

## Modified CNTs/Nafion composite: The role of sulfonate groups on the performance of prepared proton exchange methanol fuel cell's membrane

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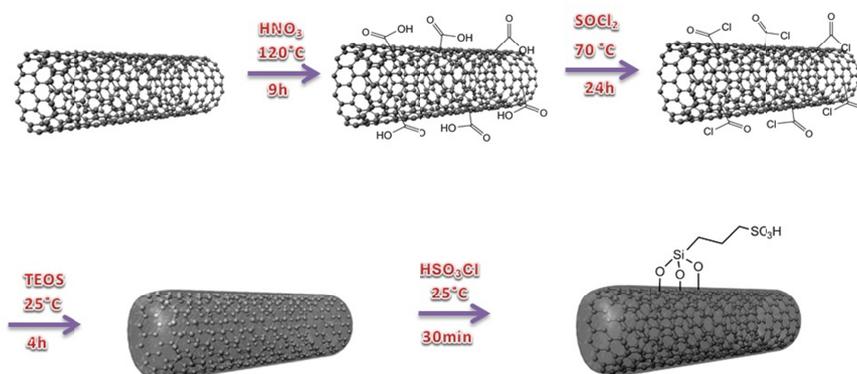
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### HIGHLIGHTS

- Functionalization of CNTs by a silica layer and sulfonated groups
- Improvement of proton conductivity and selectivity of the prepared composite membrane
- Decreasing the methanol permeability by decreasing the size of the nanochannel
- Enhancement of water uptake and ion exchange capacity by introducing the sulfonated groups

### GRAPHICAL ABSTRACT



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### ABSTRACT

A novel Nafion<sup>®</sup>-based nanocomposite membrane was synthesized to be applied as direct methanol fuel cells (DMFCs). Carbon nanotubes (CNTs) were coated with a layer of silica and then reacted by chlorosulfonic acid to produce sulfonate-functionalized silicon dioxide coated carbon nanotubes (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H). The functionalized CNTs were then introduced to Nafion<sup>®</sup>, and subsequently, methanol permeability, proton conductivity, ion exchange capacity (*IEC*) and water uptake properties of the prepared membranes were investigated. The experimental results showed that the water uptake and *IEC* of the Nafion<sup>®</sup>/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H (1 wt%) membrane increased in comparison with the recast Nafion<sup>®</sup>. *IEC* was enhanced from 0.9 meq/g for the recast Nafion<sup>®</sup> to 0.946 meq/g for Nafion<sup>®</sup>/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H, which could be attributed to the presence of sulfonate groups on the surface of CNTs. In addition, the proton conductivity of the sulfonate modified CNT/Nafion<sup>®</sup> composite was enhanced in a wide range of temperatures. Selectivity of the fabricated membrane was found to be more than 8-fold higher than that of recast Nafion<sup>®</sup> 117, demonstrating the promising potential of the produced membranes for DMFC applications.

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## 1. Introduction

With the ongoing development of industry and the progressively increasing need for consumption of energy, fuel cell technology is becoming considered as an important alternative to fossil fuel-based energy converters. Among the different types of fuel cells, direct methanol fuel cells (DMFCs) are more attractive for using as a portable power source because of their advantages such as high energy density, low molecular weight and liquid form of methanol [1].

Performance of methanol fuel cells is strongly dependent on polymer polyelectrolyte, which plays the most important role in the fuel cell. This section of the fuel cell is formed by a polymer membrane with a particular structure capable of proton exchange. The polyelectrolyte layer is located between the anode and cathode creating a preferred path for the proton transfer [2].

In addition to having proton exchange ability, this membrane should also have a minimum permeability to methanol. Moreover, the mechanical and chemical stability, flexibility and durability of polyelectrolyte membranes are very important for use in fuel cells.

