



World Scientific News

An International Scientific Journal

WSN 105 (2018) 218-224

EISSN 2392-2192

SHORT COMMUNICATION

Synthesis and Characterization of Nanocomposite Sulfonated PVDF Membrane

Juliandri^{1,*}, Rukiah¹, E. E. Ernawati¹, M. P. R. Silitonga¹ and M. Nasir²

¹Department of Chemistry, Universitas Padjadjaran, Jatinangor Sumedang 45363, Indonesia

²Research Center for Chemistry, Indonesian Institute of Science, Bandung 40135, Indonesia

*E-mail address: juliandri@unpad.ac.id

ABSTRACT

As a commercial fuel cell membrane, Nafion has disadvantages such as low stability at high temperature and low conductivity at low humidity. Sulfonated Polyvinylidene fluoride (PVDF) is known for good mechanical and thermal properties as a membrane. The purpose of this research is to synthesis a nanocomposite PVDF-TiSiO₄ membrane as a potential replacement of Nafion. PVDF sulfonation was performed using concentrated sulfuric acid. The nanocomposites TiSiO₄ were synthesized from TiCl₄ and TEOS. Ultrasonification was used to insert the nanomaterial to the sulfonated membrane. The infrared spectra analysis shows the peak for the Ti-O-Si angel. SEM-EDX analysis shows that the nanocomposite PVDF-TiSiO₄ membrane contents titanium oxide. The conductivity analysis shows the increasing of conductivity on addition of nanomaterials.

Keywords: nanocomposites, silicon oxide, titanium oxide, PVDF membrane

1. INTRODUCTION

As fossil energy resources are rapidly decreased, the alternative energy resources are developing simultaneously. The researchers did their best to produce new alternative energy resources. They tried to produce an environmental friendly resource such as fuel cell. A fuel cell is a device that transforms chemical energy to electricity power through chemical reaction. Hydrogen gas is usually used as fuel as well as alcohol. Differ from battery, fuel cell continuously produces electricity as long as the fueled gas available.

Fuel cells can be categorized into five main groups including Polymer Electrolyte Membrane Fuel Cell (PEMFC). The main part of a PEMFC is proton membrane, which allows the proton transportation through the membrane and prohibits other compounds. The membrane is a specific polymer with special properties. The membrane usually has sulfonate branch that plays important role in proton transfer. The sulfonated polymers are usually used as basic membrane for the fuel cell [1,2]. The most familiar membrane used in PEMFC is Nafion. In order to improve the properties of Nafion, researchers have added some nanomaterial to the membrane [3-6]. There are many kinds of nanomaterial that can be used in this case. Nanoparticles TiO_2 and SiO_2 for examples have been used to increase the membrane conductivity and mechanical property. Polymer nanocomposite is defined as the combination of polymer with small portion of nanomaterial. The polymer was synthesized for special purpose including for the fire resistance, oxygen protection etc.

Since few years the organic-inorganic nanocomposite membrane has been attracted the PEM researcher attention. The membrane has a significant improvement in mechanical properties and conductivities. The gas cross over is also reduced on that membrane [1,7].

The PVDF polymer is predicted to have good thermal and chemical stability as a replacement of commercial Nafion. Unfortunately the polymer is hydrophobic that decrease the PEM performances. Heo et al. [8] have suggested inserting the sulfone group in order to increase the hydrophilic property of the polymer. Kim et al. [9] reported that sulfonate PVDF membrane using concentrated H_2SO_4 at 60 °C for 4 hours has effectively increased the membrane conductivity to reach the Nafion one. Nagarale et al. [7] also reported that composite of inorganic compound with polymer membrane increased the polymer ionic exchange property. The main role of the inorganic compound in the polymer is to increase the conductivity and ion exchange property. TiSiO_4 nanocomposite has been used successfully to increase the proton conductivity of membrane [10]. The addition of SiO_2 nanoparticle to polymer membrane has improved the mechanical and thermal properties of the fuel cell membrane [11]. Devrim et al. [12] also reported that the addition of 1:1 TiO_2 : SiO_2 nanocomposite has increased the membrane conductivity.

In this research the synthesis and sulfonation procedure of PVDF is adapted from Kim et al. [9] and Kang et.al [11]. The sulfonation was performed with concentrated sulfuric acid at 60 °C for 4 hours. The SiO_2 nanoparticles were synthesized from TEOS [13-15].

2. MATERIALS AND METHODS

Deionized water, DMF, concentrated sulfuric acid, salt, sodium hydroxide, ammonia, PVDF, TiCl_4 and TEOS were used to perform the experiment. Ten mL of TiCl_4 was added drop by drop to deionized water in an ice bath. The mixture was neutralized by addition of

ammonia to reach pH of 7.5-8. The TiO_2 sol was centrifuged four times at 7000 rpm for 5 minutes. The gel TiO_2 was collected and dried at 110 °C prior to calcinations at 600 °C for 4 hours.

