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Development of a durable fiber-optic oxygen sensor for harsh underground environments

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ABSTRACT

This paper focuses on effects of protection with a silicone resin to develop a fiber-optic oxygen sensor with long-term stability and durability in harsh underground environments. Ruthenium (II) complexes were used as oxygen-sensing compounds. A uniform composite film composed of silicone resin and the Ru complex was prepared with spin coating technique. A comparison of dissolved-oxygen (DO) sensitivity between the composite film and a Ru complex film was made by exposing to hot water (80 °C). The result of the accelerated degradation test showed that sensitivity of the Ru complex film was stable; meanwhile that of the composite film increased with exposure time in a short period. In order to improve stability, the Ru complex film overcoated with silicone resin was prepared. Differences in sensitivity for saturated DO (8.5 ppm) between with and without the silicone resin overcoating on the Ru complex film were investigated by exposing to the hot water and simulated underground water. These results revealed that the sensitivities and response times of the overcoated films were stable and slow, respectively, compared to those of non-overcoated films. Then, optodes were evaluated for effects of the overcoating on sensing properties by exposing to 100 vol.% oxygen gas. The experiment showed that: (1) the response time was significantly influenced by the thickness of the overcoating; and (2) response speed of the overcoated optode was slow by a factor of about 35 compared to that of the non-overcoated. We concluded that the overcoating was effective in the application to mid- and long-term oxygen monitoring in the harsh environments.

1. Introduction

High-level radioactive wastes have potential hazards for the ecological system. Disposal of the radioactive wastes generated by a wide range of industrial, medical, and military activities is a global concern [1–3].

The long-lived high-level radioactive wastes are today expected to be stored in deep and stable underground repositories in order to isolate them from our biosphere for long-term (>1000 years). The underground disposal of the radioactive wastes is based on multibarrier system [4]: an overpack of the repository containing the vitrified radioactive wastes (first barrier), and geological barrier (second barrier). The presence of the underground water containing oxygen (O_2) near the repository can lead to an increase in corrosion risk because the repository is composed of a stainless-steel cylinder and a carbon-steel container. Hence, O_2 monitoring in the environment is crucial.

A number of studies have been reported on O_2 sensors widely used in environmental, chemical, and clinical fields [5–12]. However, there are few gaseous and/or dissolved O_2 (DO) sensors with long-term stability and robustness in the harsh underground environments (high temperatures and presence of various anions).

The objective of the present study is to develop a fiber-optic O_2 sensor with long-term stability and high durability. Compared to conventional O_2 sensors, features of the fiber-optic sensor include: (1) use of the sensor allows remote monitoring; and (2) the system provides maintenance-free operation.

Our previous papers have demonstrated that ruthenium (II) tris(4,7-diphenyl-1,10 phenanthroline)didodecyl sulfate ($[Ru(dpp)_3](DS)_2$) [13] was chosen as an excellent O_2-sensitive compound among many complexes tested [14,15]. We have made it clear its sensitivity to 100 vol.% O_2 gas. Moreover, dispersion of the Ru complex into silicone resin was effective in preventing

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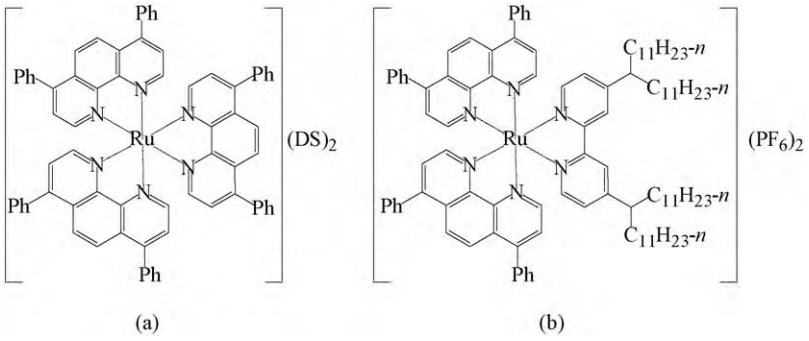

Fig. 1. Chemical structures of $[Ru(dpp)_3](DS)_2$ (a) and $[Ru(dpp)_2(4C_{11}dbpy)](PF_6)_2$ (b).

cohesion of the Ru complexes and thermal degradation of the composite film in air at high temperatures (40–150 °C).