Perfluorosulfonic acid (PFSA) based membranes, such as Nafion®, are the most common polyelectrolytes for fuel cells because of their excellent proton conductivity and also high mechanical, chemical and thermal resistance. Nafion is a semi-crystalline polymer and its structure is comprised of a hydrophobic poly-tetrafluoroethylene body with short perfluorovinyl ether side-chains which are terminated by hydrophilic sulfonate ionic groups [3]. This exceptional two-phase structure has brought a lot of attention to Nafion in recent years. Due to their hydrophilic nature of absorption of water molecules into the membrane and swelling to facilitate proton transfer, sulfonic ionic groups are leading to the formation of nano-channels. Moreover, their hydrophobic Teflon matrix creates good mechanical strength for the membrane. However, Nafion also has major disadvantages such as high methanol crossover, low proton conductivity at low humidity or high temperatures, loss of mechanical and thermal stability at elevated temperatures and restricted operating temperatures [4,5].

Modification of the Nafion membrane by incorporation of fillers is one of the best routes to improve its performance. By incorporating organic or inorganic nano-scale additives like silica, metal oxides, clay,

graphene, zeolite, and others into the Nafion polyelectrolyte matrices, the methanol permeability can be significantly reduced, but unfortunately once nanoparticles are located in the route of nano channels the proton transfer is decreased. This problem can be solved by using functionalized nanoparticles which provide new proton conduction sites on their surfaces [6].

Among the mentioned additives, carbon nanotubes (CNTs) have recently been considered as one of the best options due to their high aspect ratios, nanometer scale diameter, high specific surface area, substantial structural and their excellent mechanical and chemical properties. However, the problem of insolubility of the carbon nanotubes and the inherently poor compatibility between the carbon nanotubes and the Nafion matrix in obtaining a uniform dispersion of carbon nanotubes in the polymer matrix has limited the use of CNTs [7]. Within the past few years, several efforts have been to modify the surface of carbon nanotubes to counterbalance the mentioned issue. An effective way to ameliorate the proton conductivity and the hydration properties of Nafion at elevated temperatures is to fabricate the composite membrane with inorganic additives that have been surface modified with compounds such as hygroscopic oxides (e.g. SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>) to improve the water retention at operating temperatures above 90 °C [8]. The incorporation of hydrophilic inorganic hygroscopic oxide particles produced promising results due to their propensity to embed water in their interlayer regions which makes them more hydrophilic or more permeable to water [9]. Amjadi *et al.* [10] have studied the Nafion® 117 membranes doped with SiO<sub>2</sub> particles by in-situ sol-gel reactions. The results showed that the membranes modified with SiO<sub>2</sub> increased the fuel cell performance at 110 °C and in low humid conditions. Also, the membrane including 5-7 wt% SiO<sub>2</sub> content exhibited higher water uptake than the pure Nafion. Jung *et al.* [11] explored the proton conductivity of Nafion with different contents of SiO<sub>2</sub> and concluded that the proton conductivity was increased for the silicon oxide content of 12.4% at 125 °C. In another work, Adjemian *et al.* [12] prepared Nafion/SiO<sub>2</sub> composite membranes by the sol-gel technique, and reported high water retention characteristics above 100 °C.

Additionally, the inclusion of sulfonate into the Nafion membrane has also shown encouraging results. For example, the addition of sulfonated graphene oxide

to Nafion enhances the water retention characteristics of the membranes at higher temperatures. Chang *et al.* [13] studied the structural and functional properties of Nafion<sup>®</sup> 117 membranes filled with sulfonated graphene oxide (SGO). The composite membrane which can be implemented in direct methanol fuel cells (DMFCs) showed lower methanol permeability and water uptakes, a reduced swelling ratio, enhanced proton conductivity in low relative humidity and extremely high methanol selectivity. Moreover, Jae-Hong *et al.* [14] prepared Nafion nanocomposite membranes using sulfonated SiO<sub>2</sub> nanoparticles, and their results indicated that the addition of sulfonated SiO<sub>2</sub> nanoparticles into the Nafion matrix is very effective in improving the membrane performance including ion exchange capacity (*IEC*), proton conductivity, methanol permeability and mechanical strength.

