 grams of cerium using 10 mL of isopropyl alcohol (IPA) as the solvent. This mixture was sonicated for 30 minutes at room temperature. The variation of ABS composition in the solution used was 1%, 3%, and 5% v/v.

2.4. Membrane Printing

The ABS solution will be sonicated with s-rGO/Ce filler for each variation for 2 hours until homogeneous. The solution will then be molded using a 90×18 mm petri dish, containing 25 mL of membrane solution. All membranes were subjected to oven drying at 60 °C for 48 hours.

2.5. Membrane Characterization

2.5.1.Swelling Degree

The swelling degree was determined based on the difference in membrane length in wet and dry conditions. The wet length was determined after the membrane was immersed in water for 48 hours. The membrane surface was wiped with tissue paper and measured immediately.

$$SD = \frac{\left(L_{wet} - L_{dry}\right)}{L_{dry}} \times 100\%$$

SD, Lwet, and Ldry represent the degree of swelling in weight percent (v/v.%), and the membrane length in wet and dry conditions, respectively.

2.5.2.Ion Exchange Capacity (IEC)

Ion exchange capacity (IEC) was measured by the titration method. The membrane was cleaned with distilled water and dried with tissue paper. After that, the membrane was soaked in 50 ml of 1 M NaCl solution for 48 hours so that Na^+ ions replaced H^+ ions in the membrane. The solution from this bath was titrated using 0.01 M NaOH solution with phenolphthalein as an indicator. The IEC was calculated based on the titration results using the appropriate formula.

$$IEC\left(\frac{m_{eq}}{g}\right) = \frac{V_{NaOH} \times C_{NaOH}}{W_d}$$

V_{NaOH} is the volume of NaOH titrated (mL), C_{NaOH} is the molarity of NaOH (M), and W_{dry} is the weight of the dried membrane (g).

2.5.3.Methanol Permeability

Methanol permeability measurements were carried out using two glasses interconnected on both sides of the membrane. Glass (A) contains 100 mL of 3M methanol, while glass (B) contains distilled water. During the measurement, the solutions in both glasses were continuously stirred. The methanol concentration in beaker B was measured as a function of time using a refractometer, then compared to the calibration curve. The methanol concentration in glass B follows Fick's first law, assuming CB is much smaller than CA, so CA is considered constant.

$$Cb(t) = \frac{(A \times DK)}{V \times L} CA(t - T0)$$

CA and CB are the methanol concentrations in glasses A and B, respectively. A and L are the membrane cross-sectional area and thickness, and DK is the methanol permeability. D is assumed to be constant across the membrane surface, and K is unaffected by concentration. t is the end time, and t_0 is the start time. V is the volume of solution in beaker A.

Each test, including swelling degree, ion exchange capacity (IEC), and methanol permeability, was conducted once due to time and resource limitations during the research.

2.5.4.Fourier Transform InfraRed (FTIR)

Fourier Transform Infrared (FTIR) testing was used to identify chemical bonds in the polymer membrane. FTIR analysis was measured in the wave number range of 400 - 4000 cm^{-1} using a Jasco FT/IR - 4600.

2.5.5. Scanning Electron Microscope (SEM)

The surface morphology of the membrane was observed with a Scanning Electron Microscope (SEM) using a Hitachi SU-3500 instrument.

3. RESULTS AND DISCUSSIONS

3.1. Swelling Degree Analysis

The swelling degree test is important for evaluating membrane performance [9]. Swelling Degree refers to the degree of membrane development influenced by its physical and mechanical properties and its capacity to absorb and store water. Water in the membrane plays an important role in facilitating proton transport, which is a crucial aspect in applications such as fuel cells [10].