One gram of TiO_2 nanoparticle was added to the mixture of 5 mL ethanol, 5 mL of TEOS and 1 mL ammonia. The mixture was then put into ultrasonic bath for 1 hour. The gel was dried and calcined at 110 and 500 °C respectively to obtain nanocomposite TiSiO_4 .

One gram PVDF was dissolved in 10 mL DMF solvent to form a solution with 10 wt% PVDF. Then nanocomposite TiSiO_4 was added to the solution with a variation of 1, 1.5 and 2% (TiO_2 - SiO_2 1:1). Then the mixture was stirred with a magnetic. The mixture was then put into ultrasonic bath for 1 hour. At the last the membrane was casted. Casting process was performed by leveling the surface of the mixture that has been stipulated by using the rod so that the thickness of the membrane produced uniform.

Sulfonation was conducted by inserting the nanocomposites membrane into concentrated sulfuric acid (95-97%), and heated at a temperature of 60 °C for 4 hours. The membrane was then washed with distilled water to remove residual acid.

3. RESULTS AND DISSCUSSIONS

The nanoparticles TiO_2 was synthesized from precursor TiCl_4 based on sol gel method. TiCl_4 was added drop by drop to water in an ice bath. Due to exothermic reaction the ice bath is needed to reduce the reaction temperature. The mixture was then neutralized with ammonia. The white sol phase of TiO_2 was centrifuged several times prior to calcination.

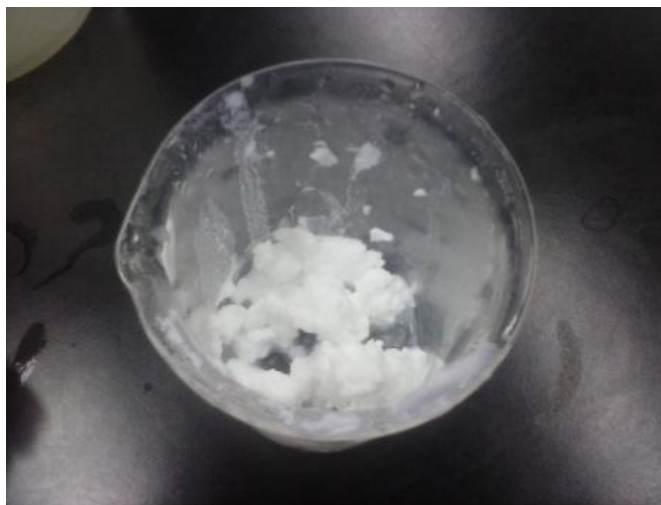


Figure 1. White TiSiO_4 sol

In this research, PVDF (Polyvinilidene Fluoride) was composited with nanoparticles of TiSiO_4 at variation of 1, 1.5, and 2%. DMSO (Dimethyl Sulfoxide) was also used as solvent. The functional group of the membrane was analyzed using FTIR spectra. The spectra prove that the sulfonation process has inserted the sulfone function to the membrane. The data are shown in Figure 2 and Table 1.

