# Preparation and Characterization of MWCNT-*g*-Poly (Aniline-*co*-DABSA)/Nafion® Nanocomposite Membranes for Direct Methanol Fuel Cells

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Multiwalled carbon nanotube (MWCNT)-*g*-poly (aniline-*co*-2,5-diaminobenzenesulfonic acid) (DABSA) reinforced Nafion® nanocomposite membranes were prepared and characterized for direct methanol fuel cells (DMFCs). The nanocomposite membranes with approximately 90 μm thickness were prepared by the water assisted solution casting method. To evaluate the properties of nanocomposite membranes for DMFC applications, the nanocomposite membranes were characterized by methanol and water uptake, thermal stability, and ion exchange capacity (IEC). Furthermore, oxidative stability measurements in terms of the hydrogen peroxide decomposition rate that represent the oxidative stability of the membranes were examined. The methanol uptake values of the nanocomposite membranes were dramatically decreased compared to the cast Nafion® membranes. The IEC values of the nanocomposite membranes were increased about 30% compared to the cast Nafion® membrane.

**Key Words :** MWCNT-*g*-poly (aniline-*co*-DABSA), Nafion®, Proton exchange membrane, Direct methanol fuel cells

## Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as a promising power device for portable electric devices. The PEMFCs such as direct methanol fuel cells (DMFCs) provide low cost and high energy efficiency in low operating temperature for various small devices.[1-3] Proton exchange membrane (PEM) is a key component in the PEMFCs that has role as a proton conductor, methanol barrier and mechanical separator between anode and cathode.[1,2,4] The Nafion® membrane is one of well-known PEMs for fuel cell applications that have microscale phase-separated structures with approximately 2-5 nm ionic channels comprised of hydrophobic backbones with hydrophilic side chains having sulfonate groups.[5] Even though Nafion® membranes have high proton conductivity with good thermal and mechanical stability caused by Teflon backbone structure, a drop-off in the fuel efficiency has been observed due to high methanol crossover in the cathodic direction. Furthermore, due to low temperature operation, carbon monoxide is adsorbed on the electrode surface negatively affects the membrane electrode assembly (MEA) performance over the long term.[6]

The following should be considered for selecting a PEM in fuel cell applications: (1) polymer backbone structures of the membranes related to the chemical and thermal stability in long-term usage, (2) microstructure of the membrane for methanol barriers and (3) selective cross linking without disrupting the ionic channels for proton conduction.[1,2] Among various nanocomposite membranes as a PEM, multiwalled carbon nanotubes (MWCNTs) reinforced Nafion® nanocomposite membranes are considered a promising approach for fuel cell applications which can exploit the synergetic effect of the Nafion® polymer. Several approaches have been proposed for preparing nanocomposites based on the Nafion® membrane with impregnated functionalized MWCNTs.[7-9] Functionalized MWCNTs grafted with sulfonate groups have resulted in improved proton conductivity in PEMs for DMFCs; thus, the membrane performance is related to the amount of ionic groups in the membrane.[10] On the previous report, a maximum of 20% of MWCNTs could be functionalized with sulfonate groups.[11] Further functionalization of MWCNTs results in damaging the MWCNTs intrinsic structural properties. The amounts of grafted sulfonate moieties in the functionalized MWCNTs have influence on the final properties of the nanocomposite for DMFCs.

Polyaniline is a water-soluble conducting polymer prepared from *p*-aminobenzoic acid.[12] Particularly, functionalization-controlled conductivity increment is one of the attractive properties related to metallic polymers and opto-nanoelectronic technologies.[13-15] Sulfonate groups can be introduced to the base polymer by direct sulfonation or by polymerization of sulfonated monomers. In addition, aniline can be used to debundle MWCNTs without damaging their

graphene structure. Aniline is very effective in debundling MWCNTs from 200 to 50 nm.[16] Thus, strategies can be developed for both debundling MWCNTs and further addition of sulfonate groups to aniline by polymerization followed by sulfonation.[17]