Here we examined the Ru complex film and the composite film for degradation behavior by exposing to hot water (80 °C). In order to achieve long-term stability of the sensors, this paper evaluated effects of silicone resin overcoating in hot water and simulated underground water containing various anions as interfering compounds or degradation promotion. Then, an optode-type O_2 probe overcoated with the silicone resin was fabricated and evaluated for sensing properties.

2. Experimental

2.1. Chemicals

Ru complexes ($[Ru(dpp)_3](DS)_2$ and $[Ru(dpp)_2(4C_{11}dbpy)](PF_6)_2$) (see Fig. 1) were synthesized in the same way as our previous paper [14] and then purified by recrystallization from acetone/water. A transparent and colorless silicone resin (XE5844, Momentive performance materials Inc.) was employed as-received.

2.2. Preparation of O_2-sensing films on quartz substrates and O_2-sensing optodes

Two kinds of O_2-sensing films (F1 and F2) were prepared in order to investigate effects of the silicone resin for the degradation behavior. F1 was prepared by spin-coating (70 rpm, 8 min) with a toluene solution of the Ru complex (2.0 mM) on a quartz substrate (ϕ 20 mm), and subsequently drying at room temperature. F2 was prepared by spin-coating with a silicone resin solution of the Ru complex (1.3 mM) on the quartz substrate and then curing at room temperature: F1 was the Ru complex film; on the other hand, F2 was the uniform composite film composed of the Ru complex and the silicone resin. F3 was $[Ru(dpp)_2(4C_{11}dbpy)](PF_6)_2$/silicone resin composite film. The preparation method of F3 was same as that of F2. $[Ru(dpp)_2(4C_{11}dbpy)](PF_6)_2$ offers high lipophilicity compared to $[Ru(dpp)_3](DS)_2$. F4 was prepared by overcoating the silicone resin on F1 in order to enhance the durability. The thickness of the overcoating was changed to investigate the sensing properties.

Optode oxygen sensors were also prepared. An O_2-sensitive uniform composite composed of $[Ru(dpp)_3](DS)_2$ and the silicone resin was immobilized on an end face of a multimode step-index (SI) optical fiber (ϕ 600 μm) with the dip-coating technique (Op1). An optode on which the silicone resin overcoating was provided (Op2) was prepared with dip-coating method. Influences of the thickness of the overcoating on their sensor responses were investigated.

2.3. Sensing characterization

Evaluation of O_2 sensitivity of these films (F1 and F2) to saturated DO was carried out with the same experimental apparatus as our previous paper (see Fig. 2a) [14]. F1 or F2 was set in a chamber and an optical fiber probe was equipped with the chamber above the sensing film. The experiments employed a 470 nm LED (Ocean Optics, Inc., LED-470) as an excitation source. Measurement of light of 610 nm with a spectrometer (Ocean Optics, Inc., USB-2000) allowed the observation of luminescence intensity changes.

Fig. 2b illustrates systematic diagram of the experimental apparatus for Op1 and Op2. The light source and spectrometer used in Fig. 2b were identical to those used in Fig. 2a.

In order to examine the films for degradation behavior, exposure tests were performed by passing hot water (80 °C), gaseous O_2, or simulated underground water containing anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, and H_4SiO_4) through the chamber. The sensitivity of the films to saturated DO was periodically measured in water at 20 °C while the exposure tests were interrupted. The exposure time was thereby defined as total duration where the films were in the test conditions.

Concentrations of HCO_3^-, SO_4^{2-}, and H_4SiO_4 in the simulated underground water were set to 1.7×10^{-1}, 1.1×10^{-4}, and 1.6×10^{-2} mol/kg, respectively. The anion concentrations of the

