Physical and Electrochemical Property of Nafion/CS Nanofiber Membranes
การศึกษาสมบัติเชิงกลและสมบัตเชิงเคมีไฟฟ้าของเมมเบรนเส้นใยนาโนแนฟฟิออน

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ABSTRACT

Nafion is commercially used as polymer electrolytes membrane (PEM) in proton exchange membrane fuel cell (PEMFC) due to its excellent chemical resistance and proton conductivity. However, mechanical properties which are water uptake and swelling ratio are depend on humidity of system. At low humidity, membrane exhibits poor proton conductivity caused by loss of water. In this work, Nafion nanofiber membrane was fabricated by electrospinning technique. The results revealed that an average diameter of Nanofiber is in the range of 200-400 nm. After that chitosan was cast onto Nafion nanofiber membrane to reduce gaps between fibers. The obtained membranes showed relatively good water uptake and proton conductivity compared to Nafion nanofiber membranes. Moreover, it exhibited relatively good proton conductivity up to 5.7 mS/cm. Therefore, this membrane has high potential to use in a PEMFC application.

บทคัดย่อ

ในปัจจุบันแนฟฟิออนถูกนำมาประยุกต์ใช้ในเชิงพาณิชย์สำหรับเป็นเยื่อแลกแปลี่ยนโปรตอนในเซลล์เชื้อเพลิงแบบเยื่อแลกแปลี่ยนโปรตอนเนื่องจากแนฟฟิออนทนต่อสารเคมีและมีคุณสมบัติเชิงเคมีไฟฟ้าที่ดี แต่อย่างไรก็ตามแนฟฟิออนยังคงมีคุณสมบัติเชิงกลและเชิงเคมีไฟฟ้าที่ต่ำลงเมื่ออุณหภูมิในการใช้งานเพิ่มสูงขึ้นเนื่องจากเมมเบรนจะเกิดการสูญเสียน้ำ ดังนั้นในงานวิจัยนี้จึงได้ศึกษาคุณสมบัติเชิงกลและเชิงเคมีไฟฟ้าของเมมเบรนเส้นใยนาโนแนฟฟิออนจากกระบวนการอิเล็กโตรสปินนิงและเมมเบรนเส้นใยนาโนแนฟฟิออนที่เติม ไคโตซาน พบว่าเมมเบรนเส้นใยนาโนแนฟฟิออนมีขนาดเส้นผ่านศูนย์กลางอยู่ในช่วง 200-400 นาโนเมตร หลังจากที่เติมไคโตซานมีเมมเบรนมีคุณสมบัติเชิงเคมีไฟฟ้าที่สูงขึ้นถึง 5.7 mS/cm และคุณสมบัติเชิงกลที่สูงกว่าเมมเบรนเส้นใยนาโนแนฟฟิออนอย่างมีนัยสำคัญ ดังนั้นเมมเบรนจากงานวิจัยนี้มีศักยภาพในการใช้เป็นเยื่อแลกแปลี่ยนโปรตอนในเซลล์เชื้อเพลิงแบบเยื่อแลกแปลี่ยนโปรตอน

Keywords: Nafion nanofiber, Electrospun, Chitosan

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Introduction

Nowadays, global warming is a critical problem for humankind. This caused by a release of carbon dioxide (CO_2) and greenhouse effect gases (SO_x, NO_x, CO) which originate from combustion of fossil fuel (Deuk Ju Kim et al., 2015). The solution of this problem is to find alternative energy including solar energy, water energy, wind energy, bioenergy, and hydrogen energy to replace fossil energy (Jin-Soo Park et al., 2017). Hydrogen energy is one of the most promising sources because it is clean and high energy density. Proton exchange membrane fuel cell (PEMFC) is a power generator device using hydrogen energy as a fuel (Jiao K, Li X., 2011). An important component of PEMFC is a proton exchange membrane (PEM) which indicates its performance (Morgan JM, Datta R., 2014). Nafion® is commercially available of PEM (Scofield, M.E. et al., 2015). It shows highly electrical, chemical, and thermal resistant of a hydrophobic part and good proton conductivity of hydrophilic part (Krishnan NN et al., 2014). However, it exhibits a low operating temperature, reduced proton conductivity at high operating temperature. This cause a need of humidification equipment which is cost added (Li J et al., 2014). The main fabrication of a PEM including solvent casting, extrusion, and electrospinning process. There are various studies referred to advantages of an electrospinning process (Hang Wang et al., 2020). Nanofiber obtained by electrospinning technique due to an electro-statics force. Sulfonate groups are aligned on surface of nanofiber due to a strong electric field caused higher proton conductivity (S.T. Arunan et al., 2017). In the past years, there are some attempts to add inorganic particles such as acid-SiO_2, Pt–G/SiO_2, Pd-SiO_2, doped TiO_2, ZrO_2, etc. to increase water retention, mechanical property, thermal stability, and proton conduction (Deuk Ju Kim et al., 2015; G. Gnana kumar et al., 2011; H.S. Thiam et al., 2013; D.C. Lee, H.N et al., 2015). Jingtao Wang et al. fabricated porous nanofiber composite membranes and cast by chitosan (CS) solution to cause acid-base pairs with $–SO_3H$ groups in matrix at interfaces. This accelerates a proton conduction at both hydrated and anhydrous conditions (H. Zhang et al., 2016). Moreover, sulfonated poly (ether ether ketone) nanofiber composite with sulfonated halloysite nanotubes mixed with CS matrix was fabricated to enhance proton conductivity of membranes. (Ping Li et al., 2020). In this work, Nafion/Polyaniline (PAN) nanofiber composite membranes were cast by electrospinning technique to improve an electrochemical property, thermal stability, and mechanical stability. Nafion/PAN membranes was cast additional layer by chitosan solution and submerged in sulfuric acid. A scanning electron microscope was used to study morphology. The mechanical properties were tested by a water uptake and swelling ratio were tested at room temperature. Electrochemical was tested by Impedance technique at room temperature.

