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An electrochemical Nafion® matrix oxygen sensor and the evaluation of oxygen permeation in coated films

Y. GAO, H. KITA

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060 Japan

Y. WATANABE, K. SIMA

Materials Research Laboratory, Central Engineering Laboratories of Nissan Motor Co., Ltd, Yokosuka 237 Japan

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A Nafion® matrix was used to prepare a small and simple oxygen sensor whose sensing electrode and counter electrode were made by r.f. sputtering of platinum deposits on both sides of the Nafion® membrane. The sensing current varied linearly with oxygen partial pressure. This sensor enabled an estimation of oxygen permeation in coated films at working conditions. The present method clarifies the correspondence between the permeation rate through the clear layer and the degree of deterioration of underlayered paint film.

1. Introduction

Deterioration of paint materials and corrosion of the iron substrate are phenomena which seriously affect the life of a car. Several reports [1–5] describe this phenomenon in which the effects of various factors such as moisture, water, oxygen, temperature and light have also been examined.

Among these factors, however, the effect of oxygen appears not to have been studied thoroughly in a quantitative manner; nor has a method of monitoring directly the concentration and permeation rate of oxygen in coated films been previously established. Thus the present paper describes a simple and useful method for the investigation of the oxygen behaviour in paint films at working conditions.

In most earlier experiments, the permeation rate has been measured by using a stripped sample of the film. For example, in the electrochemical method the stripped sample is mounted on the window of a cell facing an oxygen atmosphere and the oxygen which permeates through the sample is detected electrochemically [5]. Such a procedure includes many steps and the data are obtained indirectly. In the present study, a solid polymer electrolyte membrane is used to prepare a solution-free cell. Kuwata *et al.* [6] have already reported the use of planar-type oxygen sensor prepared with Nafion® film. An alumina substrate was coated with the Nafion® thick film and the sensing Pt and counter Au electrodes were deposited on it leaving a space in between. In the present case, platinum was deposited on both sides of a commercial Nafion® membrane. The Nafion® matrix oxygen sensor thus obtained is thin, resists heat below 200° C and operates at room temperature. The sensor was embedded inside the coated films and the oxygen permeation was observed directly at working conditions.

2. Experimental details

Figure 1 is a schematic cross section of the coated film of the car. The top layer (Fig. 1a, 1) is the clear layer which protects the underlayered paint films (2 and 3) and the iron plate.(4). Since oxygen permeability through the clear layer is expected to control the deterioration of the underlayered films and the corrosion of the iron plate, attention was focussed on the property of the clear layer. Preparation of the sensor and permeation measurements were carried out in the following way.

2.1. *Preparation of oxygen sensor and its performance*

The solid polymer ion exchange membrane (Nafion® 117, about 200 μm in thickness) was first polished by sand paper, rinsed and then dried in vacuum at room temperature. A platinum layer 80–150 nm, was deposited on both sides of the membrane by r.f. (radio frequency) sputtering. The deposited platinum layers act as sensing and counter electrodes. The sensor was then prepared by cutting off the sample at the desired size, mainly 1 cm × 1 cm. A lead-wire of copper was mounted on each Pt deposited layer by conducting silver paste. The performance of the sensor was evaluated as follows. The polarization curve was first observed in oxygen and nitrogen atmospheres by a voltage sweep method (2 mV s^{-1},

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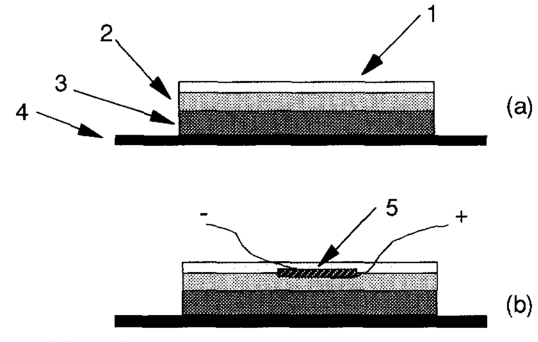

Fig. 1. Schematic presentations of coated plate (a) and embedded oxygen sensor (b). (1) Clear layer, (2) and (3) paint films, (4) iron plate, and (5) oxygen sensor.