The principal aim of this paper is to fabricate nanocomposite membranes based on Nafion by incorporating the sulfonate-functionalized silicon dioxide coated carbon nanotubes (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H) to investigate the performance of the prepared membrane. The most important aim of this research is to investigate the functionalization of CNTs and presence of sulfonate groups on the performance of the prepared membrane. To this end, the properties of the prepared membranes, such as water retention, ion exchanger, proton conductivity, methanol permeability and selectivity, were investigated and compared with pristine Nafion.

## 2. Experimental

### 2.1. Materials

Nafion<sup>®</sup> 117 was acquired from the E. I. DuPont de Nemours Company (USA) and multi-walled carbon nanotubes (MWNTs, outer diameter: 20-30 nm, inside diameter: 5-10 nm, average length: 10-30 μm and surface area: 110-130 m<sup>2</sup>/g) were purchased from Nano Amor (Houston, TX, USA). Nitric acid (HNO<sub>3</sub>, 68%) was used for oxidation of MWNTs (Merck, Germany), N,N-dimethylformamide (DMF) (Merck, Germany), thionyl chloride (Sin Chem, Indian), tetrahydrofuran (THF) (Merck, Germany), tetraethoxysilane (TEOS) (Sigma Aldrich, Germany) were used for synthesis of the silica coated MWNTs. Also, Chlorosulfonic acid (Sigma Aldrich, Germany) was used for surface modification of MWNTs and ethanol (99.7%) was used.

### 2.2. Fabrication of nanoparticle

First, CNTs were treated with nitric acid (68 wt%). For this purpose, a mixture of CNTs and nitric acid was magnetically stirred on a heater stirrer equipped with reflux condenser at 120 °C for 9 h [15,16]. In this step, COOH groups were introduced to the surface of CNTs. The resulting CNT-COOH was dispersed in thionyl chloride in a sonication bath for 1 h, and then an adequate amount of DMF (5 ml) was added to the mixture followed by stirring for 24 h at 70 °C under reflux conditions to attain the functionalized CNTs with chlorocarbonyl groups (CNT-COCl). [6].

To add the silane groups into the CNTs surfaces, CNT-COCl was dispersed into ethanol, and then stirred for 15 min. After that, NH<sub>3</sub> (4 ml, 30 wt%) and distilled water were added to the mixture of ethanol and CNT-COCl. The TEOS was quickly injected into the flask, and the reaction vessel was stirred at 25 °C for 4 h. The prepared mixture was centrifuged at 4000 rpm for 30 min to gain silicon dioxide coated CNTs (CNT@SiO<sub>2</sub>) [16,17]. In the following procedure to modify the surface of the sulfonate groups, a suction flask charged with the nanoparticles (80 mg) and equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (*i.e.*, water) was used. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas immediately evolved from the reaction vessel. After the addition was completed, the mixture was shaken for 30 min. A black solid of sulfonate-functionalized silicon dioxide coated carbon nanotubes (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H) was obtained [18]. The schematic procedure of CNT functionalization is illustrated in Figure 1.

### 2.3. Nanocomposite membranes fabrication

First, certain amounts of sulfonate-functionalized silicon dioxide coated carbon nanotubes (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H) powder were suspended in deionized water at 25 °C, stirred for 1.5 h, and sonicated for 30 min. Then, the suspensions were added to Nafion<sup>®</sup> 5 wt% (diluted by water and isopropyl alcohol) at room temperature and stirred for 3 h to gain 1 wt% of CNT@SiO<sub>2</sub>-SO<sub>3</sub>H polymer composite. The mixtures were sonicated for two sequential 30 min periods. The resultant solutions were cast on petri dishes then incubated in ambient

