

Methanol Concentration Sensitive SWCNT/Nafion Composites

Kyongsoo Lee¹, Seong-II Kim¹, Byeong-Kwon Ju^{1*}

Abstract—An aqueous methanol sensor for use in direct methanol fuel cells (DMFCs) applications is demonstrated; the methanol sensor is built using dispersed single-walled carbon nanotubes (SWCNTs) with Nafion117 solution to detect the methanol concentration in water. The study is aimed at the potential use of the carbon nanotubes array as a methanol sensor for direct methanol fuel cells (DMFCs). The concentration of methanol in the fuel circulation loop of a DMFC system is an important operating parameter, because it determines the electrical performance and efficiency of the fuel cell system. The sensor is also operative even at ambient temperatures and responds quickly to changes in the concentration levels of the methanol. Such a sensor can be easily incorporated into the methanol fuel solution flow loop in the DMFC system.

Keywords—methanol concentration, SWCNT, nafion composites

I. INTRODUCTION

THE need for high energy density electrochemical energy sources has brought about the development of direct methanol fuel cell (DMFC) systems. DMFCs employing proton exchange membrane electrolytes have gained considerable interest because of their potential for use as the power source for a wide variety of applications. The concentration of methanol in the water to be 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 efficiency of the fuel cell system. The methanol concentration for optimal performance of the fuel cell has been found to be in the range 0.5 - 2 M [1]. In this study, we report on research that a methanol sensor has been constructed utilizing dispersed carbon nanotubes with Nafion117 perfluorosulfonic acid membrane solution for the measuring the concentration of methanol. Nafion117 has played three roles in the research for developing sensors to measure the methanol concentration; these are as follows:

- Path of water/methanol permeation into the sensing materials
- Bonding material for sensor passivation
- To unravel the entangled SWCNT bundles.

Nafion has several unique properties that are most suitable for the silicon wafer bonding. For instance, the perfluorosulfonate Nafion polymers are inert and they are stable in strong bases and acids, and strong oxidizing and

* Authors are from Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea.
(e-mail: bkju@korea.ac.kr)

reducing agents at temperatures up to 125°C. Depending on the counter-ion form, the thermal stability of Nafion films is excellent to 200°C or even higher at atmospheric pressure [2].

The electronic property of single walled carbon nanotubes (SWCNTs) is a strong function of their atomic structure and mechanical deformations and such relationships make them useful when developing extremely small sensors that are sensitive to the chemical and mechanical (or physical) environments. Such sensors can be dramatically simpler in design, construction, and use and lead to highly reliabilities and sensitivities with fast responses.

II. EXPERIMENTAL

The dispersion of the carbon nanotubes are carried out using purified SWCNTs and the SWCNT powder used for this has been purchased from Hanhwa Nanotech Company Ltd; the powder comprises grains of 1-1.2 nm diameter on average, 5-20µm in length, and has 90% purity (prepared by an arc-discharge method). A 0.5wt% proton exchange membrane is prepared by diluting the 5wt% Nafion117 (Sigma-Aldrich Company) solution and the purified SWCNTs of 5 mg are then sonically dispersed in 10mL of 0.5wt% Nafion117 solution to form a suspension at a power of 200W and a pulse cycle of 1s ON and 1s OFF for 2 hours. A 10µL volume of SWCNT/Nafion composite solution is deposited onto the Pt interleaved electrode by spin-coating to ensure good-quality deposition of the SWCNTs on top of the substrate.

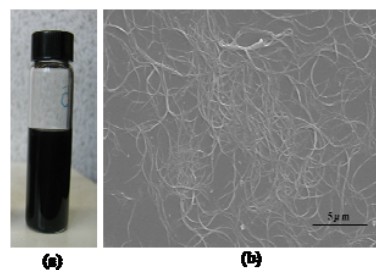


Fig. 1 (a) Aqueous solution of SWCNT/Nafion composite and (b) FE-SEM image of SWCNTs dispersed with Nafion.

Such suspensions can last for several months without precipitation and Fig.1 (a) presents images to illustrate some suspensions of SWCNTs dispersed in Nafion for 1 month. Fig.1 (b) shows the FE-SEM image of dispersed SWCNTs with Nafion117. Then diluted Nafion117 solution, not composite material, is deposited by spin-coating on the SWCNT/Nafion composite film for the role of providing a path for the water/methanol permeation. Finally, a through-etched silicon wafer is used as a mask onto the sensor to form

a window opening and passivation. The above spin-coated Nafion films are also employed in the bonding of silicon wafers at temperatures as low as 120°C [2]. The etched wafer and sensor are then pressed together by hand and a preconditioning pressure of 1 psi is applied for 5 min prior to the annealing. The bonded wafers are then placed into a preheated oven and annealed for 1 hour at 100°C. To examine the relationship between the resistance and the methanol concentration in situ measurements of the resistance are monitored by cycling solution ranging from 1M methanol to 5M methanol. The resistance of the SWCNTs is measured by using Keithley (Keithley Instruments, Inc., 4200SCS) at room temperature.