0–6 V). The difference between the currents flowing in the oxygen and nitrogen atmospheres at a constant voltage, usually 4.5 V, was recorded as a function of oxygen partial pressure for the determination of performance. The performance was not affected, even after repetitive polarization up to 6 V, showing that the films are stable at high polarization.

2.2. *Measurements of the oxygen permeation and deterioration of coated films*

One of the two sensors prepared from a common membrane carrying the platinum layers was exposed to the gas phase and used as a reference, while the other was embedded into the coating film, as follows. The sensor was placed on the newly prepared paint film, still slightly wet (about 20 μm in thickness) and covered by spraying it with a clear layer of acryl-melamine resin (Fig. 1b). It was necessary that the film should be slightly wet in order to ensure intimate contact of the membrane with the film. After application of the resin, the sample was dried in an oven at 140° C for 30 min and left in ambient conditions for two days before measurements. The thickness of the clear layer varied from 10 to 50 μm. The oxygen permeation through the clear layer was observed as a function of the clear layer thickness and the composition varied from 8:2 to 4:6 in a weight ratio of acryl to melamine. Usual methods were employed to characterize the physical properties of the clear layer, its hardness and ductility, Young's modulus, and the average molecular weight of each chain in the network.

3. Results and discussion

3.1. *Performance of the oxygen sensor*

Figures 2(a) and 2(b) show SEM pictures of the surface and cross section of the sensor. The thread like pattern observed at the surface was due to the contraction of the matrix during the Pt sputtering. The vacuum condition and an increase in the matrix temperature during the sputtering accelerates the evaporation of the water from the matrix. Such contractions cause cracks in the Pt deposits when the sample absorbs moisture after being exposed to the ambient conditions. The cracks favour oxygen transfer inside the Pt deposits. The Pt layer in Fig. 2(b) appears much thicker than would be expected from the length of the sputtering time. This was due either to an uneven Pt sputtering or to localization of the Pt deposit when the sample was cut.

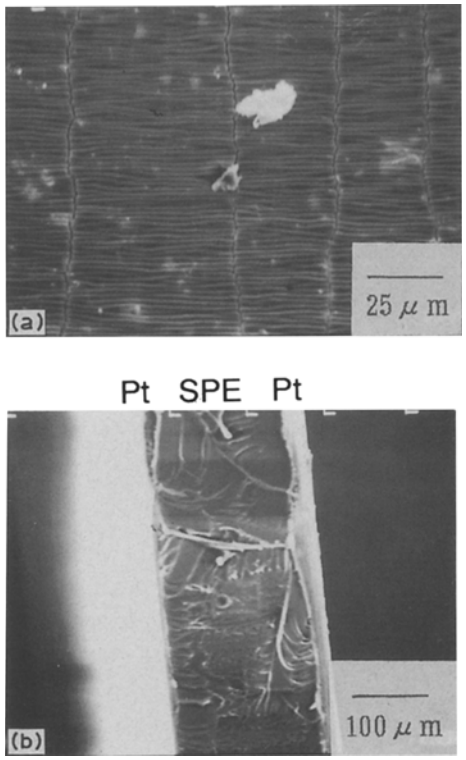

Fig. 2. SEM pictures of surface(a) and cross section(b) of oxygen sensor.

Figure 3 represents the current-voltage curves observed with the sweep rate of $2\,\mathrm{mV\,s^{-1}}$ when the sensor was exposed to oxygen and nitrogen atmospheres. The current which flowed in the nitrogen atmosphere was due to the electrolysis of

