NOVEL CORROSION SENSOR BASED ON CARBON NANOTUBE COMPOSITES FOR STRUCTURAL HEALTH MONITORING

Andy Chit Tan [(1)], Joo Joo Yong Cha [(2)] and Inpil Kang [(2)]

[(1)] School of Engineering Systems, Faculty of Built Environment and Engineering, Queensland University of Technology, George St., Brisbane, Qld 4001, Australia
[(2)] Department Mechanical and Automotive Engineering, Pukyong National University, Busan, 608-73, Korea

SUMMARY: Bridges are important infrastructures of all nations and are required for transportation of goods as well as human. A catastrophic failure can result in loss of lives and enormous financial hardship to the nation. Hence, there is an urgent need to monitor our infrastructures to prolong their life span, at the same time catering for heavier and faster moving traffics. Although various kinds of sensors are now available to monitor the health of the structures due to corrosion, they do not provide permanent and long term measurements. This paper investigates the fabrication of Carbon Nanotube (CNT) based composite sensors for structural health monitoring. The CNTs, a key material in nanotechnology has aroused great interest in the research community due to their remarkable mechanical, electrochemical, piezoresistive and other physical properties. Multi-wall CNT (MWCNT)/Nafion composite sensors were fabricated to evaluate their electrical properties when subjected to chemical solutions, to simulate a chemical reaction due to corrosion and real life corrosion experimental tests. The electrical resistance of the sensor electrode was dramatically changed due to corrosion. The novel sensor is expected to effectively detect corrosion in structures based on the measurement of electrical impedances of the CNT composite.

KEYWORDS: Carbon Nanotubes, Nano composites, Corrosion sensor, Nano Smart Materials, Structural Health Monitoring.

INTRODUCTION

It is well-known that corrosion, as a result of chemical reaction, is related to the degradation of structural strength. It reduces section thickness and increases fatigue crack growth rate, thereby changing both the steady state and dynamic response properties of structures. The costs associated with detecting, repairing, replacing and repainting corroded components are significant. If corrosion is detected at an early stage and its prediction on time to failure through structural health monitoring (SHM) system can be established, the costs of corrosion can be reduced by optimizing maintenance intervals and avoiding catastrophic failure. Traditional SHM techniques include assessment of acceleration in vibration modes, visual inspection and ultrasonic inspection may detect more advanced signs of bridge failure, they are not specifically designed to detecting corrosion and do not provide an early warning on corrosion.

The goal for future development of SHM is to use sensors which can be permanently mounted on or in the structure and can therefore provide immediate warning of the onset of a condition that will lead to failure. One of the most common measurements proposed for these *in situ* sensors is strain measurement. CNT-based sensors are emerging as a promising technology that has been investigated for this application. Carbon nanotube is one dimensional structure with a very long and slender cage and has well-defined chemical, electrical and other material properties [1]. Their distinctive high surface area, small size, unique covalent bonding and seamless hexagonal networks between molecules result in unique characteristics which make them extremely attractive for the development of chemical (including corrosion) and bio sensors. CNTs when mixed with other materials to form composite electrodes maintain their excellence electrical and mechanical properties. Recently, cyclic voltametric, amperometric, and conductance measurement have been studied to sense the characteristics of piezoresistivity properties of CNTs for chemical and bio oriented applications [2-7].

Wang and co-workers developed a production method for multi-wall carbon nanotube (MWCNT) based screen-printed electrodes and demonstrated the screen printed electrodes to electro catalytic action by means of cyclic voltametric and amperometric response analysis [3]. Sanchez et al. reported MWCNT/polysulfone composite screen-printed electrochemical enzyme biosensors based on cyclic voltametric experiments [4]. Jung et al. fabricated aligned single-wall carbon nanotubes (SWCNTs) array sensor by using AC dielectrophoresis and conventional photolithographic to detect ions and radicals [5]. They showed that p-type doping of SWCNTs by decomposed Ar ions produced drastic change in electrical conductance increment while SWCNT under fluorine radicals produced by sulfur hexafluoride plasma decomposition exhibited decrement of electrical conductance. Quang et al. fabricated a hydrogen sulfide (H_2S) gas sensor using SWCNT bundles pretreated with acid [6]. They reported that acid pretreatment not only purified the SWCNT but also improved the sensitivity of the SWCNT-based sensor due to purification and enlargement of SWCNT diameter. The acid pretreatment significantly improved the resistance of the treated SWCNT-based gas sensors. Huyen et al. studied the gas-sensing characteristics of polyaniline (PANi)/SWCNT composite sensor [7]. The physically doped SWCNT with PANi significantly improve the gas-sensing characteristics and showed that the resistance of PANi/SWCNT composite rapidly increased when it was exposed to NH_3 gas.