Objectives of the study

1. To fabricate Nafion nanofibers membrane by electrospinning technique
2. To study morphology, mechanical, electrochemical properties of Nafion nanofiber membrane

Experimental

Materials

Aqueous Nafion solution (5 wt%), polyacrylonitrile (PAN, average M.W. 150,000), N, N-dimethyl formamide (DMF), chitosan powder (medium molecular weight), and acetic acid (99.8%) were purchased from Sigma-Aldrich. Ethanol (95%) was from RCI Labscan. All chemicals are analytical grade and used as received.

Preparation of Nafion nanofiber membranes

Nafion solution was gently stirred at 40 °C to remove the solvent. After that Nafion was dissolved in DMF (10 wt%). PAN was dissolved in DMF (10 wt%). Then, both solutions were mixed. Nafion/PAN nanofiber obtained by electrospinning process following this condition: applied high-voltage is 18.6 kV, tip-to-collector distance is 15 cm, and a solution feed rate is 1 ml/h. Nanofiber membranes were compressed under 1.5 tons for 20 min at room temperature.

Fabrication of Nafion nanofiber membranes

Chitosan powder was dissolved in acetic acid aqueous solution (50:50 weight ratio for acetic and deionized water) at 40 °C. Chitosan solution was cast onto Nafion/PAN nanofiber membranes and allowed it dry at RT. Finally they were dried at 60 °C and denoted as Nafion/PAN/CS nanofiber membranes.

Characterization of nanofiber membranes

Morphology of Nafion nanofiber was evaluated by scanning electron microscope (SEM) by a LEO-1450VP after coating with gold. Water uptake and swelling ratio were evaluated by measuring the changes in weight, and thickness between dry and wet nanofiber composite membranes, respectively. Dried membranes were submerged in DI water at room temperature for 3 h. Whereafter, the weight (W_{wet}, g) and thickness (L_{wet}, cm^2) of wet membrans were re-measured instantly after removing the surface water with blotting paper. The water uptake and swelling ratio were calculated to follow equations:

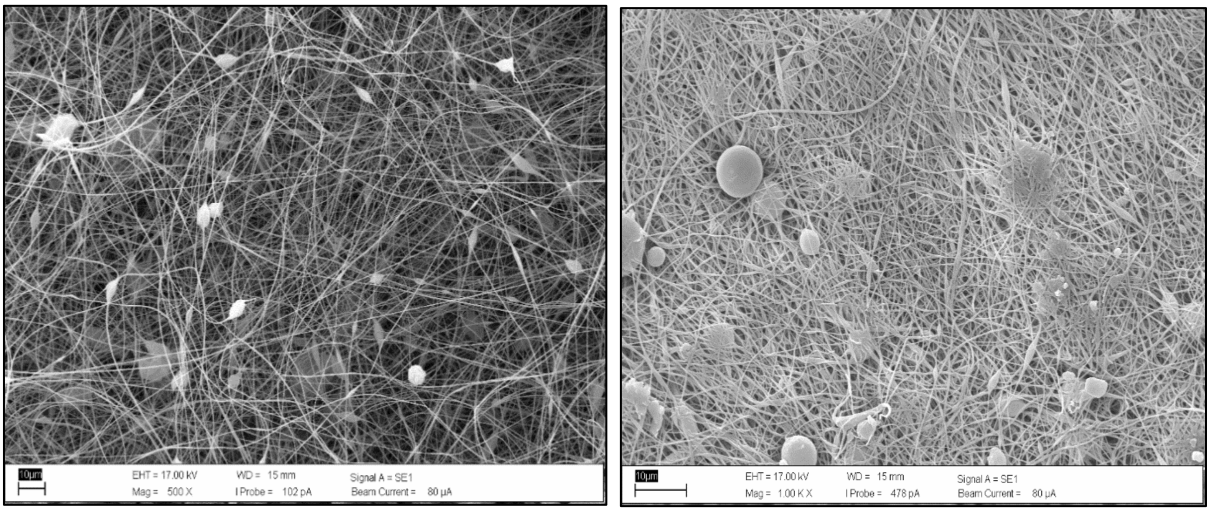
$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