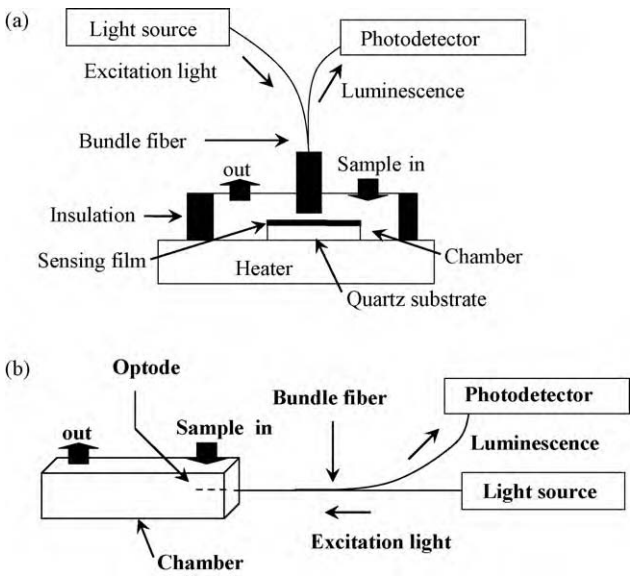

Fig. 2. (a) Systematic diagram of experimental apparatus for exposure tests to hot water and simulated underground water. (b) Systematic diagram of experimental apparatus for exposure tests to gaseous 100 vol.% O_2.

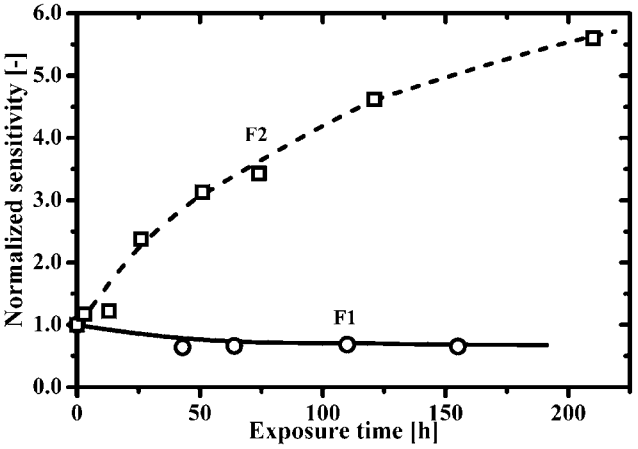

Fig. 3. Sensitivities of F1 (○) and F2 (□) for saturated DO in exposure test to hot water (80 °C).

simulated underground water were extremely higher than those of actual underground water for enhancing degradation. In these experiments, temperature and pH were fixed at 20 °C and 8.5, respectively.

3. Sensing mechanisms

Photochemical reactions in the films are as follows:

$$D + h\nu_1 \rightarrow D^*(\text{Excitation})$$

$$D^* \rightarrow D + h\nu_2(\text{Luminescence})$$

$$D^* + O_2 \rightarrow D + O_2{}^*(\text{Quenching})$$

where D and D^* are the Ru complexes at ground and excited states, respectively, and $h\nu_1$ and $h\nu_2$ are lights at 470 and 610 nm, respectively. The sensing mechanism is based on effects of luminescence quenching by O_2. Hence, measuring the variation of luminescence intensity allows O_2-sensing, and the sensors based on the mechanism are expected to offer excellent selectivity to O_2.

4. Results and discussion

4.1. Exposure test to hot water (80 °C)

Comparisons of saturated DO sensitivities between F1 and F2 were made by exposing to the hot water in order to evaluate the effects of silicone resin on sensing properties.

Fig. 3 shows relationship between normalized sensitivities and exposure times to the hot water. The sensitivity of F1 slightly decreased with exposure time, and then reached a stead state. On the other hand, the sensitivity of F2 increased consistently with time. The reason is because swelling of the silicone resin caused by exposing to the hot water probably influenced the dispersion condition of the Ru complex: increase in the apparent concentration of the Ru complex in the composite film resulted in the suppression of their self-quenching reaction.

4.2. Cyclic test (exposing to hot water/drying)

The cyclic tests employed F3 as an O_2-sensitive film. In Fig. 4, normalized sensitivities and response times of F3 to saturated DO were plotted against exposure times. The measurement confirmed that drying of F3 inevitably led to decrease in sensitivity. 90% response times (τ_{90}) of the film were determined to be from 11 to

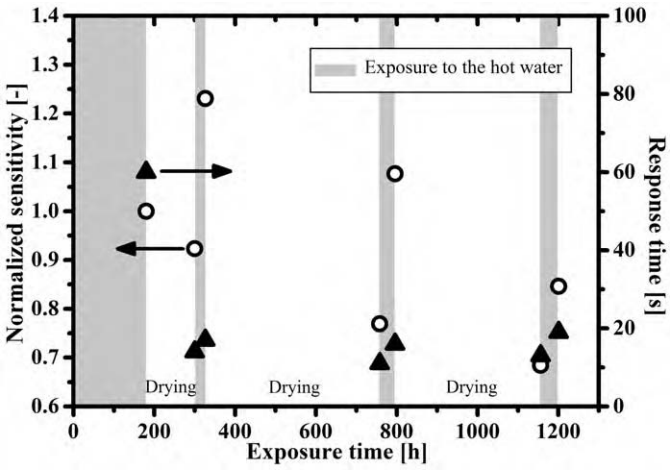

Fig. 4. Normalized sensitivity (○) and response time (▲) of F3 to saturated DO *vs.* exposing time to hot water (80 °C). The gray and white areas denote duration of exposure to the hot water and drying, respectively.