In this paper, we fabricated corrosion sensor based on MWCNT and Nafion by using traditional solution-casting technique. The electrical properties of the bulk electrodes were tested and compared for corrosion detection under laboratory conditions. In the experimental tests, various amount of chemical solution was applied to the electrodes to investigate the changes of electrical impedances and characteristics due to corrosion ionic penetration into the sensor electrodes due to corrosion and measurement of electrical properties by means of LCR meter. The results showed that the electrical resistance is highly sensitive to the chemical reaction due to corrosion. Electrical impedance measurements provide a rapid and simple sensing mechanism to detect corrosion and the MWCNT/Nafion electrode has potential to be used as a novel corrosion sensor.

FABRICATION OF CNT BULK ELECTRODES

MWCNT with Nafion composite electrodes were prepared by dispersing MWCNTs in Nafion solution, perfluorinated ion-exchange resin (Aldrich). The appropriated amounts of dispersed MWCNTs were mixed with the Nafion (Aldrich, 274704) in order to achieve a weight of 5/95% of MWCNT/Nafion composites. The MWCNTs-Nafion solutions were homogenized for 2 hours until a highly homogeneous solution was achieved. As bulk materials were hardly achieved with MWCNTs, we added Nafion to fabricate the bulk electrode because the van der Waals force interacting among the individual MWCNTs is not enough to form a film. Nafion not only combines nanotubes as a matrix but it also greatly improves the electrochemical properties. Nafion eliminates common interferences from ascorbic acids by providing a transport channel while maintaining its high sensitivity [8, 9]. Nafion has been extensively employed for the modification of electrode surfaces and for the construction of biosensor electrodes. Figure1 shows a sample of the fabricated MWCNT/Nafion bulk sensor. Is seen in its natural colour and bonded on a steel specimen using epoxy glue.

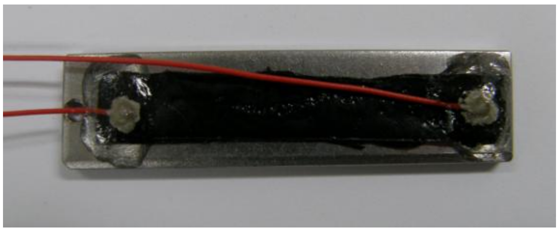

Figure 1. A sample of CNT/Nafion composite (wt. 5/95%) sensor electrode (20x50x0.02mm) on metal specimen

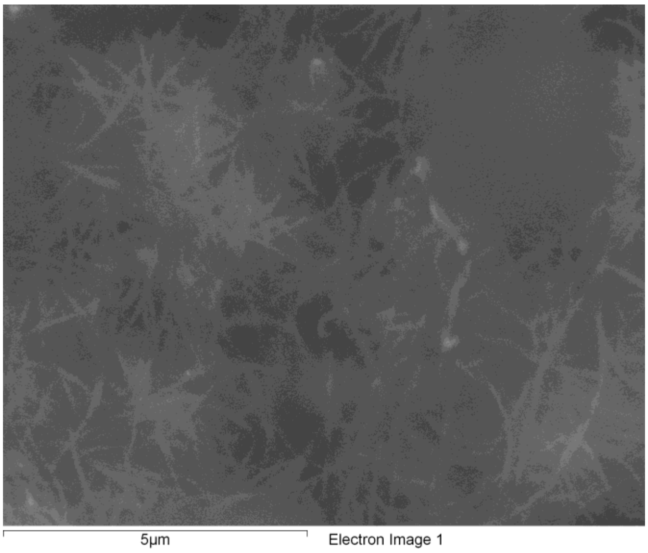

Figure 2. SEM images of the electrodes made of MWCNT/Nafion (wt. 5 %)

Figure 2 displays a typical SEM image of the MWNT/Nafion electrode sample surfaces prepared using the above procedures. The MWCNTs are entangled because of their large surface area and the van der Waals attraction. The surface of the CNT-based electrode is characterized by micro-porous structures with fairly dispersed fiber distribution. Nafion is an electrochemical agent which promotes polymeric binder. The micro porous surface of MWCNTs/Nafion composite enables the CNTs penetration to the bulk Nafion. The image shows that MWCNTs were well dispersed within the Nafion matrix and provide conductivity throughout the MWCNT-Nafion matrix.