$$\text{Swelling ratio} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \qquad (2)$$

W_{wet} and W_{dry} are weight of the hydrated and dry membranes. L_{wet} and L_{dry} are the average thickness of the hydrated and dry membranes, respectively. An electrochemical of membranes was tested by impedance spectroscopy technique at scanning the start frequency and frequency are 1 Hz and 1 MHz, respectively.

Results and discussion

Morphology of Nafion nanofiber membranes

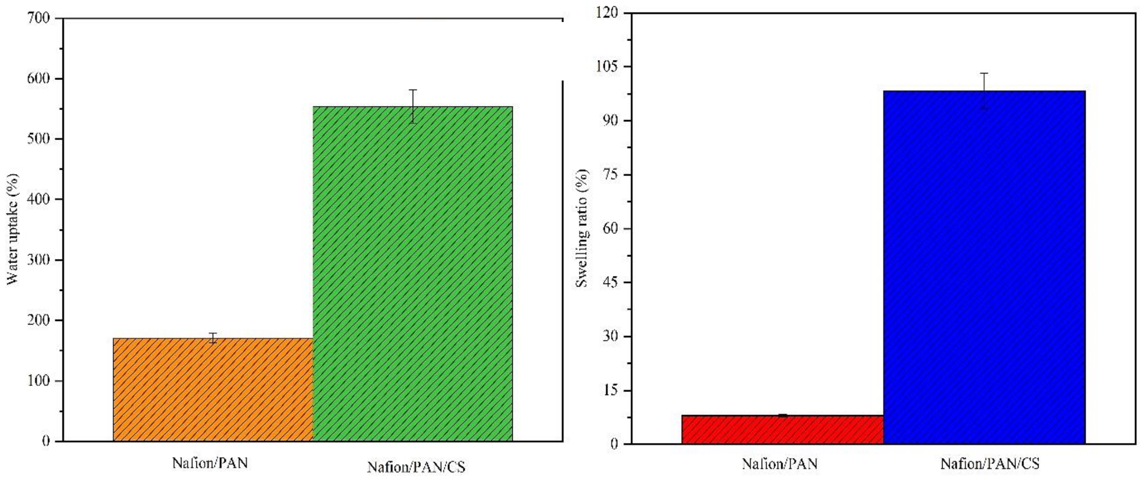


(a) (b)

Fig. 4.1 SEM image of (a) Nafion/PAN and (b) Nafion/PAN/CS

Fig. 4.1. shows SEM image of Nafion/PAN and Nafion/PAN/CS nanofiber membranes. It was found that an uniform distribution of nanofibers membranes were obtained. An average diameter of nanofibers is in the range of 200 - 400 nm. When cast chitosan solution into Nafion/PAN membranes (show as fig. 4.1 (b)), It notices that the density of Nafion/PAN/CS is increasing. Compared to the work of Ping Li et al (Ping Li et al., 2020), it was demonstrated that after cast chitosan Nafion/PAN is still be a nanofiber.

Physical properties of Nafion nanofiber membranes



(a) (b)

Fig. 4.2 (a) Water uptake and (b) swelling ratio of Nafion nanofiber membranes

Fig. 4.2 shows a water uptake and swelling ratio which is one of proton conducting part of Nafion nanofiber membranes. Nafion/PAN/CS have noticeably higher water uptake and swelling ratio than Nafion/PAN. This result occurred from hydrophilic property of SO^{-}_{3} and C≡N group of Nafion and polyacrylonitrile (R. Sigwadi et al., 2019), respectively. Moreover, it is because of an interaction acid-base pairs of the SO^{-}_{3} with -NH-/-NH_2 of Nafion and chitosan, respectively (H. Zhang et al., 2016). And finally, it notices that high water uptake and swelling ratio causes increasing in proton conductivity. (Shikai Zhang et al., 2015).

