Development of a pH-Sensitive Film Using a Porous Anodic Oxide Film of Al

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A porous anodic oxide film formed on Al was developed as a new pH-sensitive film. A porous anodic oxide film was immersed in an aqueous solution containing a pH-indicator reagent and boiled to seal it in the film. Litmus, bromthymol blue (BTB), and Congo red were used as pH-indicator reagents. The film, containing litmus, changed color reversibly within 1 s as a function of the test solution pH. The film showed superior durability in the solution at pH of 1–12 because of a stable boehmite layer covering the surface within that range. From the response of color change as a function of sealing time, it was inferred that the color change occurred mostly at the film’s surface region. For example, the film containing BTB prepared with long sealing time appeared to be green in an alkaline solution because of mixing of blue at the surface and yellow inside the film. Optimization of film thickness, the choice of pH-indicator reagent, and sealing conditions are important to prepare a highly pH-sensitive film.

Keywords: pH-Sensitive Film, Anodizing, Sealing

1. Introduction

The concentration of protons in a medium (pH) is a fundamental measure in various research fields. One method for measurement of pH is the use of glass electrodes in which a pH-sensitive glass membrane electrode and reference electrode are combined to enable quantitative evaluation of proton concentration in an aqueous solution. However, glass electrodes have various disadvantages including high cost, limitation in size and shape, mechanical fragility and temperature instability [13-19]. pH sensors using pH-sensitive metal oxide electrodes have also been developed [50-101]. However, these combined electrodes have some undesirable properties such as elution of ions from reference electrodes, resulting in contamination in the measuring system, and sensitivity of pH-sensitive electrodes to ions in the environment, which interfere with pH measurement [102]. On the other hand, a conventional pH-test paper containing chemicals to show color change with pH of the test solution has been widely used because of its easiness of use, low cost, and non-necessity of electronic equipment. However, the pH-test paper has drawbacks such as exudation of pH indicator reagents and thus short duration of service. pH-sensitive films using an organic or inorganic sol-gel film have therefore been developed to overcome these drawbacks [13-17]. Quantitative evaluation of pH using optical absorbance measurement has also been attempted. However, the development of a pH-sensitive film that fulfills the requirements of both rapid response and long lifetime has not yet been achieved [17].

A porous anodic oxide film formed on Al has been intensively investigated. Properties and morphology of the film can be optimized for various applications such as sealing of a dye for its coloration [102,103]. In the sealing process the porous oxide film on Al is immersed in boiling water to form a boehmite layer on the oxide surface. Boehmite is stable in a wide pH range and is known to penetrate protons. These properties of the porous anodic oxide film on Al seem to be suitable for sealing and holding a pH indicator reagent and for showing its color change due to proton penetration. In this study, therefore, a pH-sensitive film was developed using pH indicator reagents sealed in the porous anodic oxide film of Al. Absorbance spectra were measured as a function of pH of the test solution and the condition of film preparation.

2. Experimental

An Al sheet of 99.99% in purity and 40×20×0.3 mm in size was electropolished to obtain a mirror finish surface. The Al sheet was then fixed in a heat-adhesive laminate sheet with openings (10×10 mm in size) at both sides. One of two openings was coated with manicure and then the sheet was anodically polarized at 20 V in 4 mol dm⁻³ H₂SO₄ solution to form a porous oxide film of ca. 100 μm in thickness on the single side of the surface. The manicure coating was removed using acetone to expose the metal surface on the back side of the oxide film, and then the metal substrate at the opening was completely dissolved in etching solution containing 20% HCl + 0.1 mol dm⁻³ CuCl₂. At this time, a semi-transparent film supported in a laminate sheet was obtained. The film was immersed in boiling water containing a pH indicator reagent of 4.67 g dm⁻³ litmus, 2 g dm⁻³ bromthymol blue (BTB) or 2 g dm⁻³ Congo red for 300 s, 600 s or 1.8 ks (sealing time) at pH 7–9 to seal the pH indicator reagent in the pore. The resultant pH-sensitive films show colors of the pH indicator reagents: blue for litmus and BTB and red for Congo red. The film was put in a pyrex glass cell containing pH 2 hydrochloric acid, pH 4 phthalic acid, pH 6 or 8 sodium chloride, pH 10 carbonate or pH 12 sodium hydroxide solution, and the cell was set in a visible-light spectrometer (Shimadzu Co., model UV-3600) to measure the absorbance spectra in the wavelength range of 300 nm to 800 nm. Endurance of the films was also evaluated by immersing the film containing litmus in the solutions at various pH values for 12 ks with measurement of the absorbance at 610 nm. Surface morphology of the pH-sensitive film was observed by using an FE-SEM (JEOL Co. model JSM-6500F) and an optical microscope (Omron Co., model VC3000).