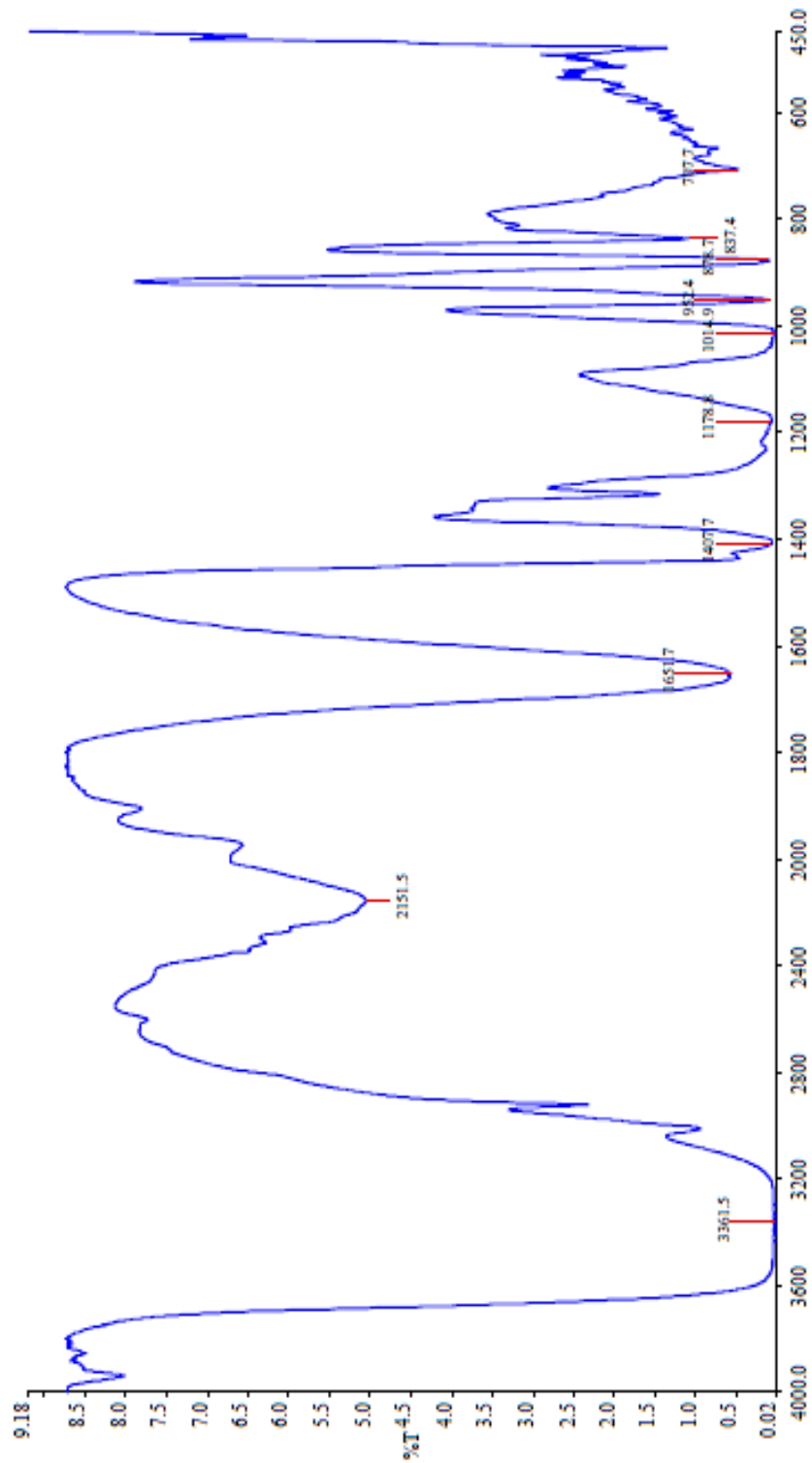


Figure 2. FTIR spectra of nanocomposite PVDF-TiSiO₄ membrane

Table 1. FTIR stretching wave number (cm^{-1}) of nanocomposite PVDF-TiSiO₄ membrane

Sulfonated PVDF-TiSiO ₄ membrane (cm^{-1})	PVDF-TiSiO ₄ membrane (cm^{-1})	Literature [16-17] (cm^{-1})	Functional group
481	483	488	Ti-O-Si scissoring
600		570-710	Asymmetric S=O stretching
838	837	837	Si-O-Si twisting
1163		1030-1275	symmetric S=O stretching

Table 1 shows the interpretation of the sample before and after sulfonation process and comparison with the reference. Sulfone group that is bound to the membrane of PVDF-TiSiO₄ can be interpreted by absorption at wave numbers of 1163 and 600 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 and 838 cm^{-1} . These prove that the membrane contain TiSiO₄ nanocomposite and sulfone functional group.

The degree of sulfonation was calculated to estimate the sulfone content in the membrane. The determination was performed by acid-base titration. The sulfonated membrane was soaked with NaCl to release the H⁺ from the membrane. The amount of H⁺ released from the sulfonated sample indicates the sulfonation degree.

Table 2. Sulfonation Degree (DS) of nanocomposite PVDF-TiSiO₄ membranes

Samples	Sulfonation Degree (%)
sPVDF	8.1
sPVDF - 1.0% TiSiO ₄	10.0
sPVDF - 1.5% TiSiO ₄	11.1
sPVDF - 2.0% TiSiO ₄	13.0

The measurement of the membrane conductivity was performed following the procedure shown by Devrim et al. [12]. The results are shown in Table 3. The highest conductivity was gained by the sulfonated membrane combined with 2% TiSiO₄ nanocomposite. Devrim et al reported that the nanocomposites help the ion exchange and proton transport inside the membrane. Our result (0.0005291 S/cm) is lower than Nafion's conductivity (0.00608 S/cm) [9].

Table 3. Nanocomposite PVDF-TiSiO₄ membrane conductivity

Samples	Conductivity $\times 10^{-4}$ (S/cm)
sPVDF	1.783
sPVDF - 1.0% TiSiO ₄	2.564
sPVDF - 1.5% TiSiO ₄	2.840
sPVDF - 2.0% TiSiO ₄	5.291

3. CONCLUSIONS

Nanocomposite PVDF membrane has been synthesized using TiCl₄, TEOS and copolymer PVDF. Infrared spectra of the membrane show the S-O bond to prove that sulfonation process. The increasing of nanocomposite content in the membrane has increased the conductivity. In the case of 2% addition of nanocomposite increases the membrane conductivity to 0.53 mS/cm.

