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Single-walled carbon nanotube/Nafion composites as methanol sensors

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Abstract

Single-walled carbon nanotube (SWCNT)/Nafion composite films were fabricated on an interdigitated electrode by using a simple casting method. Nafion acts as a polymer backbone to give stable and homogeneous cast thin films. The potential use of the composites as sensors of methanol concentration in water was investigated. The composites are operative even at ambient temperatures, and respond quickly to concentration changes. The resistance increases significantly with increasing concentration between 0.5 M and 4 M. The composites may be useful as a material to measure the concentration of methanol for direct fuel cells.

Single-walled carbon nanotube/Nafion composites as methanol sensors

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ARTICLE INFO

ABSTRACT

Single-walled carbon nanotube (SWCNT)/Nafion composite films were fabricated on an interdigitated electrode by using a simple casting method. Nafion acts as a polymer backbone to give stable and homogeneous cast thin films. The potential use of the composites as sensors of methanol concentration in water was investigated. The composites are operative even at ambient temperatures, and respond quickly to concentration changes. The resistance increases significantly with increasing concentration between 0.5 M and 4 M. The composites may be useful as a material to measure the concentration of methanol for direct fuel cells.

1. Introduction

Carbon nanotubes (CNTs) rank among the most exciting new developments in modern science and engineering. CNTs have a great potential to be used as nano-scale electronic devices, such as field effect transistors, single-electron transistors, and nano scale p–n junctions. In addition, CNTs have become promising candidates in scope tips, field emitters, and chemical sensors [1,2]. The electrical properties of CNTs come from their strong function in their atomic structure and mechanical deformations; such relationships make them useful when developing extremely small sensors that are sensitive to chemical, mechanical, or physical environments. Chemical sensors based on CNTs have recently attracted a great deal of attention. CNTs are expected to exhibit excellent properties as sensors since they have a large surface area and are known to exhibit charge sensitive conductance. Molecular interaction can change the electrical properties of CNTs at room temperature. However, a major barrier for developing such CNT-based devices is the insolubility of CNTs. It is well known that single-walled carbon nanotubes are easily entangled with substantial van der Waals attraction between the CNTs to form an agglomeration. However, their non covalent functionalization has been shown to be useful in improving their solubility and dispersibility without a degradation in their physical properties. Non covalent functionalization based on the physical adsorption of polymers such as the surface wrapping of SWCNTs with polymeric chains and surface coatings use low molecular surfactants. Nafion is known to be the most likely candidate polymer for the dispersion of CNTs. Since the hydrophilic polar group in Nafion interacts strongly with water, whereas the hydrophobic backbone in Nafion interacts with the CNTs [3,4], we expect that the CNT/Nafion composites based on electrochemical sensors offer substantial improvements in the performance of aqueous methanol concentration sensing devices. The measurement of methanol concentration is one of the most common tasks required in direct methanol fuel cell (DMFC). The methanol concentration fed to the DMFC plays a significant role in keeping a predetermined power output from the fuel cell. In fact, the methanol concentration in the fuel circulation loop of a DMFC system is an important operating parameter, because

it determines the electrical performance and the efficiency of the fuel cell system. The methanol concentration for an optimal performance of the fuel cell has been found to be in the range of between 0.5 M and 2 M [5].

In this study, we report the experimental results that demonstrate the methanol concentration capability of the composites of carbon nanotube/Nafion membranes used as sensing materials. To form a good dispersion, the single-walled carbon nanotubes (SWCNTs) were dispersed in a Nafion117 perfluorosulfonic acid solution until the sample was completely suspended in the solvent. Then, the SWCNT/Nafion membrane composites were formed on a network or mesh on interdigitated electrodes using a simple casting process, providing a large enough density of the SWCNTs to be able to achieve a sensing performance. The performance of the SWCNT/Nafion composites was characterized by typical current responses to the change of the methanol concentration in the range between 0.5 and 4 M, at room temperature.