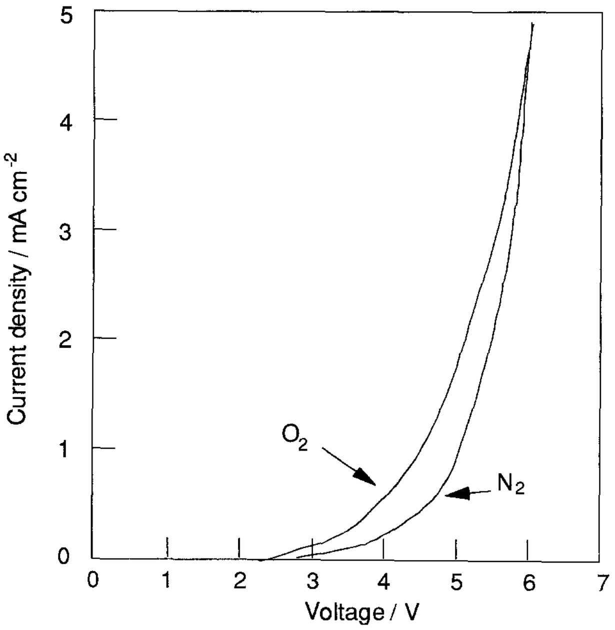

Fig. 3. Current – voltage curves of oxygen sensor in 1 atm O_2 and N_2. Sweep rate, $2\,\mathrm{mV\,s^{-1}}$.

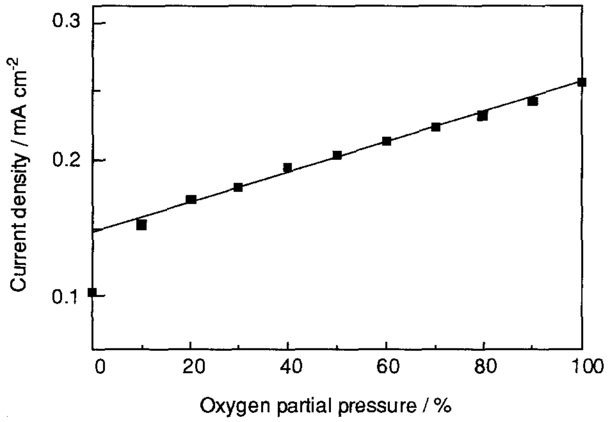

Fig. 4. Relationship between sensing current and oxygen partial pressure. Polarization: 30 min at 4.5 V.

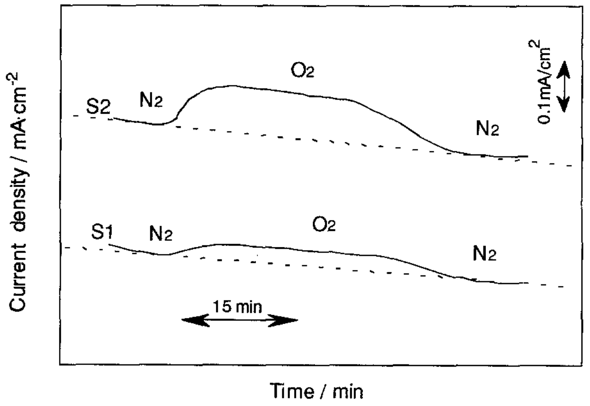

Fig. 5. Time response curve of sensors embedded in coated film(S1) and exposed in gas(S2).

water contained in the matrix. The current in the oxygen atmosphere exceeded that in the nitrogen atmosphere. This excess demonstrates that the present electrodes used are able to act as an oxygen sensor.

The oxygen is reduced at the sensing electrode (cathode) by the reaction,

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$

The resultant water migrates through the Nafion® matrix to the counter electrode (anode) and is oxidized by the reaction,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

where the protons formed migrate back to the cathode through the matrix. In consequence, the overall reaction becomes oxygen transfer through the sensor,

$$O_2(\text{sensing side}) \rightarrow O_2(\text{counter side}). \qquad (3)$$

The excess current increases with the polarization and becomes almost constant within a voltage range of 4.5–5.5 V. Since this potential independence demonstrates that the process at the sensor is not controlled by the kinetics of the electrode reactions (1) and (2), the excess current observed at 4.5 V (called sensing current) was used in the following analysis. In Fig. 4, the total current at 4.5 V in the oxygen atmosphere (polarization time, 30 min) is plotted against the oxygen partial pressure. A good straight line holds above 0.1 atm. This relation suggests that the process around the sensor is controlled by the oxygen supply to the three-phase zone at the interface between the cathode and the matrix. At lower pressures, the current deviates downward from the linear relation. The deviation was not reproducible and was not treated further in the present study.