60 s. The response times after exposing to the hot water were found to be longer than those after drying, indicating that the swelling-shrinking behavior of the composite film caused by the wet-dry cycles mainly affected the characteristics of the composite sensing films.

4.3. Long-term exposure test to hot water (80 °C)

As mentioned above, the exposure test and cyclic test demonstrated that preparation of the composite films by dispersing the Ru complex into the silicone resin led to the unfavorable sensing behavior in the hot water. For improvement of the sensors, we prepared an F4 sensor overcoated with the silicone resin. The silicone resin overcoating was expected to enhance mechanical and chemical durability of the sensor. A comparison of saturated DO sensitivity of F4 with that of F1 was performed by exposing to the hot water for about 15 days.

Scanning electron microscopy provided mean thickness of the silicone resin overcoating of 320 μm. As shown in Fig. 5, DO sensitivity of F1 hardly changed during the testing; in contrast, DO sensitivity of F4 increased steeply until 5 days, and then leveled out after about 8 days. These results revealed that the sensitivity of F4 finally remained high and stable although it increased at initial stage. Hence, development of the sensor with high stability and sensitivity is possible with the help of the pre-aging treatment.

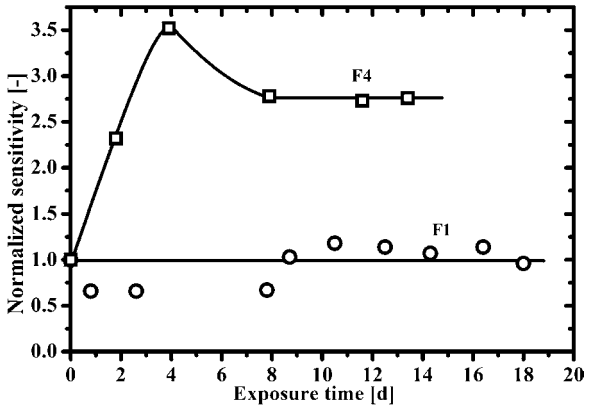

Fig. 5. Influence of silicone resin overcoating on saturated DO sensitivity. □: F4 having the silicone resin overcoating of 320 μm, ○: F1.

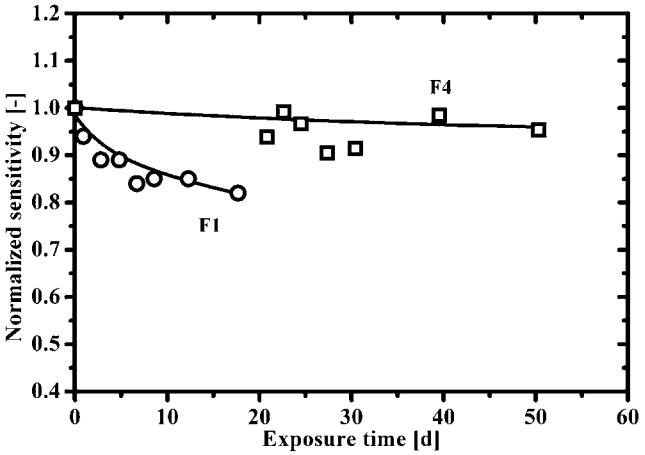

Fig. 6. Saturated DO sensitivities of F4 (□) and F1 (○) in simulated underground water.

4.4. Exposure tests to simulated underground water

The sensor with the overcoating thickness of 1300 μm could not detect saturated DO in the simulated underground water; meanwhile, the sensor having the overcoating of 320 μm permitted saturated DO sensing. This is because the thickness of the overcoating varied O_2 permeability through the silicone resin.