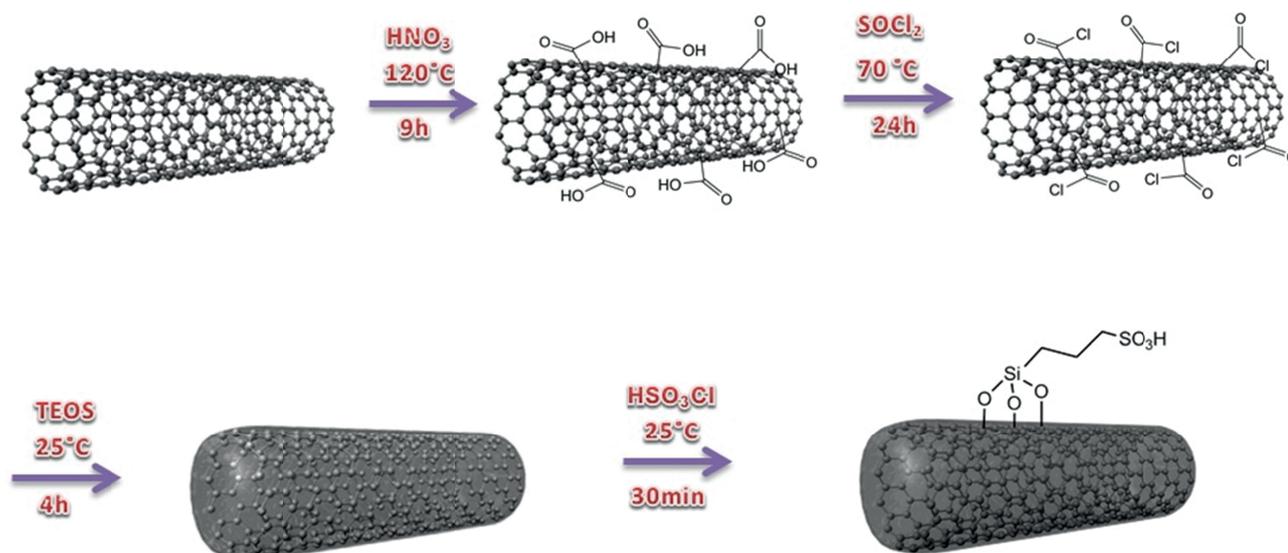


Fig. 1. Schematic of the CNTs functionalization process.

temperature overnight and further dried in 70 °C for 12 h. Lastly, the fabricated membranes were annealed at 120 °C overnight to stabilize the microstructure of Nafion. The same procedure was used to fabricate the recast Nafion.

## 2.4. Characterization

### 2.4.1. Field Emission Scanning Electron Microscope (FESEM)

A FESEM (HITACHI S-4160, Japan) is used to visualize very small topographic details on the surface or cross-section area of the fractured objects in liquid nitrogen. Prior to the analysis, the samples were coated with a thin layer of gold.

### 2.4.2. Water uptake

A vital property of any membrane is its water uptake rate ( $WUR$ ), which provides information about the water retention capacity of the membrane. Water uptake can be calculated from the difference in weights between the wet and dry samples. To attain precise results, this process was repeated several times [16]. The percentage of water uptake was then calculated by the following equation:

$$WU\% = \left( \frac{m_{wet} - m_{dry}}{m_{wet}} \right) \times 100 \quad (1)$$

where  $m_{wet}$  and  $m_{dry}$  are the weights of wet and dry membranes, respectively.

### 2.4.3. Ion exchange capacity (IEC)

The ion exchange capacity ( $IEC$ ) in meq/g is presented as the ratio of moles of sulfonic acid groups per gram of dried membrane ( $W_{dry}$ ). The titration method was employed to measure the value of ion exchange capacity ( $IEC$ ). The  $IEC$  is measured using Eq. (2).

$$IEC(\text{meq} / \text{g}) = \left( \frac{V_{NaOH} \times N_{NaOH}}{W_{dry}} \right) \times 100 \quad (2)$$

where  $V_{NaOH}$  and  $N_{NaOH}$  are the volumes of NaOH used up in titration and the concentration of NaOH, respectively.

### 2.4.4. Proton Conductivity

Ionic conductivity is usually measured based on proton conducting membrane resistance at room temperature by AC impedance spectroscopy. A four-point probe apparatus, manufactured by Bekktech Company, was employed to measure in-plane bulk conductivity. The proton conductivity was calculated by Eq. (3).

$$\sigma = L / (R \times A) \quad (3)$$

where  $L$  is the membrane thickness,  $A$  is the membrane cross-sectional area, and  $R$  is the resistance.