In this study, nanocomposite membranes with functionalized MWCNTs as a PEM were prepared and characterized for fuel cell applications. Functionalized MWCNTs were prepared with polyaniline. The polyaniline was further conjugated with 2,5-diaminobenzenesulfonic acid (DABSA) and sulfonation was done by direct mixing of mild a sulfonating agent. Polymerzation of aniline can be controlled by adding a fixed amount of aniline to the functionalized MWCNTs. For aniline polymerization, DABSA was used to obtain proper sulfonate functionality. Polyaniline conjugated with DABSA was grafted to MWCNTs (MWCNT-*g*-poly (aniline-*co*-DABSA)) and characterized by Fourier transform infrared spectroscopy (FT-IR). 1 to 5 wt % of the prepared MWCNTs based on the Nafion® polymer weight were then successfully incorporated into Nafion® membranes by the water assisted solution casting method. The sulfonation was done with the aim to obtain microphase-separated structures and ion-rich domains form channels that are favorable for proton transport. Ion rich domains can significantly boost the ion exchange capacity (IEC) of the nanocomposite membranes. Additionally, molecular level mixing between the MWCNTs polymeric chain with the Nafion® matrix can significantly decrease the methanol cross over through the nanocomposite membranes. More importantly, aniline doped polymeric material is believed to achieve more oxidative stability while a DMFC is operated at a lower temperature.[17] Water and methanol uptake of the membranes showed improved properties of the PEM for DMFC applications. Enhanced IEC of the nanocomposite membranes was obtained by thermo acidic pretreatment of the membranes. Oxidative stability of the prepared nanocomposite membranes compared to Nafion® membranes ensures the improved oxidative stability of the prepared nanocomposite membranes for long term fuel cell applications. These advanced results obtained from the nanocomposite membranes can be effectively applied to DMFC applications.

## Experimental

**Chemicals and Materials.** 2,5-Aminobenzenesulfonic acid (DABSA), diphenyl amine 4-sulfonic acid (DPASA), poly (ethylene glycol)-bis-(3-aminopropyl), thionyl chloride and ammonium persulfate (APS) from Sigma-Aldrich (St. Louis, Mo, USA). 4-vinylaniline (VA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPSA) from Alfa-Aesar (Ward Hill, MA, USA) and 5% Nafion® solution (D521) was brought from DuPont (USA). Multiwalled carbon nanotubes (MWCNTs), 30 nm in average diameter, 1-25 μm long and over 95% pure, were purchased from CNT Co., Ltd (South Korea) and used without further purification.

**Preparation of Functionalized MWCNTs.** MWCNT-*g*-

poly (aniline-*co*-DABSA) was prepared by the following stepwise procedures according to the reported method.[18-20] Briefly, MWCNTs were firstly oxidized using concentrated $HNO_3$. Oxidized MWCNTs were then refluxed with thionyl chloride under inert environment at 65 °C for 24 h to obtain MWCNT-COCl. The mixture was then stirred for 12 h at 70 °C to remove excess thionyl chloride. MWCNT-COCl was then refluxed with 2,5-diaminobenzene sulfonic acid in tetrahydrofuran at 60 °C for 48 h to obtain amine functionalized MWCNTs.[18] A little amount, 98 μL, of vinylaniline solution was reacted with the amine functionalized MWCNT for 1 h at 5 °C. After that, functionalized MWCNTs were sonicated with diphenylamine-4-sulfonic acid and 2-acrylamido-2-methyl-1-propene sulfonic acid solution for 10 min. A fixed amount of pre-cooled ammonium persulfate solution was then added to the solution.[19] Prepared MWCNT-*g*-poly (aniline-*co*-DABSA) was then washed, filtered and dried in a vacuum oven. And poly (aniline-*co*-DABSA) was prepared by the above procedures except MWCNTs. Effective copolymerization of DABSA with aniline was strongly related to the amount of DABSA treated with aniline.[20] Then FT-IR spectroscopy was employed to characterize the surface groups of MWCNT-*g*-poly (aniline-*co*-DABSA) and MWCNT-poly (DABSA).