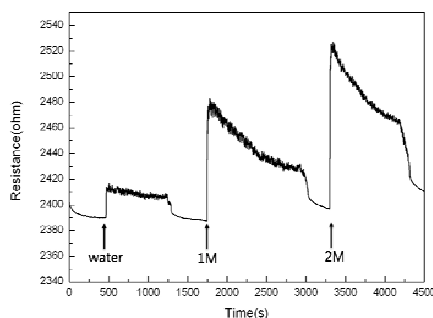


Fig. 2 Resistance changes of the sensor with droplets of 0.5ul water, 1M and 2M methanol fuel. Recovery is carried out by drying in atmospheric environment.

III. RESULTS AND DISCUSSION

The electrical properties of the SWCNTs in pure water, in 1M methanol and in 3M methanol have been investigated. It can be seen from Fig. 2 that the resistance of the SWCNTs is greatly influenced by the methanol concentration and not pure water. The sensitivity ($\Delta R/R_0$) of the sensor is calculated for pure water and different concentrations of methanol; the sensitivities of the sensor are ~1% in pure water, ~4% in 1M and ~5.8% in 3M methanol solution, respectively. Methanol fuel shows a large increase in resistance while there is little response to pure water.

According to the previous research findings on the methanol crossover, Nafion membranes have no preference for either water or for methanol [5]. Therefore, the permeability of the Nafion membrane is proportional to the concentration of methanol. For the Nafion membrane in contact with the methanol solution, the water permeation remains nearly constant while the methanol permeation increases with the methanol concentration. The water permeation in membrane remains the same as that of pure water. Therefore, Methanol permeation is thus added to the water permeation by the Nafion membrane as measured in contact with pure water [4]. The Nafion membranes contain aqueous ions (hydrophilic sulphonate ionic group clusters with a 4nm diameter) embedded in a continuous hydrophobic fluorocarbon phase. The ion clusters are interconnected by narrow channels (~1 nm diameter) that determine the transportation properties. Therefore, water and methanol reside almost completely in

these ion cluster pores and the connecting channels of the membrane and they are excluded from the hydrophobic fluorocarbon backbone due to their low solubility (non polarity between hydrophobic fluorocarbon and water molecules or methanol molecules) in that region (see Fig. 3). After all, the composition of the methanol/water mixtures within the Nafion membrane is nearly identical with that of the equilibrating solution [5-7] implying that the methanol concentration is the main factor influencing the electrical properties of the sensor.

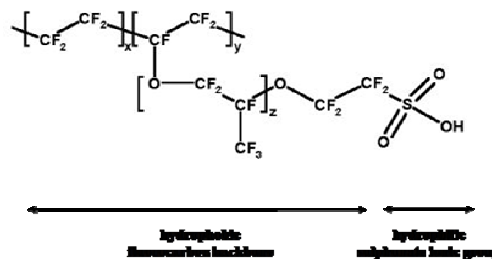


Fig. 3 Chemical structure of Nafion

The response of the sensor has been studied in various methanol solutions and the sensor response comparisons for different concentrations of methanol are shown in Fig. 4. In this case, the sensor is dipped in 1, 2, 3 and 5M methanol solutions and the sensor is perfectly recovered while the membrane is dried in normal atmosphere after dipping in each methanol solution. The sensitivity of the sensor obtained by using the dipping in solution method is much better than from using the droplet method. Fig. 5 shows the change in resistance when the sensor is dipped in 1, 2 and 3M methanol solutions continuously without recovery. These experiments have been performed to realize the optimized methanol sensor for DMFC systems; it is observed from the measurements that each concentration of methanol has its own impact on the variation of resistance, which is good for the detection of concentration changes of the methanol fuel.

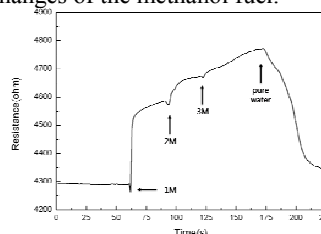


Fig. 4. Resistance changes of the sensor dipped in various methanol concentrations. Recovery is carried out by drying in atmospheric environment.

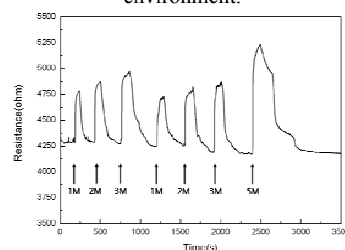


Fig. 6. Resistance changes of the sensor dipped in various methanol concentrations continuously without recovery.

IV. CONCLUSIONS

The paper has demonstrated the sensor based on SWCNT/Nafion composite for detecting the concentration level of the methanol. Nafion117 is used not only for providing a path for the permeation of the methanol and the water but also as the solution to achieve well-dispersed carbon nanotubes (CNTs). The sensor, fabricated from a random network of SWCNT/Nafion composite, shows the resistance changes by cycling methanol concentration range from 1M to 5M. The methanol dependent properties of the SWCNTs are from the methanol/water permeation through the Nafion membrane. In this way the resulting sensor can be dramatically simpler in design, construction and use. In addition, the sensor is highly reliable and sensitive with a fast response time.

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