### 2.4.5. Methanol permeability

A system including two tanks connected by a thin polymer film was used to calculate the methanol

permeability. One of the tanks was filled with methanol (cell A) and the other tank was filled with distilled water (cell B). These tanks were stirred constantly, and the concentration of methanol in the water was measured by a gas chromatography apparatus (model 890, Hewlett-Packard Company). The methanol permeability was then calculated using the Eq. (4).

$$C_{B(t)} = \frac{A}{V_B} \times \frac{DK}{L} \times C(\Delta t) \quad (4)$$

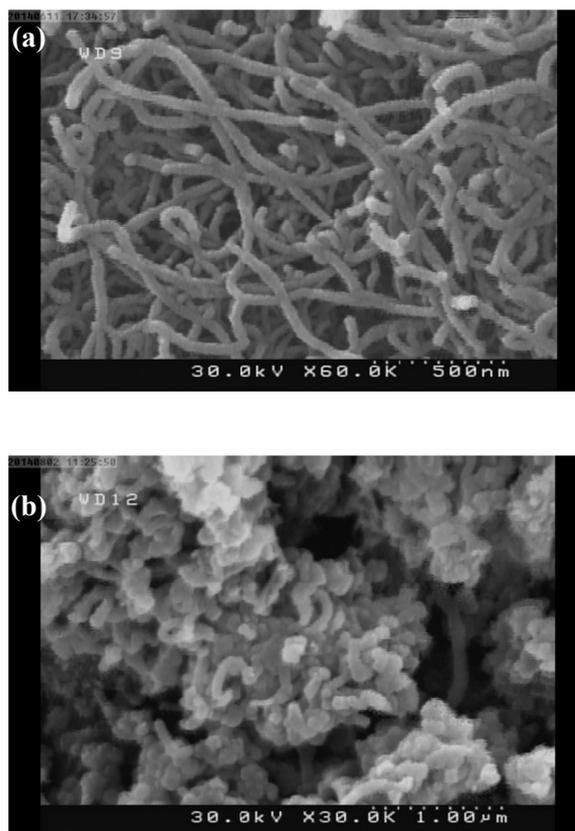
where  $C_{B(t)}$  is methanol concentration in cell B (mol/l), the product of  $DK$  is the methanol permeability of the membrane ( $\text{cm}^2/\text{s}$ ),  $C$  is the concentration of methanol in Cell A (mol/l),  $A$  is the cross-section area of membrane ( $\text{cm}^2$ ),  $L$  is the thickness of membrane (cm),  $V_B$  is the volume of each tank, and  $\Delta t$  is the time of each methanol crossover measurement.

### 3. Results and discussion

Based on the chemistry of the sulfonate group and the presence of  $\text{O}^-$  in its structure, sulfonate groups have been identified as inorganic groups which are capable of proton exchange. Accordingly, they have been investigated as proton conductors for applications in fuel cells, hydrogen sensors, and hydrogen separation membranes. Sulfonated molecules exhibit high water solubility, and consequently, protons are incorporated into the materials as charge-compensating defects when the sulfonate are doped with cations [19].

FESEM was used to investigate the surface modification of CNTs and observe the construction of the silica layer on the surface of CNTs. Figure 2 illustrates the obtained images from CNT and CNT@SiO<sub>2</sub>. Comparing the FESEM images seen in Figure 2 (a) and (b), the CNTs have been successfully coated by a thin layer of silica. As can be seen in Figure 2, the CNTs' diameter was increased by the addition of silica, which could be used as evidence for the successful coating of a silica layer on the surface of the CNTs. This layer is a substrate for future functionalization of CNTs.

The main reason for using only 1 wt% of CNT@SiO<sub>2</sub>-SO<sub>3</sub>H in preparation of Nafion membranes is due to the fact that an increase in concentration of CNT in membranes can lead to an increase in the probability of charge transferring across the prepared membranes. In order to prevent such phenomenon and minimize the risk of forming a short-circuit in the final membranes,



**Fig. 2.** Field emission Scanning electron microscope (FESEM) images of (a) CNT and (b) CNT@SiO<sub>2</sub>.

the concentration of CNTs used in PEMs must be less than the amount of the percolation threshold. The permissible limit in a polymeric membrane for percolation threshold has been reported at about 2 wt% [20].