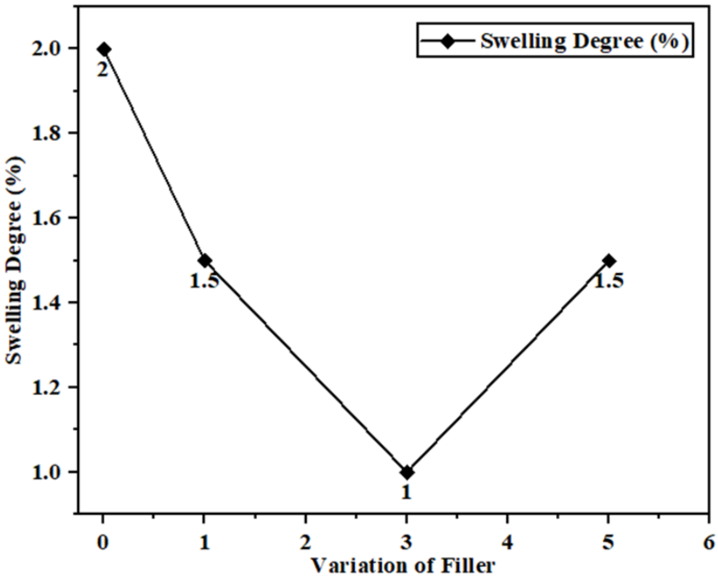

Figure 1. Swelling Degree test.

Based on Figure 1, the test results show that the filler composition variation of 3% v/v provides optimal performance with a low swelling degree (SD) value of 1%, resulting in good physical and mechanical properties of the membrane. At 5% v/v composition, the SD value increased to 1.5%, similar to the 1% v/v composition results. The increase can occur because the distribution of fillers in the ABS matrix tends to be more even, which can form microvoids or a more porous network. The presence of microvoids increases the surface area that interacts with water, thus accelerating the process of absorption and binding of water molecules in the material [11]. As a result, the greater the amount of water absorbed, the higher the swelling degree value produced.

3.2. Ion Exchange Capacity Analysis

The ion exchange capacity (IEC) test indicates the number of active groups in the polymer matrix capable of exchanging ions and directly affects the membrane's ability to transfer protons [6]. As shown in Figure 2, the pure ABS polymer membrane has the lowest ion exchange capacity (IEC), which is 0.15 meq/g. Adding filler by 1%, 3%, and 5% increases the IEC value to 0.2 meq/g, 0.3 meq/g, and 0.35 meq/g, respectively, with 5% composition showing the highest value. Analysis shows that increasing the composition of s-rGO/Ce positively impacts the IEC of ABS polymer membranes. However, excess filler can cause agglomeration, which reduces the effectiveness of ion exchange sites and decreases ion exchange efficiency.

These results are consistent with research by [12] which shows increased proton conductivity in Nafion membranes by adding graphene oxide sulfonation groups, improving proton transport and creating more efficient ion exchange sites than pure Nafion membranes. However, excessive addition of cerium can decrease proton conductivity and ion exchange capacity [9], [12] Although the addition of s-rGO and cerium fillers in this study increased the IEC compared to pure ABS membranes, the IEC value obtained was still lower than that of the Nafion 117 membrane, which has an ion exchange capacity of 0.90 meq/g [13]. Studies have shown that membranes with IEC values of 0.3–0.5 meq/g can perform efficiently in DMFC applications, particularly when complemented by low methanol permeability and good mechanical integrity [9].

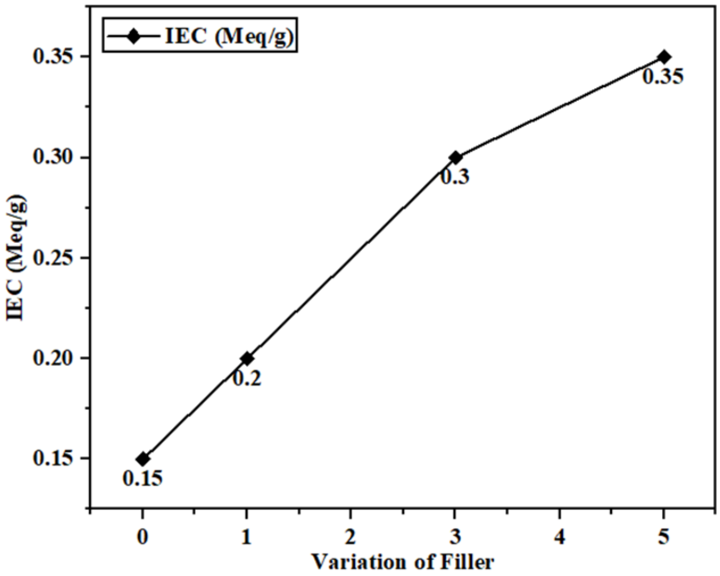

Figure 2. Ion exchange capacity test.