**Preparation of the Nanocomposites.** To prepare nanocomposite membranes, a certain amount of functionalized MWCNTs was reinforced into the Nafion® membrane by the water assisted solution casting method. An amount of the selected functionalized MWCNTs ranging from 1-5 wt % based on the Nafion® polymer weight was added to the Nafion® solution. The functionalized MWCNT (f-MWCNT) was first dispersed with a certain amount of water by sonication for 15 minutes. After that, the solution was dispersed in the Nafion® solution by sonication for 30 minutes and the well dispersed solution was then poured into a polytetrafluoroethylene (PTFE) dish and placed in a vacuum oven at 60 °C for 14 h to cast a membrane. The thickness of the prepared nanocomposite membrane was approximately 90 μm.

**Characterization of the Nanocomposites.** To investigate the membrane catalytic activity against the free radicals produced in an electrode system, the $H_2O_2$ decomposition test was performed for the membranes as reported by Xing *et al*.[21] The concentration of the $H_2O_2$ solution was determined by redox-titration with a 0.1 $KMnO_4$ solution in an acidic environment. And the prepared membranes were observed under an optical microscope (Axioplan 2, Carl Zeiss, Germany).

To investigate properties of the nanocomposite membranes for DMFC applications, water and methanol uptake and ion exchange capacity were examined in this study. Water and methanol uptake characterizations were investigated with the following procedures. For water uptake measurements, membranes (40 mm × 40 mm) were immersed in deionized (DI) water for 24 h at room temperature (RT) and the weight of the swollen membranes was measured after removing the excess water on the surface of the membranes with a paper

*MWCNT-g-Poly(Aniline-co-DABSA)/Nafion*

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towel. The weight percentage for the water uptake of the membranes was obtained with the following equation:

$$\text{Weight uptake (\%)} = (W_w - W_d)/W_d \times 100$$

, where $W_w$ is the weight of the swollen membrane and $W_d$ is the weight of the dried membrane.

The methanol uptake measurements were performed with the above procedure using 1 M methanol solution instead of DI water.

Thermo acidic pretreatment of the membranes was done to obtain proper IEC values of the nanocomposites. At first, membranes were treated with 0.5 M $H_2SO_4$ for 24 h at RT followed by reflux and washing with DI water for several times. After that, the membranes were dried in oven at 100 ℃ for 6 h. The acid treated membrane was then treated for IEC value measurements. The IEC values of the MWCNT-$g$-poly (aniline-$co$-DABSA)/Nafion®, poly (aniline-$co$-DABSA)/Nafion® and MWCNT/poly (aniline-$co$-DABSA)/Nafion® membranes were examined with a conventional titration method. Briefly, to replace $H^+$ ions with $Na^+$ ions in the membrane, nanocomposite membranes (40 mm × 40 mm) were placed in 1 M NaCl solution (100 mL) for 24 h at RT. Then, 20 mL of the 100 mL-solution having released $H^+$ ions was titrated using 0.01 M NaOH solution with phenol-phthalein indicator. The IEC value of the nanocomposite membrane was obtained by the following equation:

$$\text{IEC}_{exp} \text{ (meq/g)} = (0.01 \times V_{NaOH} \times n) / W_{dry}$$

, where $V_{NaOH}$ is the used volume of the 0.01 M NaOH solution in the titration experiment. n is the factor related to the ratio of the volume of the NaCl solution (100 mL) for the membrane immersion to the used volume (20 mL) for titration. Thus, n is 5 in this study. $W_{dry}$ is the dry weight of the following nanocomposite membrane.