In Figure 3, the value of water uptake ( $WU$ ), ion exchange capacity ( $IEC$ ),  $\lambda$  of the recast Nafion, and the prepared composite membrane containing 1 wt% of nanoparticles are depicted. The ratio of mole number of water molecules to the fixed-charged sulfonate groups, denoted as lambda ( $\lambda$ ), was calculated from the following equation:

$$\lambda = \frac{WU}{IEC \times M_{water}} \quad (5)$$

where  $WU$ ,  $IEC$  and  $M_{water}$  are the water uptake, ion exchange capacity and molecular weight of water (18 g/mol), respectively. In fact, the average number of water molecules per ionic group  $\lambda$  shows how many water molecules can be bound to the ionic groups of polyelectrolytes. Hydration of the polyelectrolytes and proton conduction across the membranes are often explained with  $\lambda$  [4].

As can be seen, by adding CNT@SiO<sub>2</sub>-SO<sub>3</sub>H to the

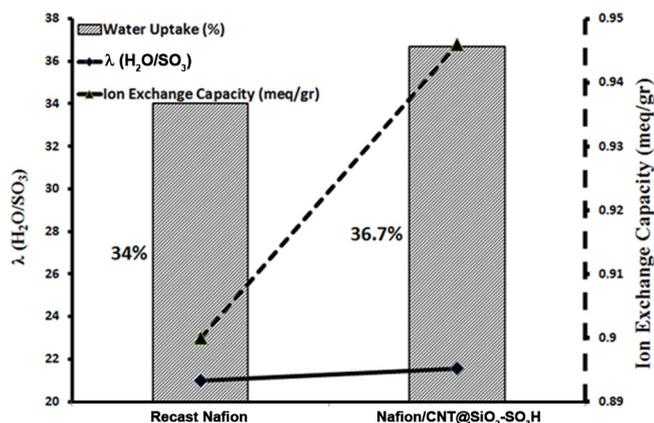


Fig. 3. Comparison of water uptake, ion exchange capacity, and  $\lambda$  in recast Nafion and Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H (1 wt%).

Nafion membrane, the water uptake increased from 34 wt% for the recast Nafion to 36.7 wt% for the prepared nanocomposite membrane. Moreover, IEC also increased and  $\lambda$  was enhanced from 0.900 to 0.945.

As a conclusion, the value of ion exchange capacity and water uptake of the membrane containing CNT@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticle is higher than those of the recast Nafion sample. Moreover, by using the sulfonate groups in surface modification of nanoparticles, in addition to be considered as an acidic proton exchanger group the water absorption in the membrane containing this nanoparticle is higher than other membranes because of a good interaction between O<sup>-</sup> groups on the surface of CNTs and H<sub>2</sub>O molecules. So, by adding the sulfonate decorated CNTs to the Nafion membrane the *WU* and *IEC* of the prepared membrane were increased.

This analysis was applied to investigate the effect of surface modified nanoparticles, especially CNT@SiO<sub>2</sub>-SO<sub>3</sub>H, on the proton conductivity of composite membrane. Figure 4 illustrates the effect of the modified CNTs on the proton conductivity of Nafion nanocomposite membranes in the range of 25-90 °C. With regard to the results, the proton conductivity of recast Nafion and Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H (1 wt%) were calculated at room temperature as 0.086 and 0.0913 S/cm, respectively. Phosphonated and sulfonated polymers are known to conduct protons at low water content [21]. An increase in the proton conductivity with the addition of CNT@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticle is related to the enhanced IEC as a result of introducing sulfonic acid groups on the surface of the nanoparticles. Moreover, CNT@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticles might absorb water on their surfaces through a strong interaction with surface -SO<sub>3</sub>H groups and the formation

of hydrogen bonds, leading to enhanced water retention and proton conductivity.

