Electrochemical and Solid-State Letters, **9** (8) H78-H80 (2006)
1099-0062/2006/9(8)/H78/3/$20.00 © The Electrochemical Society

Multiwall Carbon Nanotube Sensor for Monitoring Engine Oil Degradation

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An engine oil condition sensor based on multiwall carbon nanotubes was fabricated with the screen printing method. Carbon nanotube (CNT) paste was printed between two parallel-aligned electrodes. The conductivity change in the engine oil according to mileage was measured by using CNT oil sensor. The sensor output was compared with total acid number (TAN) to determine the remaining useful life of the engine oil. It was found that the sensor output was closely similar to TAN of the engine oil. As a result, a real-time engine oil condition monitoring sensor can be realized using CNTs as sensitive materials.
 [DOI: 10.1149/1.2209433]

Manuscript submitted February 3, 2006; revised manuscript received April 28, 2006. Available electronically June 9, 2006.

Carbon nanotubes (CNTs) have been investigated extensively because of their special geometry and unique properties.[1-4] A variety of applications have been considered such as gas sensing, nanoelectronics, gas storage, and field emission devices.[4-12]

Here, we report the realization of the CNT oil condition sensor to detect oxidation degree of the engine oil. The recommended change intervals of the engine oil have continuously been extended with the advancement in the auto industry and better engine efficiency. Engine oil reduces the friction or abrasion of lubrication parts and provides cooling, pressure distribution, and cleaning. However, the lubrication and antiwear function of the engine oil are degraded due to the contamination during use. Consequently, the engine performance decreases rapidly. Therefore, changing the engine oil is essential for environmental and financial reasons. The key parameters that determine the condition of the engine oil vary according to factors such as automobile state, ambient condition, and driving habits. Typically, oil condition (degradation of the engine oil) is determined by several physical and chemical tests such as the level of viscosity, total acid number (TAN), total base number (TBN), fuel and water dilution, metal contents, and other parameters. In particular, the total acid number is an important parameter that indicates the end of life and oxidation degree of the engine oil.[13] TAN of the engine oil is increased after its use. This change will affect the electrochemical reactivity and conductivity of the engine oil. The total current of the engine oil will change at a fixed bias voltage.

In this work, the engine oil condition sensor was fabricated using CNTs as sensitive thin films. The sensor output was compared with TAN for the same oil samples. Possible correlations between the sensor output and significant TAN parameters were investigated.

Experimental

Soda-lime glasses (1 mm thick) were used as substrates of the sensor. A pair of the Au/Cr electrode patterns for conductivity measurement in sensor device was deposited on top of the glass layer by using the shadow mask and sputtering system. Cr (50 nm thick) was used as an adhesion layer between the gold and the glass layers. The total thickness of Au/Cr electrode layers was 300 nm with 1 mm width.

CNTs as sensitive materials of the engine oil condition sensor were 95% pure multiwall carbon nanotube (MWNT) (Iljin Nanotech Co., Ltd., Korea) of ~10 to 15 nm in diameter and 10–20 μm in length, and were synthesized by using thermal chemical vapor deposition (CVD). Here, CNTs did not undergo any post-treatments such as purification, functionalization, etc., because they have already been processed by Iljin Nanotech. The CNT paste was made of an MWNT (5 wt %), a glass frit, a glass frit solvent (SEM-COM Co.), a dispersing agent, and an organic binder. The sensitive thin film was fabricated by using screen printing of CNT paste on a soda-lime glass. The paste was printed onto the glass substrate with 3 × 3 mm sensing area by using a screen printer and a screen mesh mask between the pair of electrodes. The printed CNT paste was dried at 100°C for 1 h in air ambient and then burned at 400°C for 30 min under nitrogen environment to remove any organic binder. The adhesion of CNT thin films fabricated by burning process to glass substrate was very superior and physically robust.

The fabricated CNT oil condition sensor with 8 × 5 mm in size and lead-line of the pin type is shown in Fig. 1b. This sensor was composed of a closed circuit passing through the printed CNT paste and the electrode pair. The CNT paste as a sensitive thin film acted like a variable resistor. Figure 1c shows a scanning electron microscopy (SEM) image of the random CNTs after heat treatment of screen printed CNT paste.

