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World Scientific News

An International Scientific Journal

WSN 107 (2018) 150-159 EISSN 2392-2192

Nanocomposite Sulfonated PVDF-TiO_2 Membranes as a Potential Alternative for Nafion

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ABSTRACT

Fuel cell is an alternative renewable energy source which potentially able to replace a fossil fuel. Nowadays, common fuel cell membrane generally used is Nafion. PVDF polymer is another synthetic polymer which has excellent physical and chemical properties. The purpose of this research is to synthesize an alternative fuel cell membrane, using sulfonated PVDF doped with TiO_2 nanoparticles. Sol-gel method was performed to synthesize TiO_2 nanoparticles, with $TiCl_4$ as precursor. PVDF membranes with variation of TiO_2 composition (0, 1, 1.5, and 2%) were prepared with ultrasonic method. The composite membranes then were sulfonated with concentrated sulfuric acid. The composite membranes were characterized with FTIR for functional group analysis, SEM-EDX for morphology analysis, acid-base titration for degree of sulfonation, weight difference for degree of water uptake, and four point lines for conductivity. FTIR spectra of the sulfonated membrane show the existence of sulfonic group at wavenumber of 601, 1400, and 1454 cm^{-1}. The result of SEM-EDX analysis shows that the nanoparticles of TiO_2 were not distributed homogenously. Degree of sulfonation of the PVDF-TiO_2 2% composite membrane is 19.54%, and its water uptake is 23.34%. The highest conductivity is about 3.17×10^{-3} S cm^{-1} for the PVDF-TiO_2 2% composite membrane that is very close to Nafion's conductivity, 6.08×10^{-3} S cm^{-1}.

***Keywords*:** nanocomposites, conductivity, titanium oxide, PVDF membrane

(Received 29 July 2018; Accepted 12 August 2018; Date of Publication 13 August 2018)

1. INTRODUCTION

Mankind live developments have triggered an increase in energy consumption especially fossil fuel. Therefore it is necessary to find an alternative energy source such as fuel cell. The main advantages of fuel cells are high efficiency (50-70%), no greenhouse emissions, flexible designs, and having a large selection of fuel cell (from renewable ethanol to hydrogen biomass) [1]. In the Proton Exchange Membrane Fuel Cell (PEMFC), electrolyte plays an important role in the system. The proton membrane must have several important characteristics such as high proton conductivity, high physical and chemical stability, high selectivity, and good water absorption in high temperature and low humidity [2-4]. A widely used membrane for PEMFC is Nafion (perflorosulfonic polymer). This membrane has high proton conductivity and good mechanical stability. Nafion also has several disadvantages such as high prices, low stability at high temperatures, and low conductivity in low humidity or high temperatures [5].

Poliviniliden Fluoride (PVDF) is one of the most important polymers due to its superior properties such as good mechanical strength and flexibility, high thermal stability, and fabrication efficiency. This polymer can be combined with inorganic nanoparticles such as ZrO_2, SiO_2, TiO_2, Al_2O_3 and others to enhance their characteristics [6-11]. Moreover, this polymer is considered cheaper compared to commercial Nafion membranes for fuel cell. However, PVDF has low hydrophilicity level that inhibits its application as proton transfer membrane. It is therefore very important to improve the hydrophilicity properties of the PVDF by addition of sulfonic functional groups to its structure.

The addition of nanomaterials inorganic oxides to the PVDF membrane can increase the conductivity. Srinivasan et al. [12] have proven through his research that the addition of inorganic nanotubes to Nafion membranes increase the degree of water uptake and proton conductivity of the membrane. Among the inorganic nanoparticles, TiO_2 is predicted to be a good candidate to increase water uptake and conductivity of the polymer membrane. TiO_2 molecule can maintain membrane hydration and also improve the mechanical characteristics of the membrane [13-16].

2. MATERIALS AND METHODS

Deionized water, Dimethyl Sulfoxide (DMSO), concentrated sulfuric acid, ethanol, sodium hydroxide, ammonia, PVDF, and $TiCl_4$ were used to perform the experiment. Common laboratory glassware, ultrasonic bath, centrifuge device, Burker SEM-EDX, Perkin Elmer FTIR Spectroscope were also used in the experiment.