Extrapolation of the linear relation to zero oxygen pressure gave a blank current of 0.15 mA cm^{-2}. Subtraction of the blank current from the observed one gave a sensing current for oxygen of 0.11 mA cm^{-2} at 1 atm O_2.

3.2. *Oxygen permeability of coated films.*

Since deterioration of the paint film and corrosion of the iron plate are caused mainly by air-borne oxygen, the prevention of oxygen permeation through the topmost clear layer should achieve elimination of deterioration and corrosion. Permeation through the clear layer was observed by placing the embedded sensor (Fig. 1b) in a test gas atmosphere. For comparison, the bare sensor was also placed in the test gas atmosphere.

Both sensors were first exposed to a nitrogen flow to remove oxygen from the measuring system. It took about half an hour for the embedded sensor to become free of oxygen after the polarization. Figure 5 compares the time responses of each sensor at 4.5 V when the atmosphere was switched from nitrogen to oxygen and vice versa. The embedded(S1) and bare(S2) sensors were found to respond in a similar way. The first rise of current is due to the oxygen permeation through the clear layer. Permeation includes both the dissolution and diffusion of oxygen through the clear layer. The sensing current becomes constant within several minutes. This constant current is controlled by the permeation and not by the electrode reaction discussed above. The rise time of S1 is somewhat longer than that of S2. The constant sensing current of S1 with a clear layer of acryl-melamine(7:3) resin of thickness of 22 μm was about one third of S2, and showed a fairly large oxygen permeability of the clear layer. It is interesting to note that contact of the Pt layer with the paint or clear layer does not seriously disturb the catalytic activity of the embedded electrode. The gradual decrease of the blank current may be attributed to a change in the matrix conditions following the electrolysis of water.

3.3. *Effects of thickness and composition on the permeability*

The sensing current of S1 as a function of the thickness of the clear layer was examined and this varied from 10 to 50 μm. The composition of the clear layer was 7:3 weight ratio of acryl to melamine. As expected, the sensing current at 4.5 V decreased with increase in thickness (Fig. 6a) and the plot of sensing current against reciprocal of thickness gave a straight

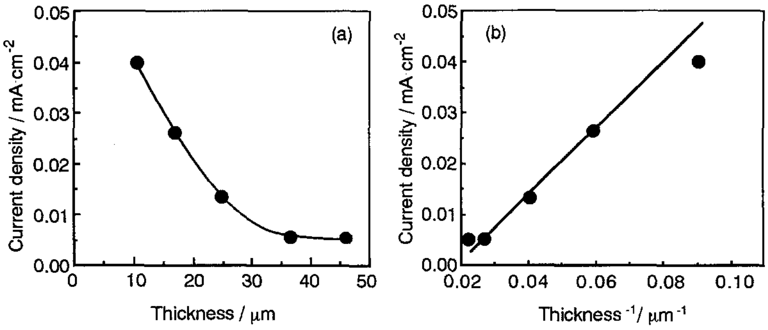

Fig. 6. Sensing current against thickness(a) and reciprocal of thickness(b) of the clear layer. Polarization: 30 min at 4.5 V.

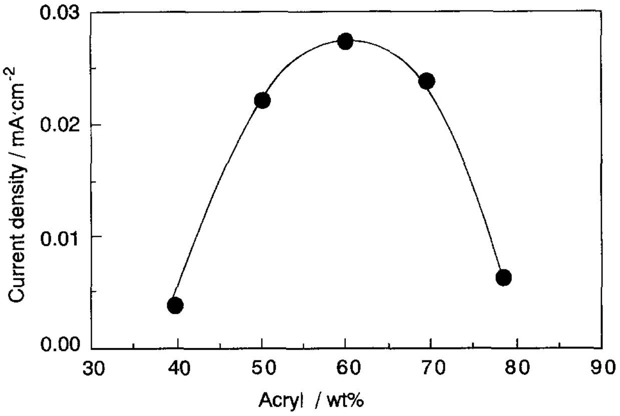

Fig. 7. Sensing current as a function of clear layer composition. Clear layer: acryl – melamine resin of 10 μm thickness, Polarization: 30 min at 4.5 V.

line (Fig. 6b). The deviation at the highest current is due to the contribution of sensor resistance.