3.3. Methanol Permeability Analysis

The methanol permeability test is one of the important tests for DMFC electrolyte membranes. It aims to determine how much methanol can pass through the membrane. In addition, methanol crossover accelerates the membrane's mechanical and chemical degradation and contributes to catalyst deactivation, ultimately reducing the DMFC's service life [14].

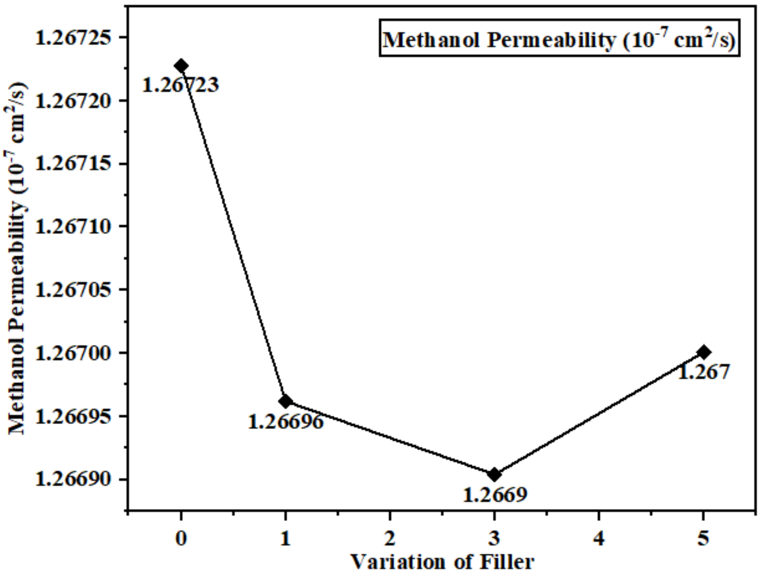

Figure 3. Methanol permeability test.

Figure 3 shows the results of the methanol permeability test on pure ABS membranes and those modified with s-rGO/Ce filler at variations of 1%, 3%, and 5%. The pure ABS membrane showed the highest permeability value of 1.26723 × 10^{-7} cm²/s. This is due to the absence of additional barriers in the ABS structure, so methanol can easily penetrate the polymer matrix. After being modified with the addition of 1% s-rGO/Ce, the permeability value decreased to 1.26696 × 10^{-7} cm²/s. A similar effect was observed with the addition of sulfonate groups to graphene oxide functionalized with polydopamine in the SPEEK membrane, reducing methanol crossover and increasing conductivity [15].

The most significant decrease in permeability occurred at a concentration of 3%, which was 1.26690×10^{-7} cm^2/s. The more even filler distribution at this concentration forms an effective barrier that can slow down methanol diffusion. In addition, the presence of homogeneously distributed sulfonate groups strengthens the interaction with methanol molecules. However, at 5% concentration, the permeability value increases again to 1.267×10^{-7} cm^2/s, which can occur due to the agglomeration of excess filler, thus creating gaps in the membrane structure. The results of this test show that both pure ABS membranes and those modified with s-rGO/Ce filler have lower methanol permeability compared to the Nafion 115 membrane (2.42×10^{-6} cm^2/s), based on testing with 3M methanol solution [7]. The thickness of all prepared membranes in this study was approximately 100 - 200 µm [16].

TABLE I. Summary of ABS-based membrane performance with s-rGO/Ce filler.