2.   The experiment

A pair of interdigitated electrodes was fabricated using conventional photolithography methods with the finger widths of 10 μm and the gap sizes of 10 μm. The interdigitated electrode fingers were made by e-beam evaporating 200 nm Pt on a layer of silicon dioxide thermally grown on top of a silicon wafer. The dispersion of the SWCNTs was carried out using purified SWCNTs; the powder was comprised of grains of 1–1.2 nm diameter on average, 5–20 μm in length, and had 90% purity (Hanhwa Nanotech. Co. Ltd., prepared by an arc-discharge method). A 0.5 wt% solvent was prepared by diluting the 5 wt% Nafion117 (Sigma–Aldrich Co.) solution and the purified 5 mg SWCNTs were then sonically dispersed in a 10 mL 0.5 wt% Nafion117 solution, forming a suspension at a power of 200 W using a pulse cycle of 1 s ON and 1 s OFF for 1 h Such suspensions can last for several months without precipitation.

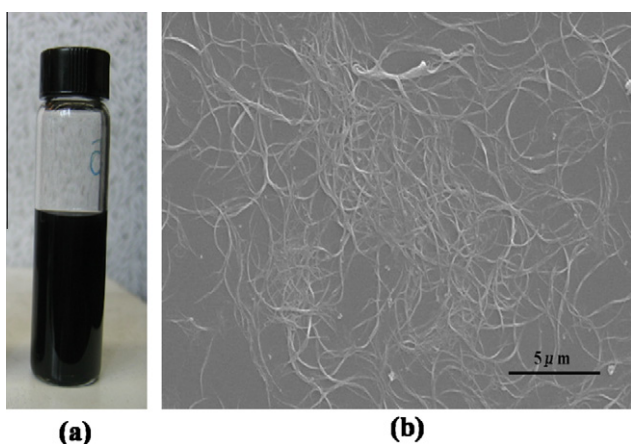Fig. 1a presents images that illustrate some suspensions of SWCNTs dispersed in Nafion117 for 1 month. Fig. 1b shows the FE-SEM image of the dispersed SWCNTs with Nafion117. The 10 μL volume of the SWCNT/Nafion composites solution was then deposited onto the Pt interdigitated electrodes by spin-coating at 1500 rpm for 30 s to ensure a good-quality deposition of the SWCNTs on top of the substrate. The obtained films were then dried at 120 °C for 1 h to increase the adhesion between the SWCNT/Nafion composite film and substrate. The spin-coated films are also employed in the bonding of the silicon wafer for packaging [6]. The window layer and the films were then pressed together by hand and a preconditioning pressure of 1 psi was applied for 5 min prior to annealing. The device was placed into a preheated oven and annealed for 1 h at 120 °C. A schematic drawing of the whole process is shown in Fig. 2.

To examine the relationship between the electrical current and the methanol concentration in the *in situ* measurements were monitored by the cycling solution in the range of 5 M. The electrical current of the SWCNT/Nafion composite film was measured using a Keithley (Keithley Instruments, Inc., 4200SCS) at room temperature.

Finally, there are numerous ways of expressing the solution concentrations according to their applicable environments. We used the aqueous methanol solution of DMFCs molarity. The definition of molarity is given in the below expression [7]:

$$\text{Molarity (M)} = \frac{\text{moles of solute (methanol)}}{\text{liters of solution}}$$

3.   Results and discussions

3.1.   The response properties

Fig. 3 shows the typical resistance response of the SWCNT/Nafion composite membrane to the methanol concentration step changes at room temperature. During the test, a constant voltage (1 V) was applied between the electrodes. A baseline of resistance was first established when deionized water (pure water) was fed through the SWCNT/Nafion composites
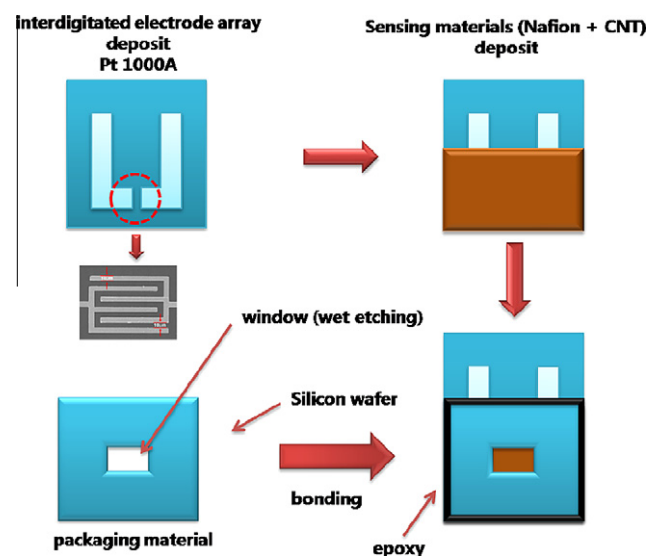