EXPERIMENTS AND DISCUSSION

Being nano-porous and electrical conductive material, electrically analogues sensor model of CNTs and their composite are represented by a parallel circuit consisting of resistance and capacitance from electrical impedance spectroscopy (EIS) test [10]. Each electrical impedance component varies under specific physical and chemical conditions. The resistance and capacitance properties of the CNT composites show very sensitive response under chemical exposure [11].

To investigate the chemical sensitivity of MWCNT/Nafion sensors due to corrosion, a simple corrosion experiment of the electrodes attached onto steel plates was performed. The sensor was attached onto steel plate by means of epoxy glue (see Fig.1). In the experimental tests, three CNT-Nafion sensors were submerged in buffer solution, saline solution and distilled water, respectively. Figure 3(a) shows the three specimens at the initial stage of corrosion with the electrodes submerged in buffer solution, saline solution and distilled water, respectively. An LCR meter (HIOKI 3522 LCR HiTESTER) was used to measure the resistivity and conductivity of the sensors.

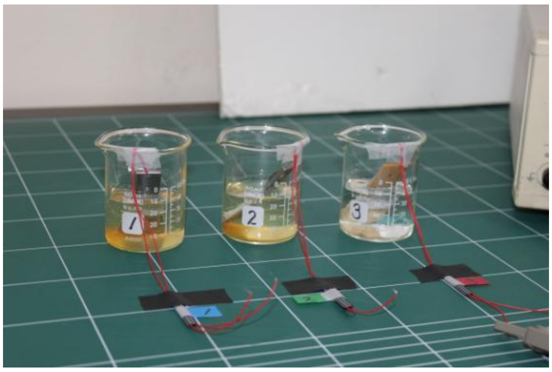

Figure 3. MWCNT-Nafion electrodes attached on steel specimens: (1) Buffer solution, (2) Saline solution and (3) Distilled water.

For the preliminary test of corrosion response, the characteristics of MWCNT/Nafion bulk materials were investigated under the change of DI water, saline and buffer solution. The electrical resistance of the composite electrodes was measured with the specimens fully soaked with the liquids. Buffer solution pH 7 (Sigma-Aldrich) was applied to the electrodes using micro pipette to simulate corrosive chemical reaction, similar to that of corrosion. In this experiment we applied an amount of 2μl /drop to the electrodes up to 10 droplets.

Figures 4 shows the electrical impedance changing patterns of the fabricated MWCNT/Nafion bulk electrodes. The figure shows that the electrical resistance of MWCNT/Nafion electrodes changes when subjected to liquid as the amount of droplet increases. It is reported that the change of resistance of bulk CNT is induced by absorbed molecules on its surface and they change the carrier

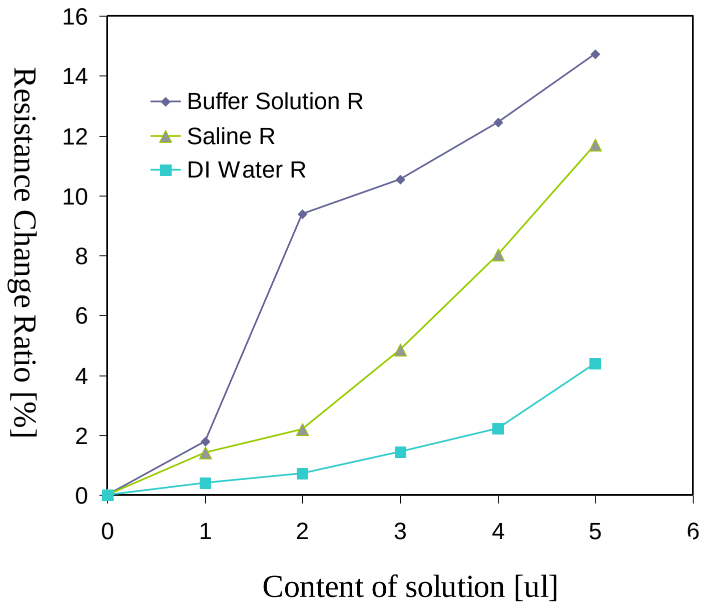

Figure 4. Changes in electrical resistance of MWCNT/Nafion composites against DI water, saline and pH7 Buffer

concentration in the outer graphene layer of the CNT [12]. After 5 drops (10ul) of liquid the electrical resistance of DI water, saline solution and buffer solution exhibits a change of about 5%, 11% and 15%, respectively. As expected buffer solution is more responsive to corrosion.

When DI water droplets were applied to the electrode, the electrical resistance shows a relatively small increment owing to its electrically insulating property and hence minimum chemical reaction. On the other hands, saline and buffer solutions exhibit larger change in electrical resistance of the two electrodes because of the doping effect to the electrodes with chemicals in the solutions. It was expected that the chemicals in buffer solution had larger doping effect than that of sodium ions in saline solution and that is the reason why the change resistance of buffer solution was larger than saline fluid.