Fig. 6 illustrates the normalized sensitivities of F4 having the silicon-resin overcoating (320 μm) and F1. The sensitivity of F1 decreased dramatically with exposure time, and then peeling of the sensing film from the quartz substrate was observed; in contrast, F4 could detect saturated DO for about 50 days. Moreover, decreasing rate of the sensitivity of F4 was sufficiently slow compared to that of F1. Hence, the protection using the silicone resin was effective in obtaining stable sensitivity in actual environments.

The measurement revealed that τ_{90} of F1 was determined to be about 10 s; meanwhile τ_{90} of F4 was found to be about 190 s, implying that the silicone resin overcoating increased the response time. However, the performance of the protection was sufficient and useful in practical application because the rate of change in DO in actual underground water was probably slow.

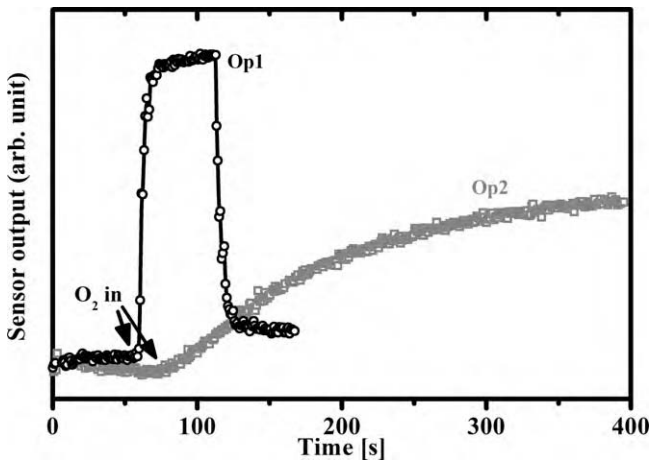

Fig. 7. Typical response behavior to gaseous 100 vol.% O_2. □: Op2 having silicone resin overcoating of 320 μm, ○: Op1.

4.5. Sensitivity of optode sensors to 100 vol.% gaseous O_2

Fig. 7 shows sensor responses of Op1 and Op2 to 100 vol.% gaseous O_2. The results revealed that Op1 exhibited sufficiently higher sensitivities and shorter response times ($\tau_{90} < 10$ s). The detection limit to gaseous O_2 was determined to be 450 ppb and the sensitivity behavior showed good reproducibility. In contrast, sensitivity of Op2 with the silicone resin overcoating of 320 μm was lower than that of Op1. Moreover, response speed of Op2 was slow by a factor of about 35 compared to that of Op1.

Our experiments revealed that the overcoating thickness of 100 μm or less did not influence the response time because of high oxygen permeability of the silicone resin. In contrast, the overcoating thickness of 1000 μm or more resulted in remarkably slow response and reduced the sensitivity by a factor of 2. These results suggested that adjustment of the overcoating thickness allowed fabrication of the sensor with desired sensing characteristics for mid- and long-term O_2 monitoring in the harsh aqueous environments.

5. Conclusions

The sensor whose sensing mechanism is based on luminescence-quenching reaction by O_2 was evaluated for long-term stability and durability. In our experiments, Ru complexes were employed as O_2-sensitive compounds. The Ru complex film and composite film composed of the Ru complex and silicone resin were prepared and examined for degradation behavior by exposing hot water (80 °C). The exposure test revealed that sensitivity and response time of the composite film tended to fluctuate.

In order to improve their sensing properties, we prepared the Ru complex film overcoated using the silicone resin. A comparison of saturated DO sensitivities between the overcoated and non-overcoated films was made by exposing the hot water and the simulated underground water containing various highly-concentrated anions. The exposure test to the simulated underground water showed that: (1) the film with the overcoating thickness of 320 μm could detect saturated DO; (2) sensitivity of the non-overcoated film decreased steeply with exposure time; (3) τ_{90} s of the overcoated and non-overcoated films were determined to be about 190 and 10 s, respectively; and (4) the sensing performance of the overcoated film remained unchanged for at least approximately 50 days.

Moreover, the optode overcoated with silicone resin by dip-coating were evaluated its sensing characteristics. The experiments confirmed that: (1) the response times significantly depended on the overcoating thickness; and (2) response time of the overcoated optode was slow by a factor of 35 compared to that of the non-overcoated. We concluded that the silicone resin overcoating was sufficiently effective in the application to mid- and long-term O_2 monitoring in the harsh underground environments.

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