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3. Results and discussion

3.1 Dependence of absorption spectra on reagents

Fig. 1 shows absorption spectra of pH-sensitive films containing three different pH indicator reagents measured in solutions at various pH values. Sealing time of all films was 1.8 ks. In the absorption spectral measurement, intensity of transmitted light was not reproducible because the color density, i.e., concentration of the reagents was not uniform in the films. However, the shape of the spectra was reproducible and the heights of two absorption peaks could be quantitatively compared.

The film containing litmus (Fig. 1a) showed a sudden change in spectra between 4 and 6, and the color of the film was red at pH lower than 4 and blue at pH higher than 4. The color of the film was similar to that of the litmus-containing solution. On the other hand, the spectra of the film containing BTB (Fig. 1b) changed gradually with pH. The color of the film was yellow at pH lower than 4 and green at pH higher than 4. These colors differ from that of the solution containing BTB, which was yellow at pH lower than 6 and blue at pH higher than 8. The spectra of the film containing Congo red (Fig. 1c) changed between pH 3 and 5.2. However, the color change was not clear for the naked eyes. The color of the solution containing Congo red was blue at pH lower than 3.0 and red at pH higher than 5.2.

The difference in color of the pH-sensitive films and solutions containing BTB or Congo red is probably caused by partial color change of the films occurring only at the surface region. On the other hand, similar color of the film and solution containing litmus indicates that the litmus reagent containing dye and fine powder derived from lichen was fixed and partially embedded in the surface region of the boehmite layer. Such distribution of reagent in the film provides clear color change and also provides response of color change within a few seconds. For the purpose of pH sensor fabrication, however, continuous change of absorbance with pH, as observed for the film containing BTB, is required.

3.2 Dependence of absorption spectra on sealing time

Absorption spectra of the film containing BTB were measured as a function of sealing time to find suitable conditions for preparation of the pH-sensitive film. In the plots shown in Fig. 2, baselines were subtracted from the measured spectra to indicate clear changes in peak height. As can be seen in these figures, changes in peak height at 450 nm and 620 nm were observed. The height change at 450 nm was clear for the film sealed for 300 s and 600 s and became unclear for the film sealed for 1.8 ks. On the other hand, the height change at 620 nm showed an unusual dependence on sealing time.

Fig. 3 shows the peak height at 450 nm and 620 nm as a function of pH of the test solution using data presented in Fig. 2. For the film sealed for 300 s (Fig. 3a) or 600 s (Fig. 3b), peak height at 450 nm gradually decreased with pH. The film sealed for 1.8 ks (Fig. 3c) also showed a gradual decrease in peak height with pH accompanied by a large fluctuation. In contrast, peak height at 620 nm did not show reproducible dependence on pH change. These results indicate that the film sealed for a shorter time shows better pH response of absorbance peak height at 520 nm, although the color of the film sealed for a longer time was dense.

Fig. 4 shows cross-sectional SEM images of the surface region...
of the porous films sealed for 300, 600 and 1800 s. As can be seen in these images, the films sealed for 300 s (Fig. 4a) and 600 s (Fig. 4b) were hardly sealed, while the film sealed for 1.8 ks was completely sealed. Even if the pore was not closed for the former films, the surface of the film is thought to be covered with a boehmite layer to hold pH indicator reagents.

These results indicate that the pH-sensitive film containing BTB sealed for 300 s showed better performance for pH evaluation with absorption measurement at 450 nm. Better performance of color change was obtained for the film prepared for a shorter sealing time because the color change occurs mainly in the surface region rather than the inner part of the film. It is thought that the porous anodic oxide film provides a larger surface area to increase the density of color change. On the other hand, comparison of absorbance changes at two wavelengths is necessary for quantitative evaluation of pH of the test solution. For this purpose, however, reproducibility of absorption peak height at 620 nm was insufficient, as seen in Fig. 3. Therefore, further optimization of film preparation conditions is necessary to obtain reproducible absorbance changes.

3.3 Endurance test
Durability of the pH-sensitive film was examined by measuring absorbance change of the film containing litmus sealed for 1800 s in test solutions at various pH values for 1.2 ks, as shown in Fig. 5. In all solutions, absorbance decreased gradually due to slow exudation of the reagent from the film or dissolution of the film itself. The relatively rapid decrease of absorbance at the initial immersion was probably due to exudation of the reagent from insufficiently sealed film or detachment of the reagent loosely absorbed to or embedded in the boehmite film. The faster decrease of absorbance at pH 12 than at other pH values is caused by chemical dissolution of the oxide film in alkaline solution. After 12 ks of the endurance test, all films showed sufficient absorbance and reversible color change capability with change in pH of the test solution, even for the film immersed in pH 12 solution. From these results, we conclude that the pH-sensitive film obtained in this work possesses superior potential for use as a pH indicator with rapid response and long lifetime and with less contamination due to slow exudation of the reagent.

4. Conclusion
A new pH-sensitive film was developed using a porous anodic oxide film formed on Al and a pH indicator reagent sealed in it.
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The film shows fast response and long durability in the pH range of 1 to 12. Color change occurs in the surface region rather than inside the film. For use of the film in quantitative analysis of pH, however, optimization of the conditions for film preparation is necessary.

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