**Results and Discussions**

**Characterization of Functionalized MWCNTs.** The functional groups on the surface of functionalized MWCNTs were characterized by FT-IR spectroscopy. The FT-IR spectra of MWCNT-$g$-poly (DABSA) and MWCNT-$g$-poly (aniline-$co$-DABSA) were respectively shown in Figure 1. The two band peaks at 3338 and 3405 cm$^{-1}$ in Figure 1(a) were assigned to the primary amine attached to the MWCNTs. After conjugation followed by polymerization with aniline, the two peaks disappeared and produced one broad peak over 3400 cm$^{-1}$ in the Figure 1(b) usually assigned to the hydroxyl groups due to presence of water while experiment. The presence of the secondary amide groups on the oxidized MWCNT surface was characterized for further polymerization with aniline. The two band peaks at 1600 and 1621 cm$^{-1}$ were due to carbonyl amide (C=O stretching) in MWCNT-$g$-poly (aniline-$co$-DABSA) and MWCNT-$g$-poly (DABSA) respectively. The peaks around 1500 cm$^{-1}$ in the Figure 1(b) were assigned to secondary amide could be resulted for successful polymerization to the amine function-alized MWCNTs with aniline.[22-24] The medium band peaks
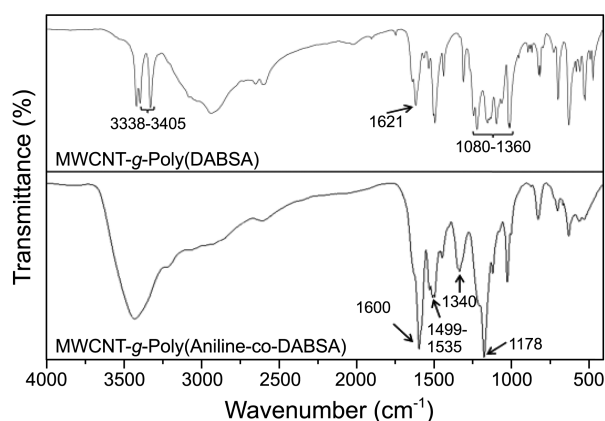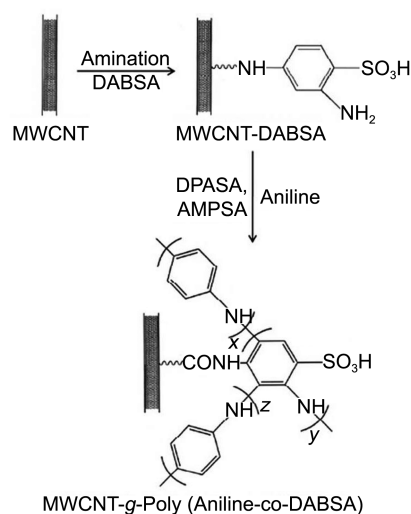


**Figure 1.** FT-IR spectra of (a) MWCNT-$g$-poly (DABSA) and (b) MWCNT-$g$-poly (aniline-$co$-DABSA).

around 1080-1360 cm$^{-1}$ in Figure 1(a) were assigned to C-N stretching due to DABSA attached to the MWCNTs which was not present in the MWCNT-$g$-poly (aniline-$co$-DABSA) nanocomposites due to the sulfonation by ammonium persulfate, resulted in peaks at 1178 and 1340 cm$^{-1}$ as shown in Figure 1(b).

**Dispersion of the Functionalized MWCNTs.** The pre-pared functionalized MWCNTs were reinforced into the Nafion membrane to prepare MWCNT/Nafion nanocompo-site membranes. Dispersion of the MWCNTs in the Nafion membrane is related to the physical properties of the nano-composite membranes. Thus, well-dispersion of MWCNTs in the membrane is necessary to obtain enhanced properties and stability of the nanocomposite membranes in long-term usage. Sulfonated MWCNTs could well dispersed in the Nafion membrane because the same functional groups were on the Nafion polymer chain.[10] MWCNT-$g$-poly (aniline-$co$-DABSA) with large amount of sulfonate groups attached to the MWCNTs by copolymerization. From the chemical structures of functional groups in the schematic diagram (Scheme 1), it could be expected that one amine functional