The Arrhenius equation was used to prove the dependency of proton conductivity to temperature in different membranes. According to the following equation,  $E_a$ ,  $\sigma$  and  $\sigma_0$  are the activation energy of proton conduction, the proton conductivity, and pre-exponential factor in this equation, respectively.  $T$  is the absolute temperature and  $R$  is the universal gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>).

$$\sigma = \sigma_0 e^{-E_a/(RT)} \quad (6)$$

Arrhenius plots of conductivity (logarithm of conductivity v.s 1/ $T$ ) for the recast Nafion<sup>®</sup> and modified Nafion<sup>®</sup> membranes at different temperatures are shown in Figure 4 (b). Activation energy was calculated using the Arrhenius plot and Eq. (6). The slope of these plots

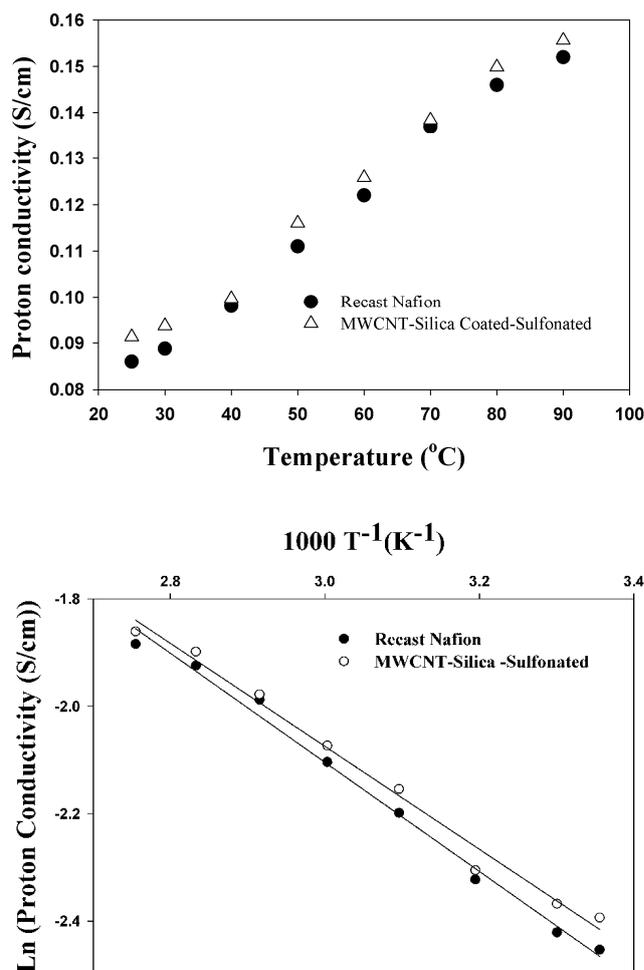


Fig. 4. (a) Proton conductivity of Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H in the temperature range of 25-90 °C in comparison with recast Nafion. (b) Demonstrates the Arrhenius amount of proton conductivity for Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H in comparison with recast Nafion.

denotes the activation energy ( $E_a$ ) of the proton exchange at different temperatures.

According to the results from the Arrhenius plots, the activation energies of recast Nafion and Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H are calculated as 0.1140 and 0.1066 (kJ/kmol), respectively. As can be seen, the activation energy of the composite membrane, which includes sulfonate groups, is lower than that of the recast Nafion membrane. Sulfonate groups reduced the activation energy of O-H bond by exposing the ionic groups locating on the chains of Nafion facilitating the movement of protons through the Grotthus mechanisms.

Figure 5 compares the amount of methanol permeability for the prepared membranes at room temperature. The values of methanol permeability are equal to  $2.25 \times 10^{-6}$  and  $2.91 \times 10^{-7}$  cm<sup>2</sup>/S for Nafion and Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H, respectively. It is seen that the methanol permeability of the membrane including Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H has been noticeably reduced in comparison with the recast Nafion, this is mostly due to shrinking and stretching out of the route of methanol diffusion. The greatest reduction in methanol permeability occurs in the membrane including CNT@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticles and could be attributed to the reduced size of nano channels and obstruction of methanol's permeation route in the Nafion matrix by the presence of CNTs and also to the barrier role of these particles against methanol transfer [14].