Chemical composition of Nafion nanofiber membranes

From FTIR result exhibits that the characteristic peaks at 1230, 1140, and 1060 cm^{-1} occurred from O=S=O of -SO_3H groups in Nafion nanofiber membranes (Y. Yin et al., 2016). In comparison, the peak intensity of -SO_3H groups for Nafion/PAN/CS decrease because the formation of -NH-/NH_2 groups of chitosan and -SO_3H groups of Nafion. Interaction of acid-base occurred from strong electric field cause to observed weakened intensity (Ping Li et al., 2020).

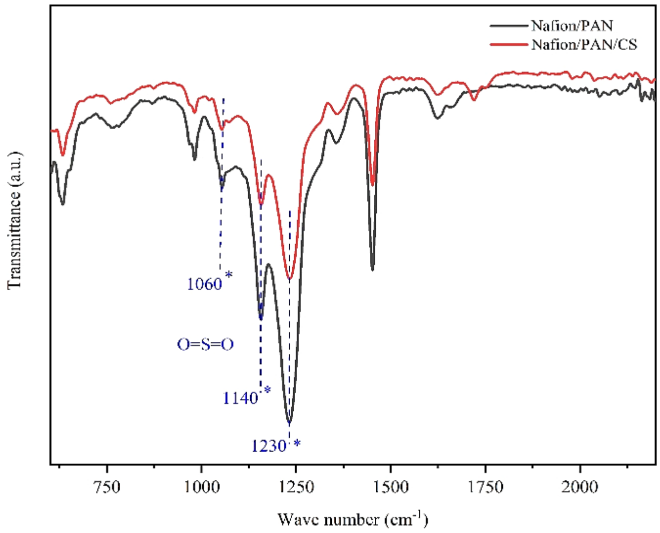
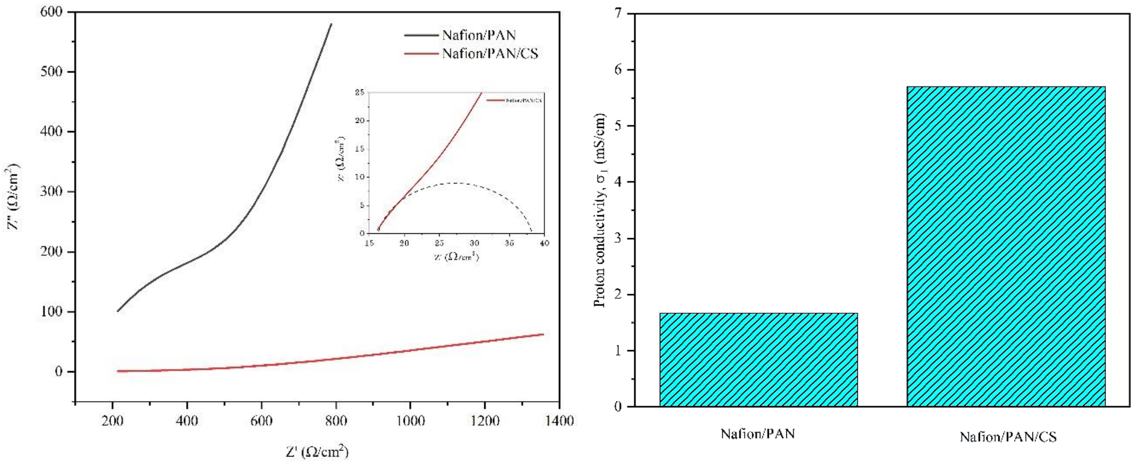


Fig. 4.3 FTIR spectra of Nafion nanofiber membranes

Proton conductivity of Nafion nanofiber membranes

Fig. 4.4 shows proton conductivity of Nafion nanofiber membranes at fully hydrated and room temperature conditions. Nafion/PAN/CS show higher proton conduction than Nafion/PAN, 5.7 mS/cm and 1.67 mS/cm respectively. An increase in proton conductivity significantly occurred from acid-base pairs between -NH/-NH_2 with -SO_3H which causes low-barrier pathways of proton transfer through the nanofiber (Ping Li et al., 2020)



(a) (b)

Fig. 4.4 (a) Impedance curve and (b) Proton conductivity of Nafion nanofiber membranes

Conclusions

Nafion nanofiber membrane was fabricated by electrospinning technique. an average diameter of Nanofiber is in the range of 200 - 400 nm. Chitosan was cast onto Nafion nanofiber membrane which showed relatively good water uptake and proton conductivity compared to Nafion nanofiber membranes. Moreover, it exhibited relatively good proton conductivity up to 5.7 mS/cm due to an interaction between -NH/-NH_2 of chitosan and -SO_3H of Nafion confirm from FTIR. This suggested that membrane has high potential in a PEMFC application.

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