In the laboratory, the CNT oil sensor was dipped into the engine oil inside a sealed flask to measure the electrical conductivity of the engine oil. The flask was placed on the hot plate and heated in the range between room temperature and under 160°C. The temperature of the engine oil was measured with the Pt temperature sensor (Pt 100), which was installed together with the CNT oil sensor. Generally, a range of the engine oil temperature inside engine pan of automobile is kept ~80 to 120°C by cooling water and pumping. All of the engine oil samples were the same oil (ZIC A, SK Corp., Korea; API SL, SAE 5W30, Ashland Inc., Lexington, KY) and were collected from several automobiles with the same engine displacement according to mileages from 0 km (fresh oil) to 6000 km. The sensor output was measured by using a Keithley 2400 source meter

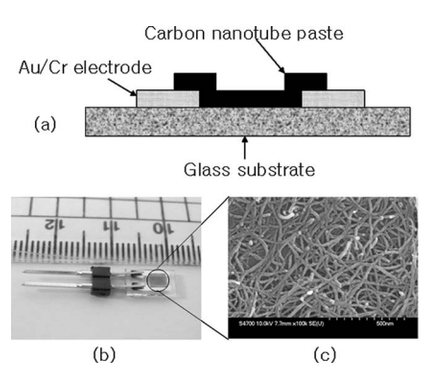

Figure 1. (a) Schematic drawing and (b) real image of a CNT oil sensor, (c) SEM image of multiwall carbon nanotubes as sensitive thin films.

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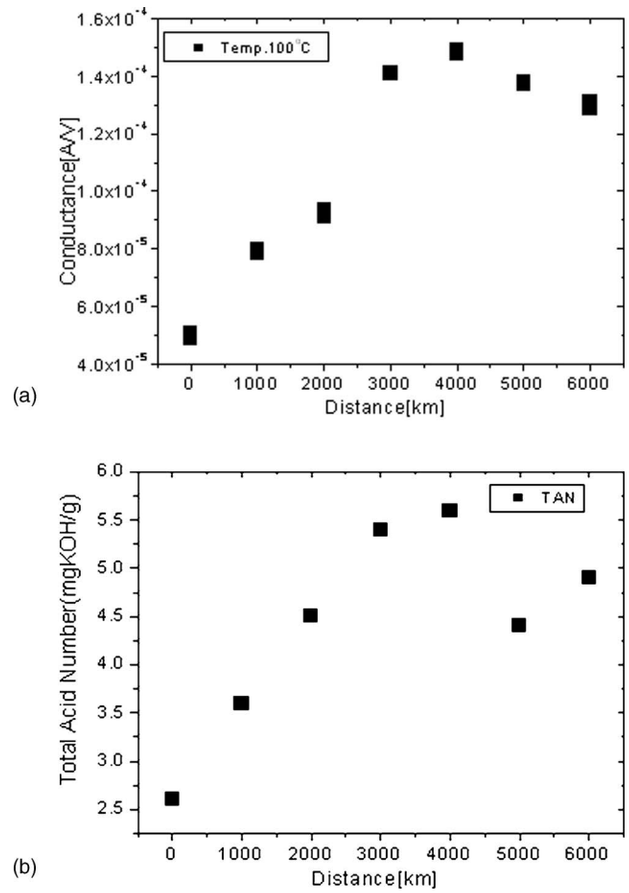

Figure 2. (a) Electrical conductance of the engine oil was measured according to mileage at 100°C. (b) The total acid number was measured in accordance with the national standard (KSM ISO 6618:2003).

and LabVIEW (National Instruments Corp., Austin, TX) software. The input voltage was fixed at 1 V, and the heating rate for the engine oil was 8°C min^{-1}.

At the road test, the CNT oil sensor was fixed at the end of the dipstick, and was contacted with the engine oil at the inner oil pan of the automobile through dipstick. The in situ CNT oil sensor was fabricated using a paste with twice the density (10 wt %) of our previous paste to improve the sensor output. The CNT oil sensor and Pt sensor were installed inside the vehicle engine oil pan. In addition, the sensor was always kept deep within the engine oil. The automobile had the driving distance of ~6000 km for the period of two months. The installed sensor in the oil pan was operated only at a temperature of 100°C.

On the other hand, the capacitive oil sensor was fabricated to be compared with the CNT oil sensor. The sensor was composed of interdigitated metal electrodes and glass substrate. The width and gap of electrodes were 40 and 40 μm, respectively, which were fabricated by using microelectromechanical systems processing. The capacitance in the engine oil was measured only by using the capacitive oil sensor with electrodes. In operation, an ac bias source was applied between two interdigitated electrodes. The frequency employed was 15 kHz and the sensor output was measured by using LCR meter.