**Scheme 1.** Preparation procedures of MWCNT-$g$-poly (aniline-co-DABSA).
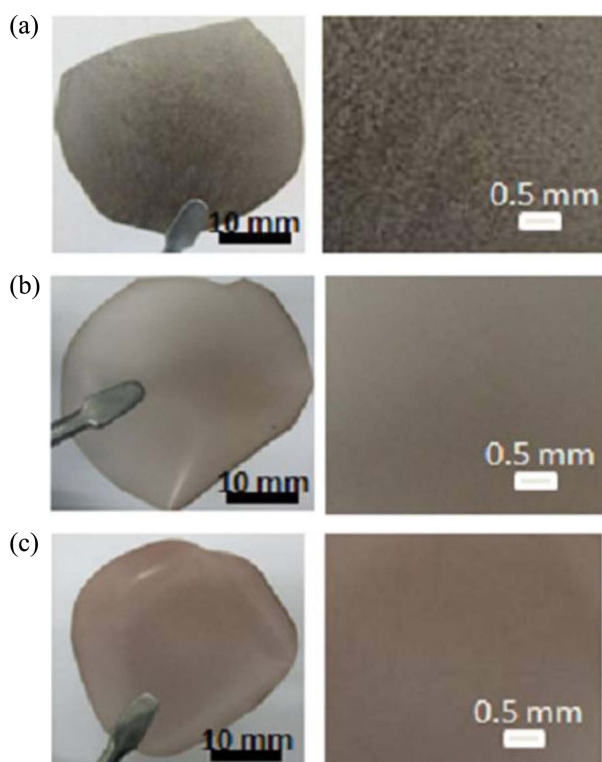
**Figure 2.** Dispersion of 3 wt % MWCNTs in the nanocomposite membranes by observing optical images of the membranes. (a) MWCNT/poly (aniline-*co*-DABSA)/Nafion®, (b) poly (aniline-*co*-DABSA)/Nafion® and (c) MWCNT-*g*-poly (aniline-*co*-DABSA)/ Nafion® membranes.

group of MWCNTs can incorporate at least 3 sulfonate groups through successful copolymerization. Figure 2 shows the dispersion of the three types of MWCNTs in the nanocomposite membranes. To investigate the dispersion effect, 3 wt % of functionalized MWCNTs was reinforced into the Nafion polymer solution followed by solution casting. As shown in Figure 2(a), MWCNTs were blended with poly (aniline-*co*-DABSA) at a 1:1 ratio, followed by incorporation into the Nafion polymer. The MWCNT dispersion was not good due to the inherent self-assembly property of the MWCNTs for the solution casting procedure. On the other hand, poly (aniline-*co*-DABSA) and MWCNT-*g*-poly (aniline-*co*-DABSA) showed good dispersion in the nanocomposite membranes because of the functional groups (Figure 2(b) and 2(c)).

**Oxidative Stability Test.** Reduction of the performance of PEMs in fuel cell applications was directly related to the formation of HO and $HO_2$.[25-27] Aniline is much more stabilized while doped with sulfonic acid resulting in a high tolerance against free radicals produced during membrane electrode assembly (MEA) operations in DMFC applications. Here in Figure 3, we examined the oxidative stability of the prepared nanocomposite membranes compared to the Nafion membrane. To understand the oxidative stability as well as the catalytic activity of hydrogen peroxide decomposition, the prepared nanocomposite membranes were treated in 5 wt % of $H_2O_2$ solution. The results of the $H_2O_2$ decomposi-
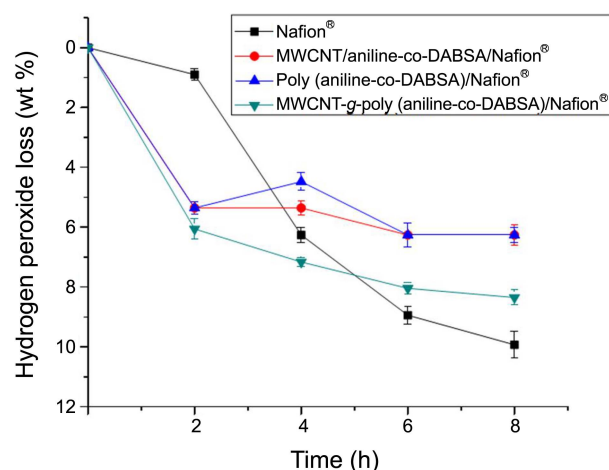


**Figure 3.** Decomposition rate of $H_2O_2$ in the three kinds of nanocomposite membranes.

tion rate for the nanocomposite membranes showed that the nanocomposite membranes were more resistant to $H_2O_2$ decomposition. After 24 h of immersion in $H_2O_2$ solution, the treated membranes were dried in oven and weighed. MWCNT-*g*-poly (aniline-*co*-DABSA)/Nafion membrane lost 0.1678%, where Nafion membrane lost 0.271% and MWCNT/aniline/DABSA/Nafion membrane lost around 1.285% based on the initial dried weight. Thus, a lower $H_2O_2$ decomposition rate for the MWCNT-*g*-poly (aniline-*co*-DABSA)/Nafion membrane shows that the resistivity against the oxidative radicals produced during MEA operations in DMFCs.

