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Copper-Ion Responsive Chemical Bimetal

Takeshi YAMADA
Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606

A new type of sensor, called "Chemical Bimetal", has been developed. Chemical Bimetal uses the "Bimetal effect" and can effectively amplify the expansion or the contraction of materials. The copper-ion responsive Chemical Bimetal was constructed from polyethylene terephthalate (PET) membrane and polyvinyl chloride (PVC) membrane which contains 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (Kelex 100) as a reactant. This Chemical Bimetal responds to copper ion concentration from 0.2 to 1 mM.

The ordinary Bimetal is composed of two metal plates which have different rates of expansion with temperature change. By using this Bimetal effect, a new type of sensor, called "Chemical Bimetal," has been developed. The Chemical Bimetal consists of the combination of two kinds of plates having different characteristics depending on the chemical or physical properties of its surroundings. By the theoretical calculation, when a Chemical Bimetal of 40 mm length and 0.6 mm thickness contracts 0.5 mm, the amount of change in position (ACP) is 16 mm (32 time's amplification).

In this report, a copper ion responsive Chemical Bimetal was investigated. One plate (PET membrane of 0.1 mm thickness) does not react. The other plate (PVC membrane which contains Kelex 100) reacts with copper ion. When the Chemical Bimetal is dipped in sample solution, Kelex 100 forms copper-Kelex 100 chelate and the formed chelate deposits. Then, the Kelex 100 concentration in the PVC membrane decreases. The decrease of Kelex 100 concentration in the PVC membrane causes a little decrease of the PVC membrane length. Then, the small decrease of length is amplified to a large amount in the change in position of the Chemical Bimetal due to the Bimetal effect. Amounts of change in position show almost a linear relationship with the copper ion concentration.

The Chemical Bimetal was made using the following procedure.[1] Kelex 100 (donated by Sherex Chem. Co.) was purified by Lakshmanan's method.[2] 2 g of Kelex 100 and 3 g of dioctyl phthalate (DOP) was dissolved in 71 ml of 7% PVC-tetrahydrofuran (THF) solution. This mixed solution was cast onto a PET membrane (Fuji-Xerox OHP sheet V515) for 3 days, using a glass ring with an inner diameter of 13.5 cm . This cast plate was cut into the 8 cm square. Next, the cut plate was hot-pressed at 100 kg· cm^{-2} for 20 s. with two aluminum plates and a 0.7 mm thickness stainless steel spacer to remove curvature. The pressed plate was cut into a 1 cm x 4 cm rectangle.

The measurement was performed using the following procedure. One end of the Chemical Bimetal was fixed on a plane plate and the distance between one plate and the other end of the Chemical Bimetal was measured using a digital caliper (Mitsutoyo; No. 500-301) to obtain the amounts of change in position. At first, the initial

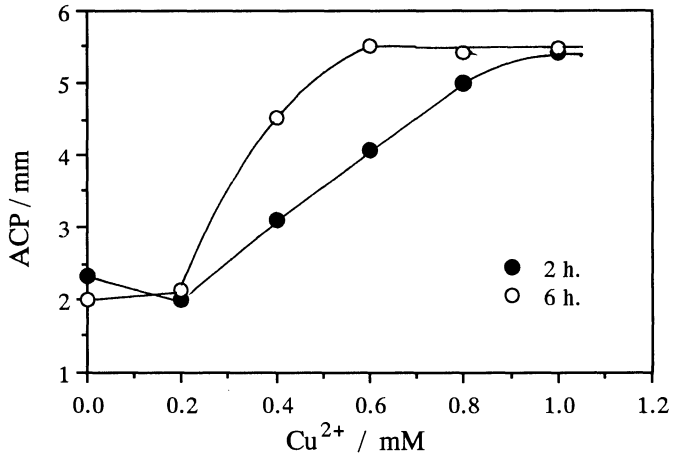

Fig. 1. Calibration curves of copper-ion responsive Chemical Bimetal.

curvature was measured before the reaction. The Chemical Bimetal was then soaked in a 30 ml vial bottle with 25 ml of sample solution at pH 5. After 1, 2, 3, 6, and 24 hours, the Chemical Bimetal was picked up, attached water was removed by paper, and curvatures were measured. Amounts of the change in position were obtained by subtracting the initial curvature. The composition of PVC membrane was chosen to be 20% Kelex 100, 30% DOP, and 50% PVC and the spacer thickness was chosen to be 0.7 mm, because of its high sensitivity. The sensitivity for copper ion was constant from pH 3.5 to pH 5.0. Calibration curves of the copper-ion responsive Chemical Bimetals are shown in Fig.1. From Fig.1, this Chemical Bimetal shows an almost linear response from 0.2 to 1.0 mM (1 mM = 10^{-3} mol dm^{-3}) copper ion concentration and does not respond from 0 to 0.2 mM. In this zero response zone, the copper-Kelex 100 chelate is extracted in PVC membrane. While, in the higher copper ion concentration range, the solubility of copper-Kelex 100 chelate is limited by the solvent power of the PVC membrane. Then, only a little portion of copper-Kelex 100 chelate is extracted in PVC membrane and the rest of the chelate forms oil-like drops on the PVC membrane surface. Thus, the decrease of Kelex 100 concentration in the PVC membrane causes the decrease of volume and length of the PVC membrane. The Chemical Bimetal then curves due to the Bimetal effect. The effects of other metal ions on the amounts of change in position were investigated. Nickel(II), cadmium(II), and aluminum(III) ions did not interfere. Zinc(II) and iron(III) ions interfered 12% and 8% after 3 hour soaking, respectively. Cobalt(II) ion interfered 47% after 3 hour soaking and 130% after 24 hour soaking. This result is due to slow chelate formation rate[3] and low solubility of cobalt(II)-Kelex 100 complex in PVC membrane.

These results suggest that the Chemical Bimetal works as a sensor. Further applications of Chemical Bimetal, such as reversible Chemical Bimetal, photosensitive Chemical Bimetal, parts of micro machine etc. is currently being investigated. Also, this phenomenon in the biological movement is currently being studied.

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References

1) T. Yamada, E. Yamada, K. Nishiyama, J. Kato, and M. Sato, *Prog. X-Ray Anal. Jpn.*, **16**, 51(1985).
2) V. I. Lakshamanan and G. J. Lawson, *J. Inorg. Nucl. Chem.*, **35**, 4285(1973).
3) E. Yamada, T. Yamada, and M. Sato, *Prog. X-Ray Anal. Jpn.*, **18**, 149(1987).

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