The synthesis of TiO_2 nanoparticles was performed by sol-gel method using $TiCl_4$ as precursor. Into a chemistry glass containing 20 mL deionized water was added 10 mL of $TiCl_4$ drop by drop while stirring. The solution is then adjusted to neutral pH with the addition of NH_4OH solution. The resulting sol TiO_2 was then centrifuged at 7000 rpm for 5 minutes four times to produce gel TiO_2. The gel was then dried at 100 °C and calcined at 600 °C for 4 hours to produce white powder of TiO_2 nanoparticles.

The membrane preparation in this study was performed based on the procedure performed by Devrim et al. (2012). One g of PVDF powder was dissolved in 10 mL of DMSO solvent to form a mixture with 10% (w/v) PVDF. Into the solutions were added with

TiO_2 nanoparticles with a variation of 1, 1.5, and 2% (w/w). Then each mixture was stirred with a magnetic stirrer and sonicated for one hour at a frequency of 30 Hz. The polymer mixture was poured onto the glass plate to synthesis a thin layer membrane. The membrane was dried in an oven with a temperature of 30 °C to remove the solvent.

Sulfonation method used in this research is based on Kim et al's study[6]. Initially the sample of PVDF membrane, PVDF-1%TiO_2, PVDF-1,5%TiO_2 and PVDF-2%TiO_2 were each immersed in 20 mL concentrated sulfuric acid at 60 °C for 4 hours. Then each membrane was rinsed with distilled water to remove sulfuric acid from membrane's surface. Sulfonated composite membrane hereinafter called sPVDF-TiO_2.

3. RESULTS AND DISSCUSSIONS

The hydrolysis reaction of the $TiCl_4$ is shown below.

$$TiCl_4\,(aq) + 2H_2O\,(l) \rightarrow TiO_2\,(aq) + 2Cl_2\,(g) + 4H^+\,(aq)$$

This reaction is exothermic and produces harmful chlorine gas. The addition of $TiCl_4$ precursor to water was carried out in an ice bath drop by drop to avoid explosion. At the condensation stage, the H^+ ions of the hydrolysis react with OH^- ions from NH_4OH to produce water.

The centrifugation is carried out for the separation of the sample from the residual ions. Distilled water can be used as a Cl^- ion binder solution due to its high polarity. The Cl^- anion is easily move to water rather than stays in TiO_2 sol. The white crystals of TiO_2 were formed after the calcination process. According to Devrim et al. [14], the calcination process can remove remaining organic impurities to obtain stable TiO_2 crystals.

A functional group analysis was performed to confirm the existence of sulphonate (-SO_3H) groups in the composite membrane. Infrared spectra of PVDF-TiO_2 composite membrane before and after sulfonation are shown in Figure 1 and 2.

Table 1 shows the interpretation of the sample before and after sulfonation process and comparison with the reference. Sulfonate group that is bound to the membrane of PVDF-TiO_2 can be interpreted by absorption at wave numbers of 1454, 601 and 1400 cm^{-1} which are for the stretching of asymmetric and symmetric S=O respectively. The nanocomposite existence in the membrane was indicated by the absorption at 481 cm^{-1}. These prove that the membrane contain TiO_2 nanoparticles and sulfonate functional group.

In order to determine the sulfonation degree of membrane, the immersion step with NaCl is aimed to ion exchange. The H^+ ions of sulfonate group in the membrane were changed with Na^+ ions from the NaCl solution. The amount of detached H^+ ions is proportional to the amount of sulfonate groups present in the membrane (degree of sulfonation). This value can be determined quantitatively by titration method using NaOH solution. The sulfonation degrees of the sulfonated membranes are shown in Table 2.