Membrane	**Swelling Degree (% v/v)**	**Ion Exchange Capacity (meq/g)**	**Methanol Permeability ($\times 10^{-7}$ cm^2/s)**
ABS Pure	2	0.15	1.26723
ABS + s-rGO/Ce 1%	1.5	0.20	1.26696
ABS + s-rGO/Ce 3%	1	0.30	1.26690
ABS + s-rGO/Ce 5%	1.5	0.35	1.267

3.4. FTIR Analysis

The FTIR test results present the difference between the pure ABS membrane and the ABS membrane that has been modified with 5% s-rGO/Ce. Figure 4 presents the difference in the FTIR test between the pure ABS membrane and the ABS membrane modified with 5% s-rGO/Ce. In the pure ABS membrane, there is a strong absorption appearing in the range of 2920 cm^{-1}, which indicates the aliphatic C-H vibrational bond and a peak at 2237 cm^{-1}, which indicates the presence of a nitrile group (C≡N) from acrylonitrile [17]. In addition, the absorption peak at 1493 cm^{-1} indicates the C=C double bond of styrene, while the absorption peak at 1451 cm^{-1} indicates the C=C double bond of butadiene [18]. Deformation of the C-H bond of the hydrogen atom bound to the alkene carbon is seen at 965 cm^{-1} for 1,4 butadiene and 911 cm^{-1} for 1,2 butadiene [18].

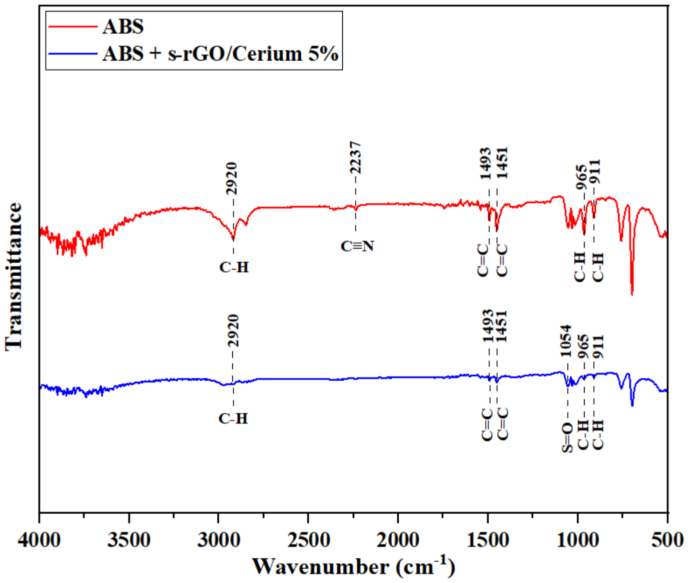

Figure 4. FTIR spectra of ABS and ABS + s-rGO/Ce.

In the ABS membrane with 5% s-rGO/Ce filler, the test results show that the intensity of the aliphatic C-H bond peak becomes weaker in the range of 2920 cm^{-1}. Other interactions also resulted in slight changes in the FTIR bands of ABS + s-rGO/Ce membrane, especially in nitrile groups (C=N) and aromatic groups (C=C). This indicates that the s-rGO/Ce filler interacts with the ABS matrix, which can disrupt the electronic charge distribution, thus affecting the vibrational intensity in the FTIR spectrum [19]. In Addition, the 1054 cm^{-1} range peak indicates the presence of sulfonate groups (S=O) [8]. These results demonstrate that the r-GO sulfonation process was successfully embedded in this membrane. The peak intensity for cerium ions looks very weak in the polymer, mainly because the amount of cerium used is relatively small [19].

3.5. SEM Analysis

Identification was carried out through a scanning electron microscope (SEM) to determine the morphology formed on the surface of the ABS + s-rGO/Ce polymer membrane. The results of membrane morphology identification are shown in Figure 5 and 6.