From the above tests, saline fluid was used to conduct long term effect of the electrodes to monitor the rate of corrosion of the steel specimens. Figure 5 shows the results of electrical resistance change of MWCNT/Nafion electrodes submerged in liquid and pure electrode attached onto a piece of timber and electrode attached onto a steel specimen, respectively. As expected the change in electrical resistance of the electrode fixed onto the steel specimen exhibits larger resistance change than on the timber specimen. At about 35 hours of exposure in liquid, the change of resistance of the steel specimen in saline solution is about 3 times higher than the timber specimen. The corrosion of the steel specimen subjected to saline solution is caused by the ions in the solution penetrating into the electrodes surface and form a double layer charge on the nanotube surface. This chemical doping changes the impedance of the CNTs and can be detected by changes of the electrodes' electrical properties. Having a large surface area, the electrical resistance of the MWCNT/Nafion electrode can change remarkably when the ions are in contact with liquids.

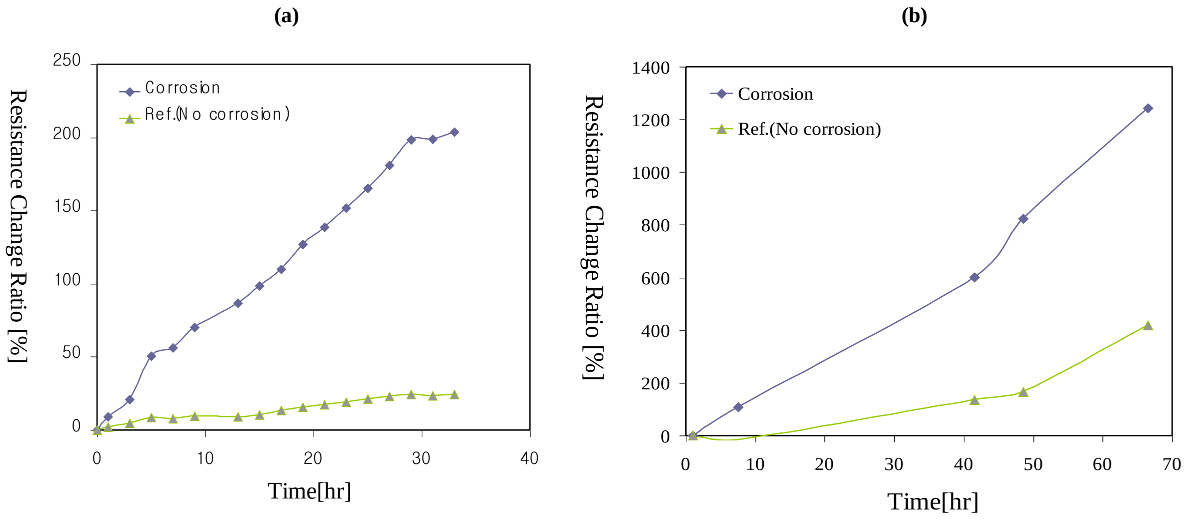

Figure 5. Changes in Electrical Resistance - (a) Distilled Water and (b) Saline Fluid

From this preliminary corrosion test with MWCNT/Nafion sensors in liquid, we expect the novel MWCNT/Nafion corrosion sensor can be developed to detect corrosion by measuring the change of electrical resistance of the sensor electrodes.

CONCLUSION

Electrical impedance properties of carbon nanotubes based bulk electrodes have been investigated for use as chemical (including corrosion) sensor. The bulk composite electrodes were fabricated with multi-wall carbon nanotubes involving ionic conducting host polymer, Nafion, by using of traditional solution-casting techniques. Under the various amount of buffer, saline and distilled solutions to simulate corrosion, resistance of the electrodes were measured with LCR meter and their characteristics due to ionic conducting host polymer were investigated by means of electro kinetic analysis. For the MWCNTs with Nafion, the resistance value showed drastic change when submerged in buffer and saline solutions. The resistance measurements can be used to assess the occurrence of corrosion in structures. Long term experiments to monitor the rate of corrosion using the fabricated MWCNT/Nafion composites on steel specimens show that there is a remarkable difference in electrical resistance when the sensors are submerged in liquid, especially in corrosive fluids. The results confirm our hypothesis as corrosion occurs on the metal surface the corrosive ions penetrate into the surface of the CNTs and changes the electrical resistivity. This paper has shown that our corrosion sensors can be economically manufactured for SHM and without the use of expensive and complicate conventional corrosion sensors.

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