Fig. 1 – (a) An aqueous solution of the SWCNT/Nafion composites and the (b) FE-SEM image of SWCNTs dispersed with Nafion.
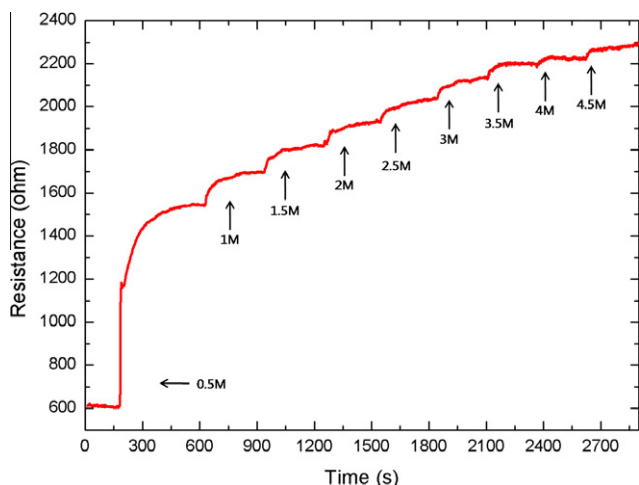

Fig. 2 – Schematic of the process.

Fig. 3 – The resistance changes of the SWCNT/Nafion composite membrane to the concentration of methanol step changes at room temperature.

membrane on an interdigitated electrode with stirring to distribute the nanotubes uniformly (a methanol and water mixture). The resistances were recorded during the feeding of the methanol concentration as it was increased by switching to a different solution every 5 min. The resistance increased significantly with an increasing concentration of between 0.5 and 4 M. The resistance shows some fluctuation with time, but the average remains relatively constant. This may be caused by the fluctuation related to the stirring of the solution.

Nafion is used not only for providing a path for the absorption of the water and methanol molecules but also as a solvent to achieve well-dispersed single-walled carbon nanotubes. It is well known that the surface wrapping of SWCNTs with Nafion and surface coatings have been shown to be useful for improving solubility and dispersibility. Nafion contain aqueous ions (hydrophilic sulphonate polar group clusters with a 4 nm diameter) embedded in a continuous hydrophobic fluorocarbon chain (Fig. 4).

The polar group clusters are interconnected by narrow channels (~1 nm diameter) that determine the transportation properties of the water and methanol molecules [8,9]. The SWCNTs dispersion with Nafion implies that the hydrophilic polar group in Nafion interacts strongly with water, whereas the hydrophobic backbone in Nafion interacts with the surface of SWCNTs. However, this surface wrapping of the SWCNTs with Nafion may cause a degradation of the electrical properties, because of the interference interactions between the surface of SWCNTs and the methanol molecules. In this case, the water and methanol absorption in Nafion is the main factor of the electrical changes of the SWCNTs. However, the absorption of Nafion has no preference for either water or methanol. Therefore, the absorption of the solution to the Nafion membrane is proportional to the concentration of methanol.

Fig. 5 shows that water and methanol molecules are excluded from the hydrophobic fluorocarbon backbone channels in the Nafion to the surface of SWCNTs due to their low solubility (a non-polarity between the hydrophobic fluorocarbon and water molecules or the methanol molecules). The hydrophobic surface of the fluorocarbon backbone provides a stronger repulsive force on the water and methanol molecules near the surface than that provided by their surrounding water and methanol molecules. The water adsorption remains nearly constant whereas the methanol absorption increases with the methanol concentration in the Nafion membrane. This means that the methanol adsorption is thus added to the water absorption by the Nafion in contact with pure water. After all, the composition of the solution within the Nafion is nearly identical with that of the equilibrating solution, implying that the methanol concentration is the main factor influencing the electrical properties of the SWCNTs [10,11,7].