**Water and Methanol Uptake, and IEC of the Nanocomposites.** Water uptake values of the nanocomposites membranes are shown in Figure 4. The results show that water uptake values of MWCNT-*g*-poly (aniline-*co*-DABSA)/ Nafion membranes were slightly increased when the impregnation was 1-3 wt %. The ionic channel distribution for water diffusion through the membrane is important when different amount of loading is applied. Membrane properties can be significantly improved when the reinforced functionalized MWCNTs on loading ranges from 1-5 wt % based on
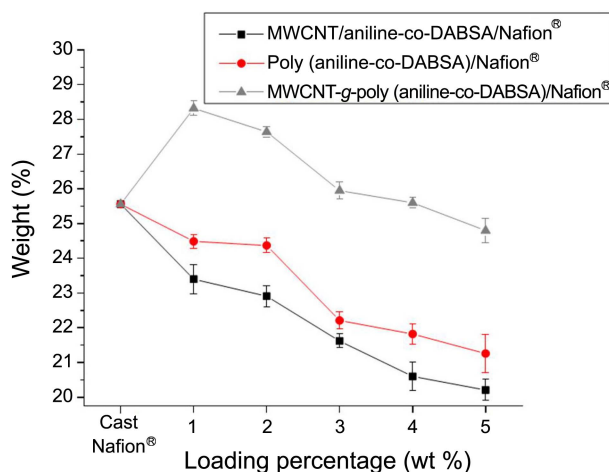


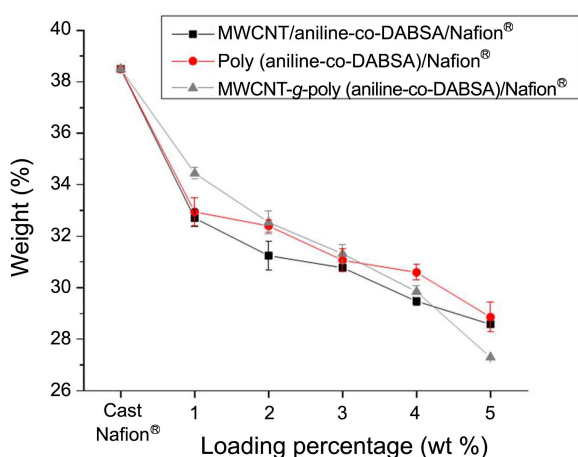**Figure 4.** Water uptake values of the nanocomposite membranes.

**Figure 5.** Methanol uptake values of the nanocomposite membranes.



**Figure 6.** Ion exchange capacity values of the nanocomposite membranes.

the Nafion polymer weight.[28] MWCNT-*g*-poly (aniline-*co*-DABSA)/Nafion nanocomposite membranes showed enhanced water uptake values up to 1-2 wt % loading of the f-MWCNTs. Afterward, further loading of the f-MWCNTs on the Nafion membranes did not improved in the water uptake values. For poly (aniline-*co*-DABSA)/Nafion and MWCNT/poly (aniline-*co*-DABSA)/Nafion nanocomposite membranes, the water uptake properties showed a similar trend with a decrement in the water uptake values compared to Nafion membrane. Functionalized polymeric group or just mixed with MWCNTs into the Nafion membranes resulted in lowering the water uptake values. The inherent water diffusion channels of Nafion polymer were disrupted with the addition of the two added materials resulted in decrement of the water uptake values of Nafion nanocomposite membranes and intensified with higher loading.