Results and Discussion

The individual CNTs can be visualized as a hollow cylinder formed by rolling graphite sheets. Bonding in nanotubes is basically sp^2. CNTs have excellent absorption properties to other molecules.

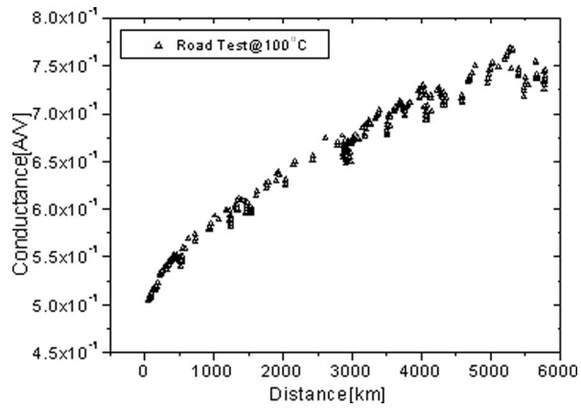

Figure 3. Electrical conductance of the engine oil under on-road driving test was measured by using in situ CNT oil sensor in the engine oil pan at 100°C.

Generally, they exhibit a hole-doped semiconductor characteristics.[4] Oxygen (O_2) exposure has a significant effect on electronic properties of semiconducting nanotubes,[14] e.g., converts semiconducting tubes into apparent conductors.[5] In addition, they respond to hydrogen peroxide, and their response current is increased according to the higher concentration of hydrogen peroxide.[15]

A model for oil oxidation inside combustion engines is as follows.[16] Engine oil oxidation is initiated by free radicals, which are derived either from combustion or from decomposition of primary oxidation products such as hydroperoxides (ROOH). These free radicals react with the oil (RH) to extract hydrogen and form alkyl radicals (R′), which in the presence of oxygen form peroxy radicals (RO_2')

$$ROOH \rightarrow RO' + {}'OH$$

$$RO' + RH \rightarrow ROH + R' \xrightarrow{O_2} RO_2'$$

The peroxy radicals further react with the oil to form hydroperoxides (ROOH) and alkyl radicals (R′). This process continues in a chain reaction, which can result in the formation of a high concentration of hydroperoxides. Formation of hydroperoxides is followed by radical formation from thermal and catalytic decomposition of hydroperoxides, which initiate and accelerate the oxidation.[16] In addition, oxidation of the engine oil in the internal combustion engine led to an increase in the electrical conductivity of CNTs. Generally, the TAN from the engine oil is used as an oxidation degree. The life of the engine oil corresponded to the value of TAN. Thus, the life of the engine oil can be determined by comparing the output of CNT oil sensor and TAN.

Figure 2 shows the sensor response according to mileage at 100°C. The measured temperatures of the engine oil were in the range between room temperature and below 160°C. The conductance values in the collected oil samples were measured by using the CNT oil sensor in the laboratory (Fig. 2a). TAN values for the same oil samples as those used in the CNT oil sensor were measured in accordance with the national standard (KSM ISO 6618:2003) (Fig. 2b). TAN value increased at 4000 km and decreased at 5000 and 6000 km, respectively. The reason is that the oil samples were collected from respective vehicles under different driving conditions, which can influence the degradation level of engine oil.[13] On the other hand, comparing Fig. 2a and b shows that the CNT oil sensor output is similar to TAN. Namely, the output of the CNT oil sensor corresponded to the degradation level of the engine oil. Therefore, CNTs can be useful as sensitive materials of the engine oil sensors.

Figure 3 shows the road test results according to mileages from 0 to 6000 km, where the more engine oil is degraded, the more sensor output is increased. If the oil condition was not changed, the

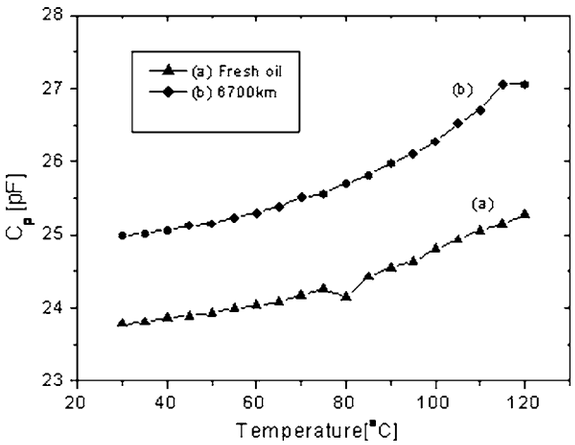

Figure 4. Capacitance variation in the capacitive oil sensor to the oil samples according to mileage. The capacitance difference in the sensor output was ~1.5 to 2 pF.