It is also well known that swelling of surfactants and polymers will also affect the electrical conductivity of the SWCNTs. Nafion, in particular, is very sensitive to swelling in water and organic solvents [11]. Swelling of Nafion due to the solution absorption may also increase the volume and thus increase the distance between SWCNTs. The increase of contact resistance between SWCNTs becomes promoted by the increment of the distance between adjacent SWCNTs.

If the swelling of Nafion is influenced by immersion time, the swelling is one of serious problems in detecting methanol concentration. Fig. 6 shows the resistance changes of SWCNTs/Nafion composites after long time immersion in 1 M methanol solution. It shows the extent of the swelling (Fig. 6 inset), and hence we can conclude that the electrical response, hardly depends on the immersion time. No resistance changes were detected except in the early stage. In other words, swelling of Nafion happens rapidly and reaches a stable state immediately after the immersion of the composites into the solution. It means that most of responses, including swelling effect, are influenced by rapid water and methanol molecules absorption into the composites in a short time. If the swelling of Nafion does not depend on the time, the swelling is not an important
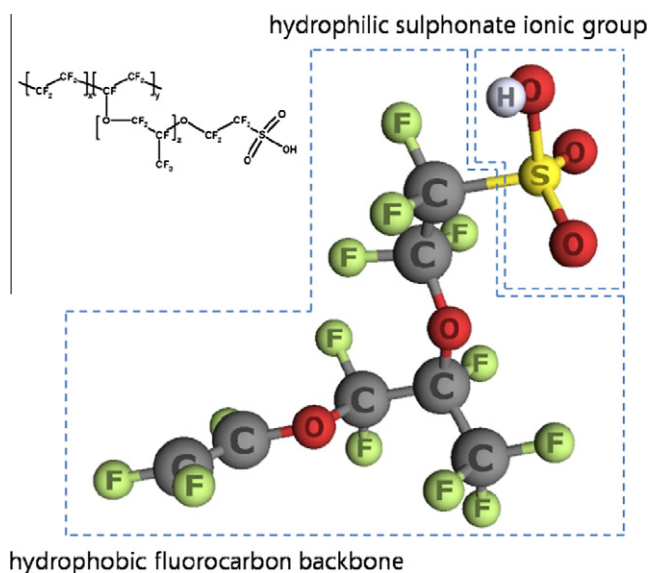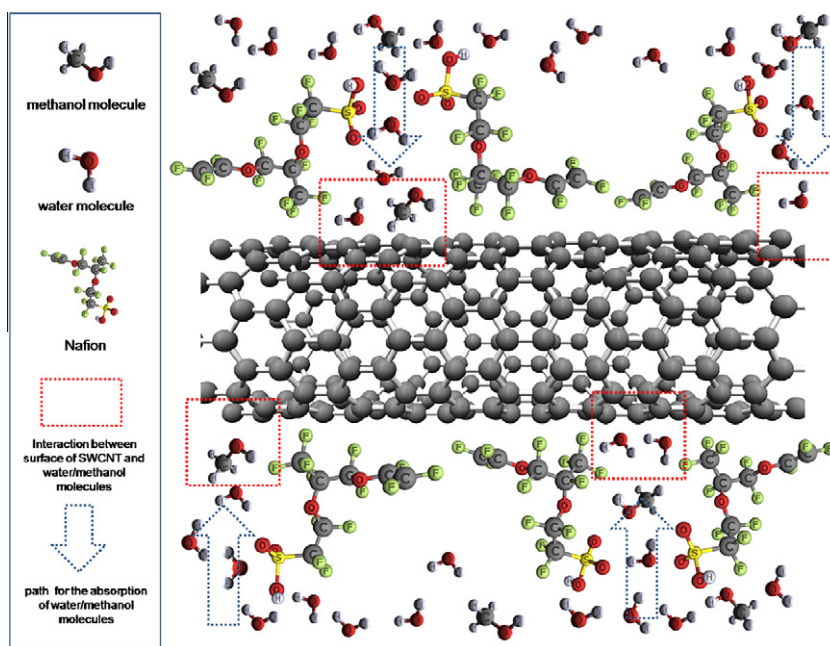

Fig. 4 – The chemical structure of Nafion.