With regard to membranes' modification, two factors, namely, proton conductivity and methanol permeability are simultaneously concerned. In fact, potential of the new composite membranes for direct methanol fuel cell (DMFC) is evaluated using the ratio of proton conductivity to methanol permeability, called selectivity

( $\phi$ ) (S.s/cm<sup>3</sup>). Generally, membranes exhibiting higher selectivity than Nafion® 117 indicate a higher potential to improve electrochemical cell performance. This is impossible unless high performance membrane electrode assemblies (MEA) can be manufactured using novel composite membranes which include organic or inorganic materials with higher selectivity. The selectivity of membrane was calculated by the following equation:

$$\text{Selectivity}(\phi) = \frac{\text{Value of Proton Conductivity}}{\text{Value of Methanol Permeability}} \quad (7)$$

The value of  $\phi$  for the recast Nafion and Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H (1 wt%) are calculated at 38222 and 313745 S.s/cm<sup>3</sup>, respectively, at room temperature. As can be noted in Figure 5, the membrane modified by CNT@SiO<sub>2</sub>-SO<sub>3</sub>H has higher selectivity in comparison to the recast Nafion.

As mentioned above, the addition of modified CNTs to the Nafion membrane can cause the methanol permeability to be decreased because of the barrier role of inorganic added CNTs in the route of methanol transfer. On the other hand, the presence of sulfonated groups on the surface of modified CNTs improved the interaction of H<sup>+</sup> and nano channels of the Nafion structure as well as increased the proton conductivity of the prepared modified membranes. Decreasing the methanol permeability and increasing the proton conductivity in a wide range of temperatures caused the selectivity of the prepared membrane, one of the most important performance parameters of PEMs, to be improved.

#### 4. Conclusion

The sulfonate-functionalized silicon dioxide coated carbon nanotube (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H) nanoparticles were successfully synthesized from tetraethoxysilane (TEOS) and chlorosulfonic acid. According to the results attained from proton conductivity, methanol permeability, ion exchange capacity and other analyzes, the nanocomposite membranes prepared with Nafion and (CNT@SiO<sub>2</sub>-SO<sub>3</sub>H) nanoparticles exhibited a higher level of proton conductivity, higher water retention and lower methanol permeability as compared to the recast Nafion membrane. Proton conductivity was higher in the modified-CNTs/Nafion membrane than the Nafion membrane in a wide range of temperature. Methanol permeability decreased from  $2.25 \times 10^{-6}$  cm<sup>2</sup>/S for the Nafion membrane to  $2.91 \times 10^{-7}$  cm<sup>2</sup>/S for the modified composite membrane.

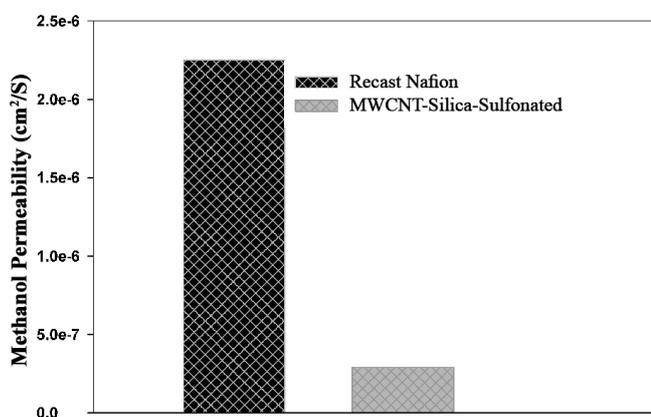


Fig. 5. Methanol permeability of Nafion/CNT@SiO<sub>2</sub>-SO<sub>3</sub>H in comparison with recast Nafion selectivity (S.s/cm<sup>3</sup>).

Moreover, the selectivity of this fabricated membrane base on Nafion and CNT@SiO<sub>2</sub>-SO<sub>3</sub>H nanoparticles is more than 8-fold higher than that of the recast Nafion<sup>®</sup> 117, demonstrating its promising potential for DMFC applications.

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