According to Table 2, the sulfonation degree of membrane increases with the addition of the TiO_2 nanoparticles percentage. This proves that TiO_2 nanoparticles play important role in increasing the sulfonation degree of membrane. According to Peighambardoust et al. [5], TiO_2 nanoparticles can improve the hydrophilic properties of membrane surfaces so that hydrophilic groups such as sulfonates are easily bonded to the membrane.

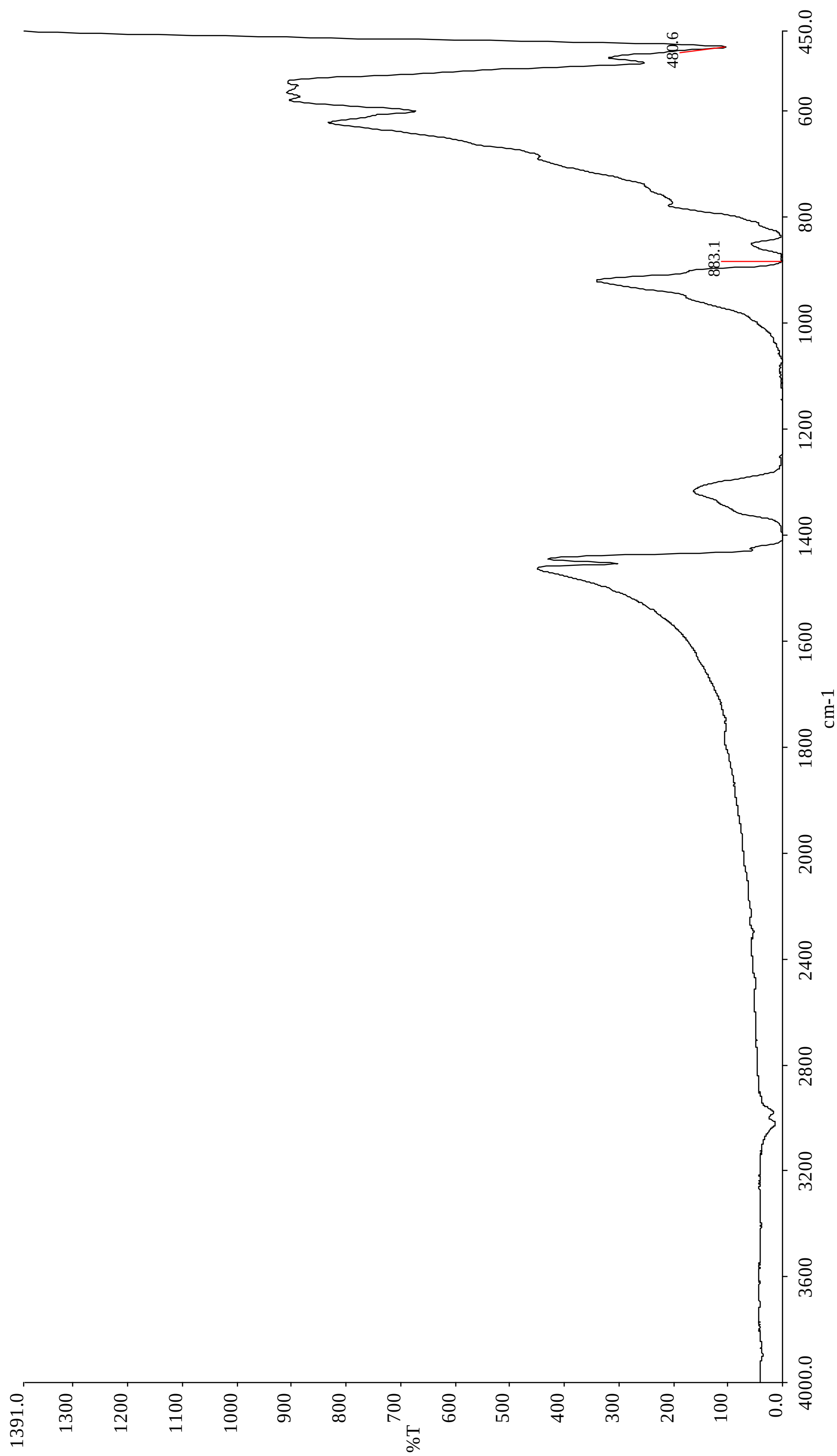

Figure 1. FTIR spectra of nanocomposite PVDF-TiO_2 membrane before sulfonation

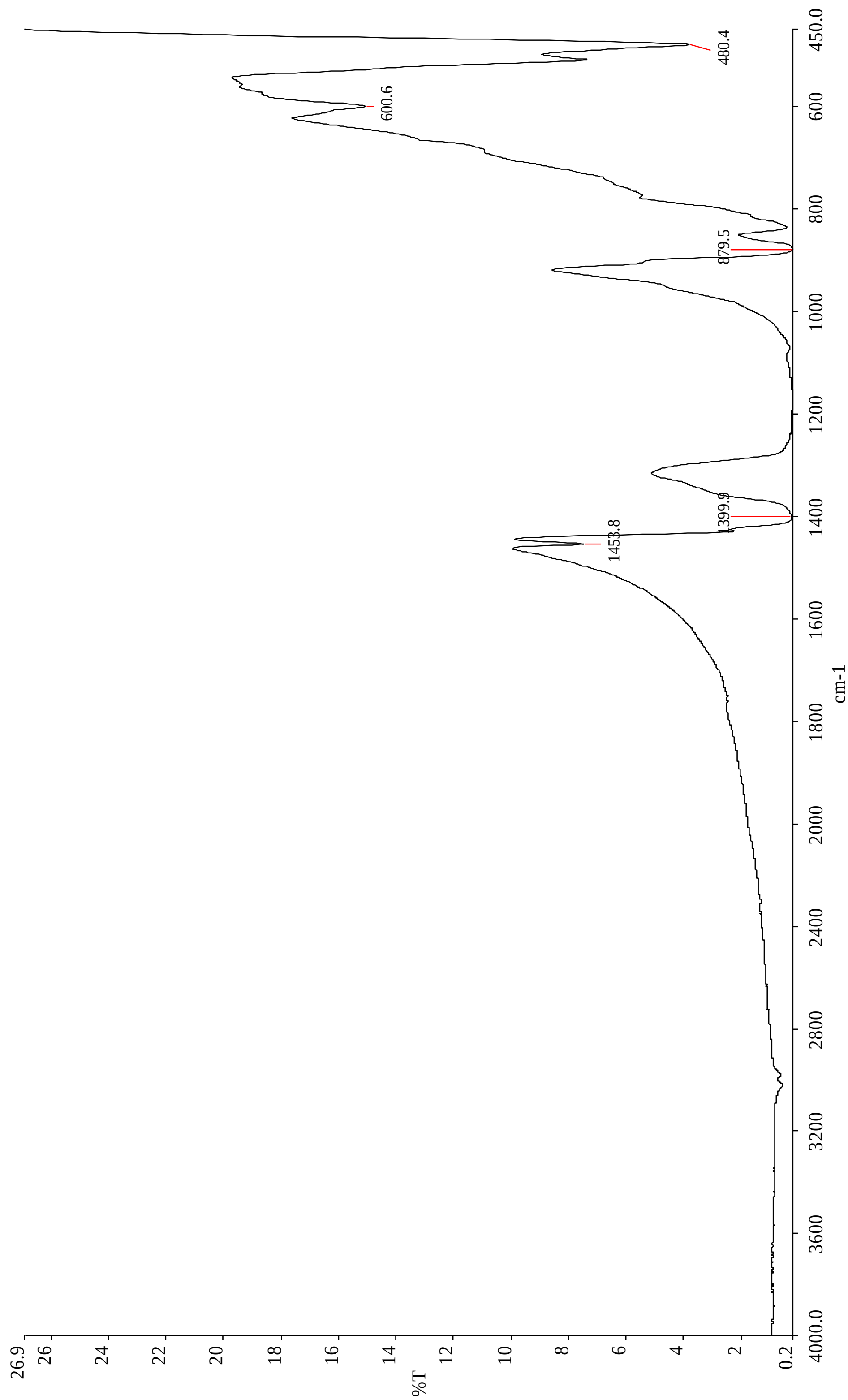

Figure 2. FTIR spectra of nanocomposite PVDF-TiO_2 membrane after sulfonation

Table 1. FTIR stretching wave number (cm^{-1}) of nanocomposite PVDF-TiO_2 membrane