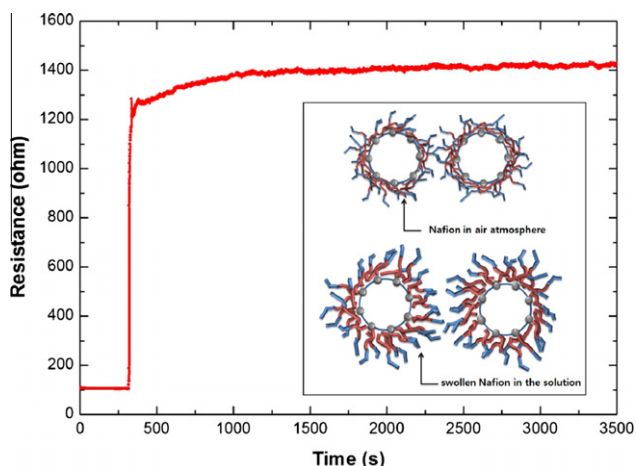**Fig. 5 – The path of the water/methanol absorption into the Nafion.**

Fig. 6 – The resistance changes versus time in 1 M methanol concentration solution.

problem anymore in DMFC operation because the sensor always could operate in bulk liquid solution.

Methanol molecules also affect to the swelling of Nafion. In previous work [12,13], Nafion swelled to a greater extent in a number of organic solvents than it did in water. Water molecules interact only with the hydrophilic domains rather than with the hydrophobic domains of Nafion. However, the great better interactions between methanol molecules and the hydrophilic/hydrophobic domains of Nafion would result in greater extent swelling of Nafion. So, methanol concentration would be considered as the major cause of the resistance changes. In chemical analysis by using infrared spectroscopy, the swelling of Nafion depends strongly on the intermolecular interaction like as the hydrogen bonding between methanol/water molecules and hydrophobic/hydrophilic domains in Nafion. Those interactions were more observable in highly swollen Nafion. However, there are no conspicuous intermo-

lecular interaction between methanol/water molecules and the Nafion membrane in low methanol concentrations. Therefore, less methanol molecules are not attributed to the swelling of Nafion. Swelling of Nafion is the only problem in higher concentration over 6 M methanol solution.

3.2. Recovery properties

In the above investigations, the response to each concentration methanol was small. This may be due to the reduced surface area of the SWCNTs. Here, we have to consider the side surfaces of the SWNCTs in a bundle. Namely, the response and recovery characteristics depend on how we can untangle the SWCNT bundles to utilize the side surface area of the SWNCTs. We must also take into account that the SWCNTs are usually in a bundle form where the van der Waals forces make them gather. In other words, it is necessary to consider the undesirable reduction of surface area due to the formation of these bundles. In our experiment the SWCNTs were ultrasonically dispersed in the Nafion solution for 1 h. When a longer time is employed for the ultrasonic treatment, it leads to a more pronounced untangling and hence to a good response for each concentration. To confirm this effect, the SWCNTs were ultrasonically treated for 2 h, and the 1 M methanol concentration was tested.

Fig. 7 shows the result of the stability and recovery properties of the SWCNT/Nafion composite membrane. The voltage applied between the electrodes was maintained at a constant voltage (1 V) throughout the test. The recovery was performed perfectly while the film was in deionized water after dipping in 2 M methanol by turns.