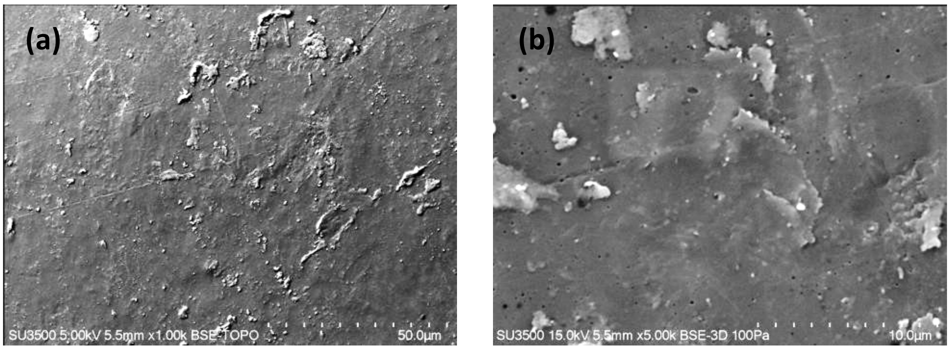

Figure 5. SEM results of pure ABS polymer membrane, (a) 1000x and (b) 5000x magnification.

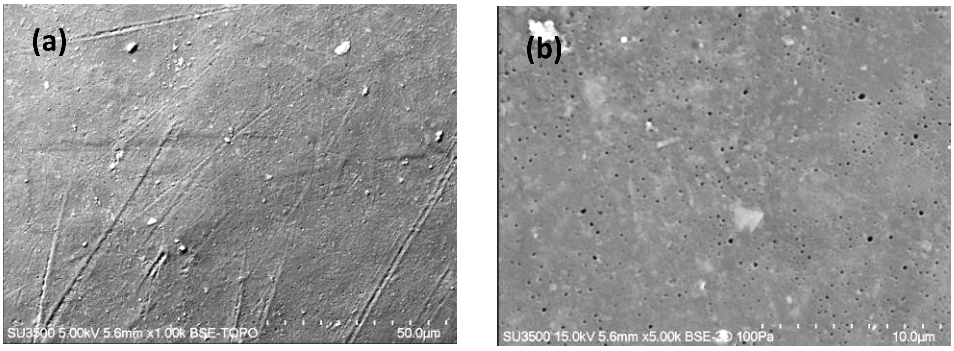

Figure 6. ABS polymer membrane with s-rGO/Ce filler, (a) 1000x and (b) 5000x magnification

The surface morphology of the pure ABS membrane as displayed in Figure 5, shows a wavy and slightly porous structure. These wave patterns reflect topographical variations at the microscopic scale. At 1000x magnification, there is a buildup of particles indicating agglomeration. Poor mixing during membrane fabrication can lead to nanofiller agglomeration, resulting in uneven particle distribution that may hinder proton transport and reduce membrane conductivity [20]. Meanwhile, at 5000x magnification, microvoids or small pores can be seen, which can increase the hydrophilic properties of the membrane but also make the structure more fragile [21]. Generally, solubility mismatches between components in organic-inorganic systems can lead to unstable or defective membrane morphologies [8].

Figure 6 shows the morphology of the ABS membrane modified with s-rGO and 5% v/v cerium at 60°C. Observation at 5000x magnification shows a more even surface and a greater number of pores compared to the pristine membrane, due to the addition of fillers [16]. The higher number of microvoids is expected to increase water absorption, thus supporting proton transport and conductivity during fuel cell operation [11]. The addition of s-rGO and cerium fillers to the ABS polymer membrane can provide a surface morphology that tends to be porous and wavy, thus actively providing better results than pure ABS polymer membranes.

4. CONCLUSIONS

The ABS membrane containing 5% filler showed a swelling degree of 1.5%, indicating sufficient water uptake while preserving structural integrity. Although the 3% filler membrane had the lowest swelling, the 5% membrane demonstrated a higher ion exchange capacity (0.35 meq/g), crucial for proton conductivity in DMFC applications. Its methanol permeability was slightly higher than that of the 3% membrane, likely due to filler agglomeration, but still within an acceptable range for practical use. FTIR analysis confirmed the presence of sulfonate groups at 1054 cm^{-1}, and SEM images revealed a uniformly porous structure that supports improved membrane performance.

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