Sulfonated PVDF-TiO_2 membrane (cm^{-1})	PVDF-TiO_2 membrane (cm^{-1})	Literatures [17-19] (cm^{-1})	Functional groups
481	483	450-800	Ti-O stretching
601		570-710	Asymmetric S=O stretching
880	883	850-1000	C-F stretching
1400		1398	symmetric S=O stretching
1454		1451	Asymmetric S=O stretching

Table 2. Sulfonation degree and water uptake of nanocomposite PVDF-TiO_2 membranes

Samples	Sulfonation Degree (%)	Water uptake (%)
sPVDF	4.4	59.4
sPVDF-1.0%TiO_2	7.4	43.7
sPVDF-1.5%TiO_2	11.3	26.1
sPVDF-2.0%TiO_2	19.5	23.3

Table 2 also shows the water uptake of sulfonated PVDF membranes. The water uptake is inversely proportional to the number of TiO_2 nanoparticles concentration. The TiO_2 nanoparticles fill the membrane matrix by covering the pores on the membrane surface, while one of the water binding positions is in the membrane pores. Thus, the more nanoparticles added, the less the water binding on the membrane pores. According to Devrim [13], the hydrophilic TiO_2 nanoparticles occupy the hydrophilic side of the composite membrane, the sulfonate group, thereby decreasing the degree of water uptake of the membrane.

Table 3 shows that the membrane conductivity increases with the addition of TiO_2 nanoparticles. This is due to the hydrophilic and semiconducting nature of TiO_2 nanoparticles can assist ion exchange processes that occur in the membrane.

The membrane's conductivity is also linear to the increasing sulfonation degree. According to Kim et al. [15], the conductivity of proton membranes is also proportional to the degree of water uptake. In this study, the degree of water uptake is inversely proportional to the conductivity of protons. This means that TiO_2 nanoparticles and sulfonate group give dominant influence to the conductivity of proton of membrane. The highest membrane's conductivity is for the sulfonated PVDF-2%TiO_2 composite membrane, ie 3.17×10^{-3} S cm^{-1}. The conductivity of commercial Nafion membrane (NAF NR212) according to Kim et al. [15] is 6.08×10^{-3} S cm^{-1}. This means from the view of conductivity, sPVDF-TiO_2 membrane is very potential to be used as an alternative fuel cell membrane.

The SEM-EDX analysis was performed to observe the morphology of the membrane surface and its composition. The nanocomposite membrane analyzed through SEM-EDX is a composite membrane with the highest conductivity value (sPVDF-2.0%TiO_2). The SEM results of the PVDF-2%TiO_2 composite membrane is shown in Figure 3 and 4. There are coagulated structures of TiO_2 nanoparticles at certain positions.

The EDX analysis results show the presence of Ti from TiO_2 nanoparticles on the membrane even in small amounts with the composition of 0.037%. Other atomic compositions detected on the composite membrane are carbon (48.037%), fluorine (51.09%), oxygen (0.709%), and sulfur (0.126%). The carbon and fluorine elements are found from the PVDF polymer main chain, so the numbers are predominant. The oxygen element of the membrane is derived from the sulfonate group ($-SO_3H$) and from the TiO_2 nanoparticles.