In previous works [14,15], the mechanism was thought to be related to the electro-chemical adsorption or to the reaction of the methanol solution. However, in this paper, the mechanism is found to be on the basis of the polar interaction of methanol on the SWCNT surface. Since the SWCNTs/
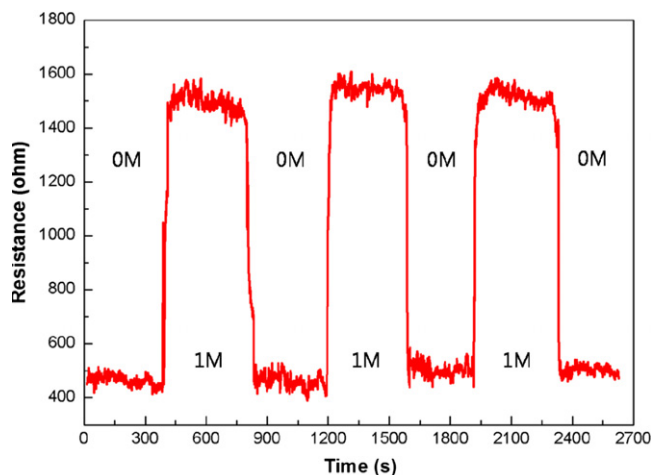
Fig. 7 – The recovery property of the SWCNT/Nafion composite membrane in a 1 M concentration of methanol.

polymer composite based sensing materials have been tested with similar results, it is strongly believed that the sensing mechanism can be explained by the variation of the electrical properties of the semiconductor SWCNT surface which occur by the charge transfers induced by the adsorption of the polar organic molecules, such as acetone and methanol. The adsorption of such molecules is caused by the interaction between the polar molecules and the polar groups on the SWCNT surface from the dipole–dipole interactions, including hydrogen bonding. The SWCNT surfaces contain polar functional groups which can absorb water and methanol molecules. The solution forms hydrogen bonds with the polar groups on the SWCNT surface. In conclusion, it seems that the adsorption or reaction of the methanol molecule dopes the SWCNTs. However, according to the literature, water is a more strongly polar molecule than the methanol molecule (Fig. 8).

It seems that water prefers to interact with the surface of the SWCNT compared with methanol. Thus, it looks like that the main factor of the sensing mechanism is water molecules not methanol molecules. But the strong hydrogen bonds
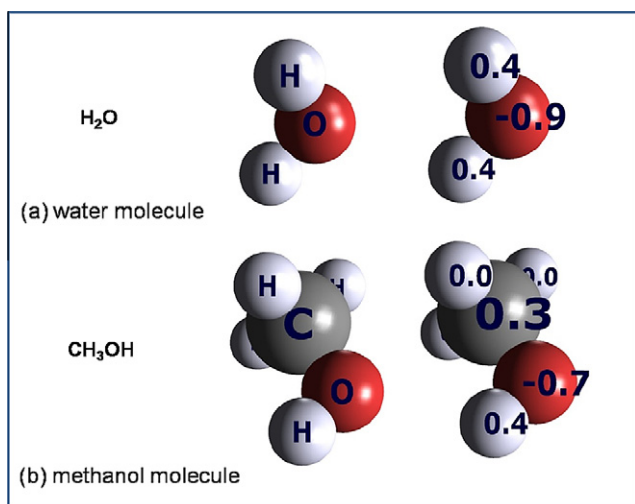
between the water molecules and hydrophilic sulphonate polar group clusters found in Nafion slow down water molecular motion, whereas methanol is easily transported faster than water because of the weaker methanol–Nafion (hydrophilic sulphonate polar group clusters and hydrophobic fluorocarbon backbone) interaction [16,17].

4. Summary

A random network of the Nafion coated SWCNT has shown a change in conductance towards different methanol concentrations in water. The Nafion membrane provides a path for the transportation of water and methanol molecules to the surface of the SWCNTs. The sensor, fabricated from a random network of SWCNT/Nafion composite, shows the resistance changes by cycling methanol concentration range from 0.5 M to 5 M. Methanol solution shows a large increase in resistance while there is little response to pure water. The methanol dependent properties of the SWCNTs arise from the difference in methanol/water transport properties through the Nafion membrane because of difference in polarity of the molecules. The polar functional group on SWNTs interacts with both methanol and water, however, with the Nafion membrane, selectivity towards methanol had been achieved. Membrane coatings on the highly sensitive SWNT such as the technique above should be widely employed in other complex chemical environments in order to highly enhance the selectivity of sensors.

Acknowledgements

Fig. 8 – The chemical structures of water and methanol molecules and their charges.

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