In Figure 5, the methanol uptake values of the nanocomposite membranes are shown for DMFC applications. High methanol permeation through the Nafion membranes results in decreased fuel efficiency in fuel cells. As shown in the Figure, all the prepared nanocomposite membranes were effective against methanol diffusion through the membranes. Approaches for controlling the microstructures of the Nafion membrane *via* sufficient cross-linking by the groups attached to the nanomaterials are promising. The main polymeric chain of poly (aniline-*co*-DABSA) was very effective in reducing the methanol uptake values through the membranes.

It is important to consider the electrochemical properties of a PEM in DMFCs. Figure 6 shows the IEC values of the nanocomposite membranes. The three kinds of prepared nanocomposite membranes showed a significant increment in IEC values. MWCNT/poly (aniline-*co*-DABSA)/Nafion® membranes showed very small increment in the IEC value up to 4 wt % of the blended nanocomposite loading to the Nafion® matrix. The increment was mainly due to the copolymerization of DABSA to MWCNTs which resulted in the tuning of the synergetic effect for the H⁺ mobility of the sulfonate group in the nanocomposites. A similar trend was observed for poly (aniline-*co*-DABSA)/Nafion® nanocom-
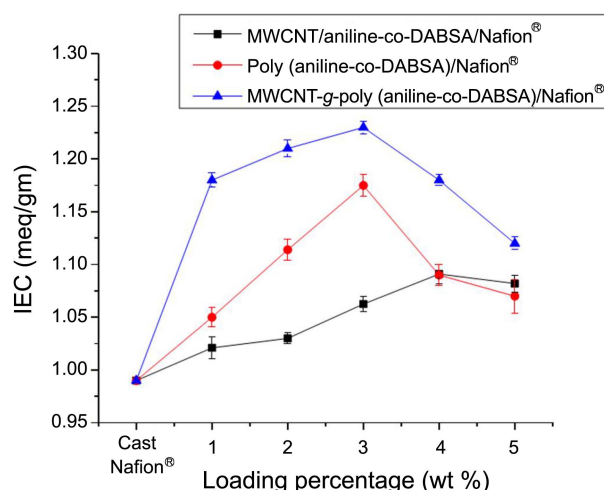
posites. In the case of MWCNT-*g*-poly (aniline-*co*-DABSA), IEC values were significantly increased due to the effective grafting of ion rich channels. Higher loading of f-MWCNTs, over 4 wt %, into the Nafion® polymer matrix resulted in lowering the IEC values due to the excessive functional groups of MWCNTs. Polymerization of aniline conjugated with DABSA has resulted in a higher degree of sulfonation (DS). From the IEC value of MWCNT-*g*-poly (aniline-*co*-DABSA)/Nafion® membranes we can assume the 30% DS value was obtained for the prepared nanocomposites. Therefore, the above results mean that the methanol crossover of the Nafion® membrane could be reduced by the amount of the prepared functionalized MWCNTs added. Water uptake properties were enhanced by the addition of MWCNT-*g*-poly (aniline-*co*-DABSA) to the Nafion® membranes. Furthermore, the IEC values of the MWCNT-*g*-poly (aniline-*co*-DABSA)/Nafion® membranes increased dramatically when the functionalized MWCNTs loading ranged from 1-4 wt %.

**Conclusion**

Functionalized MWCNTs with aniline and DABSA were prepared and reinforced into the Nafion® membranes as a PEM for DMFC applications. The prepared nanocomposite membranes were prepared by the solution casting to increase the IEC value and decrease the methanol permeability. Increased IEC values of the nanocomposite membranes were evaluated as a higher DS value of the prepared MWCNT-*g*-poly (aniline-*co*-DABSA) nanocomposite. Methanol uptake values of the membranes decreased by a fold compared to the Nafion® membrane. Additionally, dispersion of the prepared nanocomposites into Nafion® polymer was enhanced by the increased sulfonate groups of the nanocomposites. The measured oxidative stability in terms of the $H_2O_2$ decomposition rate represents the tolerance against free radicals produced in the fuel cells. Thus, in the range of 1-4 wt % loading of MWCNT-*g*-poly (aniline-*co*-DABSA) to Nafion® membrane can be commercially useful for DMFC applications.

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