The effect of the composition was studied by varying the weight ratio of acryl to melamine from 8:2 to 4:6. The observed sensing currents at 4.5 V were normalized to the values at a thickness of 10 μm based on the linearity of Fig 6(b). The results are plotted against the weight ratio of acryl in Fig. 7. The oxygen permeability of the clear layer reaches a maximum at a ratio at 6:4, when it becomes more than ten times larger than that of 4:6 or 8:2.

To examine factors controlling permeability, such physical properties of the clear layer as hardness, ductility, Young's modulus and the average molecular weight of the chain in the network were observed as a function of composition. The results are shown in Fig. 8(a) to 8(d). The average molecular weight plays a decisive role and hardness and Young's modulus do not show any systematic correspondence with the permeability. The sensing current reaches a maximum level when the average molecular weight drops to a minimum. Thus the degree of crosslinking controls the permeability. A smaller average molecule weight indicates a denser network of linkages. Such a network provides channels for oxygen permeation.

3.4. *Oxygen permeation and deterioration of paint films*

The present results demonstrate that deterioration of coated films can be directly monitored by measuring oxygen permeation with an oxygen sensor embedded below the clear layer of the coats. This method enables direct measurements to be made at working conditions without stripping the films, which the previous method required. The improvement of the

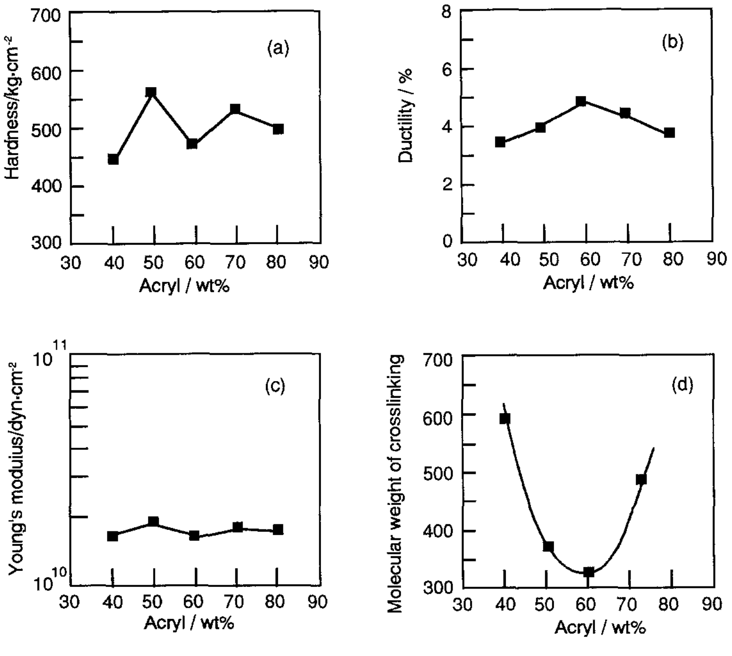

Fig. 8. Hardness(a), ductility(b), Young's modulus(c) and molecular weight of crosslinking(d) as a function of clear layer composition.

clear layer is the prime requirement for proofing paint films and iron plate against disintegration.

4. Conclusions

An oxygen sensor with a Nafion® membrane matrix as an electrolyte was prepared. This sensor records the linear output performance with respect to the oxygen pressure. The present sensor is a thin layer type and available in any size and shape. The performance was not affected by the coating treatment, being free from erosion of the paint solvent and resistant to heat treatment at 140° C. As it is embedded, it is also free from air contaminants.

The present sensor is thus able to provide direct information on oxygen permeation, which is the principal cause of the deterioration of paint films. The results indicate that the control of deterioration and corrosion phenomena will be enhanced if the permeation of oxygen through the clear layer can be suppressed.

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