References

- [1] Shin, D. W., Kang, N. R., Lee, K. H., Coo, D. H., Kim, J. H., Lee, W. H., Lee, Y. M., Proton conducting, composite sulfonated polymer membrane for medium temperature and low relative humidity fuel cells. *Journal of Power Sources* 262 (2014) 162-168.
- [2] Yekyung, K., Sung-Hee, S., In Seop, C. & Seung-Hyeon, M., 2014. Characterization of uncharged and sulfonated porous poly(vinylidene fluoride) membranes and their performance in microbial fuel cells. *Journal of Membrane Science* 463 (2014) 205-214.
- [3] Kim, D. J., Jo, M. J. and Nam, S. Y., A review of polymer–nanocomposite electrolyte membranes for fuel cell application. *Journal of Industrial and Engineering Chemistry* 21 (2015) 36-52.
- [4] Sriram, K., Arthanareeswaran, G., Ismail, A. F. & Paul, D., Effects of special nanoparticles on fuel cell properties of sulfonated polyethersulfone membranes. *International Journal of Polymeric Materials and Polymeric Biomaterials* 65 (2016) 294-301.
- [5] Das, S., Kumar, P., Dutta, K. & Kundu, P. P., Partial sulfonation of PVdF-co-HFP: A preliminary study and characterization for application in direct methanol fuel cell. *Applied Energy* 113 (2014) 169-177.
- [6] Devrim, Y. and Devrim, H., PEM fuel cell short stack performances of silica doped nanocomposite membranes. *International Journal of Hydrogen Energy* 40 (2015) 7870-7878.

- [7] Nagarale, R. K., W. Shina, P. K Singh, Progress in ionic organic-inorganic composite membranes for fuel cell application. *Polymer Chemistry* 1 (2010) 388-408.
- [8] Heo, Y., H. Im, J. Kim, The effect of sulfonated graphene oxide on sulfonated poly(ether ether ketone) membrane for direct methanol fuel cells. *Journal of Membrane Science* 425-426 (2013) 11-22.
- [9] Kim, Y., S. Shin, Chang, Moon. 2013. Characterization of uncharged and sulfonated porous poly (vinylidene fluoride) membranes and their performance in microbial fuel cells. *Journal of Membrane Science* 463 (2014) 205–214.
- [10] Jun, Y., Z. Hadiz, F. Michael, C. Zhongwei, Functionalized titania nanotube composite membranes for high temperature proton exchange membrane fuel cells. *International Journal of Hydrogen Energy* 36 (2011) 6073-6081.
- [11] Mhisra, K. M., B. Saswata, K. Tapas, H. K. Nam, H. L. Joong, Silicate-based polymer-nanocomposite membranes for polymer electrolyte membrane fuel cells. *Progress in Polymer Chemistry* 37 (2012) 842-869.
- [12] Devrim, Y., E. Serdar, B. Nurcan, and E. Inci, Improvement of PEMFC Performance with Nafion/Inorganic Nanocomposite Membrane Electrode Assembly Prepared by Ultrasonic Coating Technique. *International Journal of Hydrogen Energy* 37 (2012) 16748-16758.
- [13] Walid, H. A., T. Kashiwagi, A. B. Morgan, J. M. Antonuchi, M. M. van Landingham, R. H. Harris, and J. R. Shields, Thermal and flammability properties of a silica–poly(methylmethacrylate) nanocomposite. *Journal of Applied Polymer Science* 89 (2003) 2072–2078.
- [14] Jal, P. K., M.Sudarshan, A.Saha, Sabita Patel, B.K.Mishra. Synthesis and characterization of nanosilica prepared by precipitation method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 240 (2004) 173-178.
- [15] Jazarzadeh, M., Rahman, I. & Sipaut, C. Synthesis of silica nanoparticles by modified sol–gel process: the effect of mixing modes of the reactants and drying techniques. *Journal of Sol-Gel Science Technology* 50 (2009) 328-336.
- [16] Farrokhzad, H., T.Kikhavani, F.Monnaie, S.N.Ashrafizadeh, G.Koeckelberghs, T.Van Gerven, B.Van der Bruggen, Novel composite cation exchange films based on sulfonated PVDF for electromembrane separations. *Journal of Membrane Science* 474 (2014) 167-174.
- [17] Shahzadi, A., Ahmed, R. Shidiq, M., 2014. Synthesis and characterization of Nafion/SiO₂ - MO_x (M = Ti, Zr, W) nanocomposite membranes by sol-gel reaction for fuel cells. *IOP Con. Ser. Materials Science and Engineering*, 60 (2014) 012033.