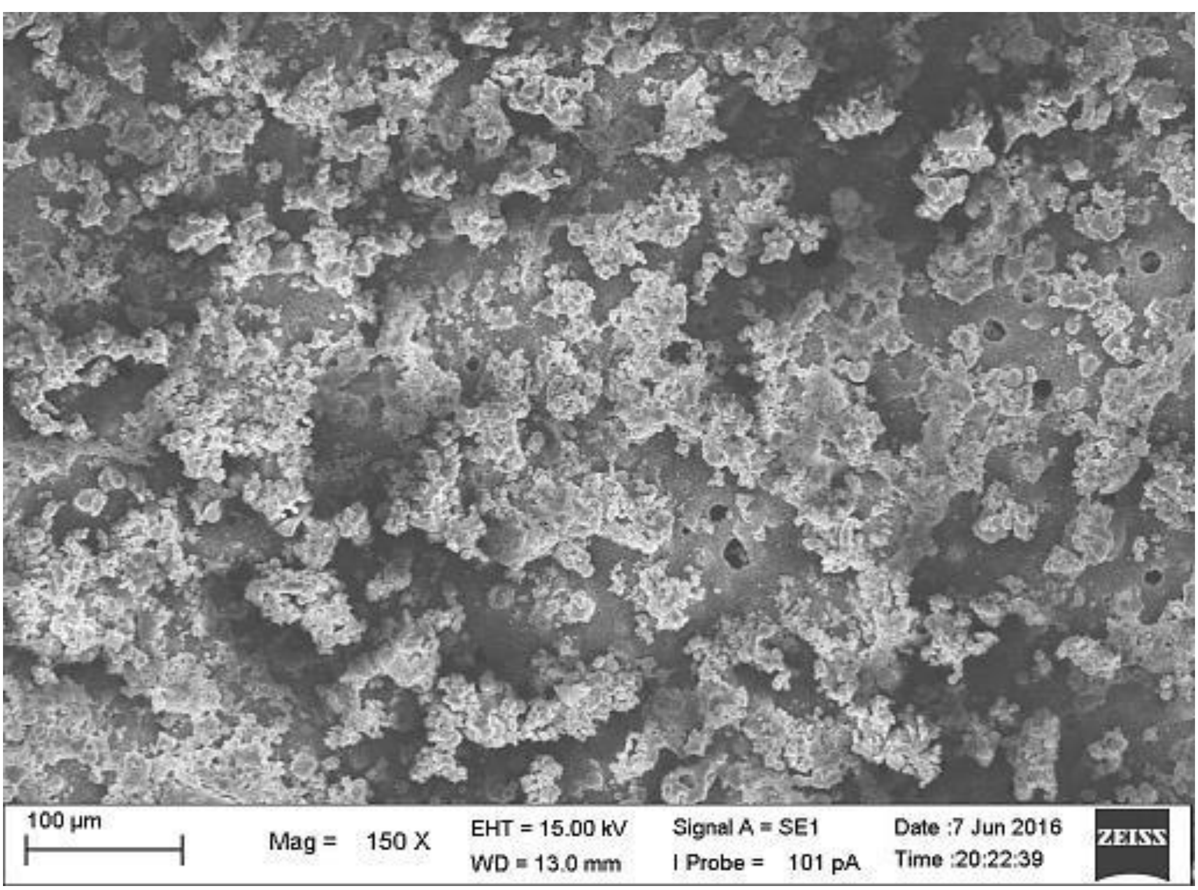

Figure 3. SEM analysis of sPVDF-2%TiO_2 membrane morphology at 150 ×

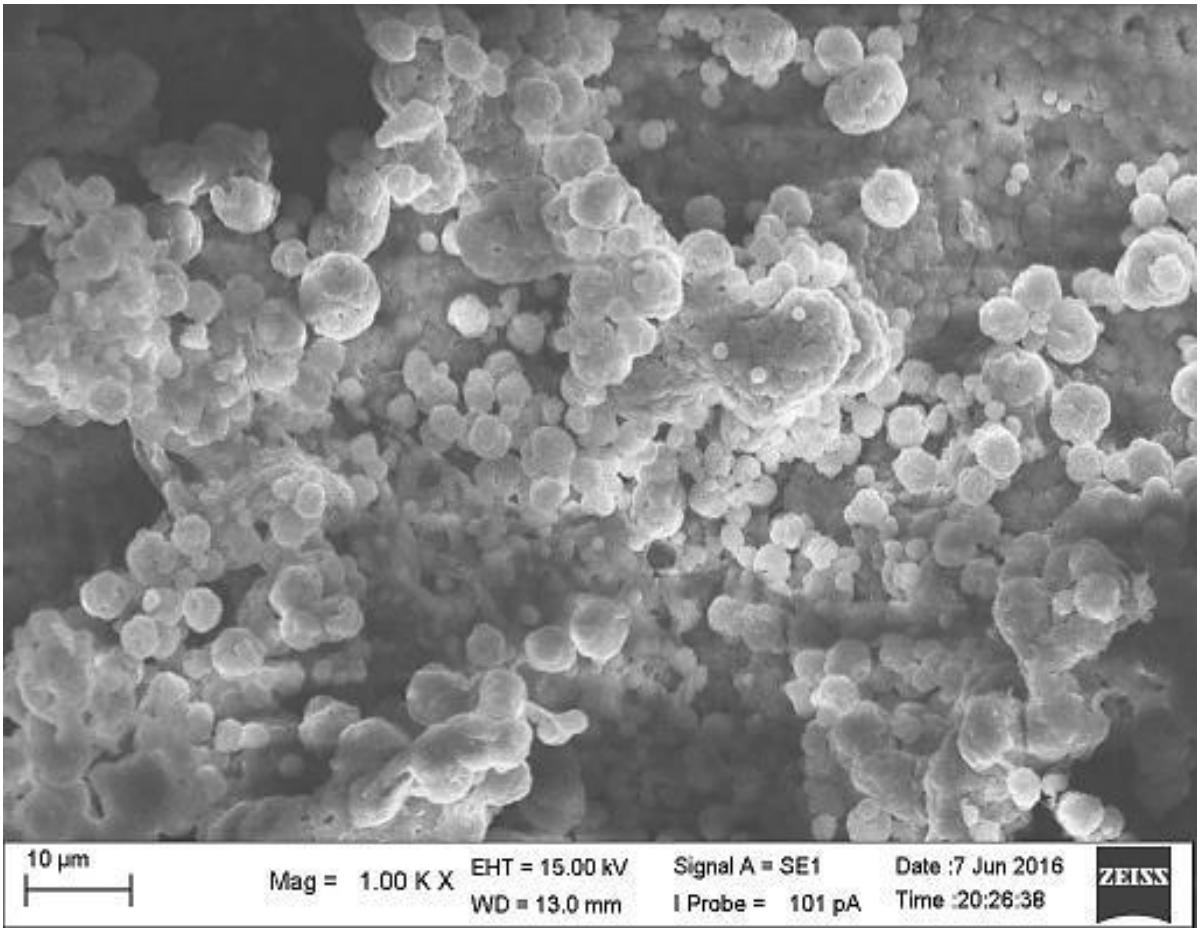

Figure 4. SEM analysis of sPVDF-2%TiO_2 membrane morphology at 1000 ×

Table 3. The conductivity of nanocomposite PVDF-TiO_2 membranes

Samples	Conductivity × 10^{-4} (S/cm)
sPVDF	1.78
sPVDF-1.0%TiO_2	3.75
sPVDF-1.5%TiO_2	15.20
sPVDF-2.0%TiO_2	31.70

4. CONCLUSIONS

FTIR spectra show the absorption at wave numbers of 601, 1409 and 1454 cm^{-1} for the SO_3-H functional group of the sulfonated PVDF-TiO_2 membrane to confirm the successful sulfonation. SEM-EDX analysis shows the surface morphology of PVDF-TiO_2 membrane with composition of carbon atoms is 48.04%, fluorine is 51.09%, oxygen is 0.71%, sulfur is 0.13%, and titanium is 0.04%. The addition of the TiO_2 nanoparticles to the PVDF membrane increases the degree of sulfonation and conductivity. The conductivity of PVDF-2%TiO_2 proton membrane is 3.17×10^{-3} S cm^{-1} while the Nafion's is 6.08×10^{-3} S cm^{-1}, thus the membrane has potential to become a fuel cell membrane alternative.

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