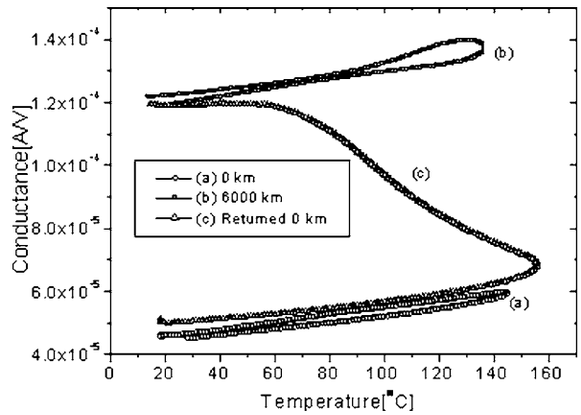

Figure 5. Reversible properties of the CNT oil sensor. (a) Fresh oil, (b) used oil (6000 km), and (c) returned fresh oil.

CNT oil sensor always kept the last conductance value in the engine oil. Consequently, when conductance value will be measured again, last conductance in the engine oil becomes the starting point in the output of CNT oil sensor. The sensor performance was not degraded, and at this time, the temperature of the engine oil was kept at an average temperature of 100°C. The maximum temperature was 130°C. The conductance of in situ CNT oil sensor in the oil pan was continuously increased according to mileage. When the CNT density was increased, initial conductance of in situ CNT oil sensor increased greatly more than that of our previous sensors. Therefore, the CNT density can be manipulated to change the conductivity of the CNT oil sensor. As a result, the output of the CNT oil sensor was continuously increased when the internal combustion engine was operated.

Figure 4 shows the response of the capacitive oil sensor to the oil samples according to mileage. The initial capacitance of fresh oil was 23.7 pF and was compared with that of the used oil (6700 km). The capacitance difference in the sensor output was ~1.5 to 2 pF. The sensing ability of the capacitive oil sensor depends on the dielectric constant of the engine oil between two electrodes.[13] This result shows that it is hard for the capacitive oil sensor to separate noise occurred in operation. We know that the CNT oil sensor had excellent performances than electrode-type capacitive oil sensor, because of easy process, few noise effect, and higher sensitivity.

Reversibility data in the CNT oil sensor is shown in Fig. 5. In the range from room temperature to 160°C, reversible test method was measured in sequence of fresh oil, used oil (6000 km), and returned fresh oil. The conductance in the CNT oil sensor was increased as engine oil temperature rose up. As mentioned above, the output of the CNT oil sensor was continuously increased when the internal combustion engine operated. However, in the returned fresh oil sample, the conductance of the CNT oil sensor was decreased nonetheless because temperature was increased. Conductance in the returned fresh oil sample was similar to that in the fresh oil sample while the temperature was falling. Therefore, the key parameter that affects sensitivity in the CNT oil sensor is oxidation level in the engine oil. We know that the CNT oil sensor had reversibility and linear property.

Conclusions

We have fabricated an engine oil sensor using multiwall carbon nanotubes. The CNT oil sensor was fabricated by using screen printing method with CNT paste. The output of the CNT oil sensor corresponded to TAN, which is one of factors to determine the end life of the engine oil. The CNT oil sensor can estimate the end life of the engine oil by scientific method in real time in situ for internal combustion engine. The sensitive thin film was not influenced by the maximum temperature of 160°C in the engine oil for several hours. We can confirm that the degradation of the CNT oil sensor was not generated during repetitive measurement in the engine oil at high temperature. In addition, the CNT oil sensor has reversibility and linear property, and so is used several times. The CNT oil sensor can be applied to other oil because the oxidation reaction in most types of lubricant oil is the same. This sensor is expected to be useful in several commercial and industrial applications.

Acknowledgment

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, funded by the Ministry of Science and Technology of Korea.

Korea University assisted in meeting the publication costs of this article.

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