Development of A Novel Solid-State pH Sensor Based on Tin Oxide Thin Film

Taher M. El-Agez[a], Manal R. Al-Saraj[b], and Monzir S. Abdel-Latif[b]

[a] Physics Department, Islamic University of Gaza, P. O. Box 108, Gaza, Palestine
[b] Chemistry Department, Islamic University of Gaza, P. O. Box 108, Gaza, Palestine

Reprint requests to Prof. M. S. Abdel-Latif. E-mail: mlatif@mail.iugaza.edu

Z. Naturforsch. **59b,** 877 – 880 (2004); received December 15, 2003

A solid-state pH sensor was fabricated using a transparent conductive tin oxide film on a glass substrate. The coating of the glass substrate was achieved by a novel simple chemical vapor deposition (CVD) procedure. The response time of the pH sensor was substantially reduced when a thin graphite film was deposited onto the tin oxide conductive film. The sensor slope was found to increase as the temperature of the solution was increased. The performance of the sensor was investigated in the pH range from 0.3 to 11.0. A straight-line calibration graph was achieved throughout the whole range tested, especially when the solution temperature was 80 °C. The working pH range was found to decrease on the expense of the lower range as the temperature was decreased. Results obtained by the suggested sensor compares very well with conventional pH electrodes where the square of the correlation coefficient was 0.999.

Key words: pH Sensor, Tin Oxide, Conductive Thin Film

Introduction

The area of ion-selective electrodes (ISE) continues to expand as the need for reliable sensors increases. Many versions and configurations of ISEs were suggested emphasizing better selectivites, lower cost, ruggedness, simplicity and miniaturization possibility [1 – 12]. The requirement for low cost sensors is of prime importance when measurements in harsh conditions or in hostile environments are required. Different strategies and significant efforts were focused on developing reliable pH sensors where tridodecylamine, as well as other compounds, were used as the major constituents of the sensing element in pH electrodes [13 – 26]. Conductive polymers, like polyaniline, containing alkyldibenzylamine were used in solid contact pH electrodes [27]. Several reports on the application of tin oxide thin films as pH sensing elements were also reported in the literature [28, 29]. Yin *et al.* described an enzyme field effect transistor sensor (ENFET) for glucose [30] based on indirect pH sensing of tin oxide films. Preparation of conductive oxide thin films is also an important area of extensive research. Tin oxide thin films, doped and undoped, were prepared by several methods and precursors [31 – 36]. These methods are usually troublesome and, in most cases, require well controlled conditions and instrumentation.

In this work, we present a novel and simple method for the preparation of transparent conductive tin oxide films on a glass substrate. Diluted headspace tin tetrachloride vapors were focused on preheated glass substrates. The formed solid-state conductive material is used as a pH sensor. Experimental conditions and details of the sensor fabrication and the performance are detailed.

Experimental Section

Undoped conductive tin oxide (SnO_2) films were prepared on cleaned soda-lime glass plates with the dimensions 100 mm×50 mm×2 mm. Glass plates were cleaned physically by wiping the solid surface with Ethanolamine wetted cotton cloth. Moreover, the plates were chemically cleaned by dipping in concentrated chromic acid for 15 minutes followed by rinsing with distilled water. The glass substrates were placed on a preheated custom-made hot plate. The hot plate was fabricated out of black granite thick pieces with a heating element rated at 1750 W, 220 volts. The plate's temperature was monitored with a Chromel Alumel thermocouple and controlled electronically from 350 to 550 °C.

Fumes of concentrated tin chloride (99%, Riedel de Haën, Seelze, Hannover), carried by 99.9% oxygen gas, were forced to flow at a rate of 5 l/h through two rows of fine pipettes (melting point capillary tubes). Each row consisted of 50 tubes 10 cm long and 0.1 mm internal diameter.

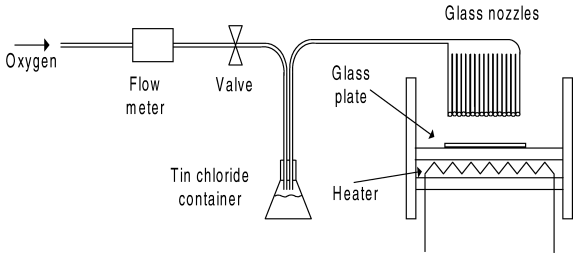

Fig. 1. Experimental setup for preparation of the tin oxide conductive thin film.

The prepared tin oxide coated glass plates were cut into small pieces (100 mm×3 mm) and the lower part (about 10 mm) was covered with a colloidal graphite suspension (Aquadag, Acheson, England). The formed graphite film was annealed at 200 °C for 30 min. The resulting sensor was washed with distilled water and stored in 0.4 M aqueous KCl. The measurement of the pH of different solutions (acetate, phosphate, and ammonia buffers as well as HCl and NaOH solutions) was done by placing the sensor in the test solution and connecting it to a saturated calomel electrode (SCE). The potential developed was measured using a Hanna pH/mV meter and the resulting potential was correlated to pH using a calibration curve in the pH range from 0.3 to 11.

Results and Discussion

Preparation of tin oxide thin film

The preparation of the conductive film was executed using a rather simple procedure and equipment. The headspace vapor of fuming tin chloride was driven throughout a set of glass capillary tubes made in two rows using 99.9% oxygen gas. The outgoing gaseous mixture was allowed to hit a preheated glass plate for few minutes. Fig. 1 show a schematic of the experimental setup that was used for the preparation of the conductive glass plates. The resistance of the formed tin oxide film was measured between the ends of the coated surface using a Fluke 87 digital multimeter. A substantial decrease in the resistance to few kilo ohms was achieved in just few minutes. Details of this process as well as the different parameters affecting the outcome will be the focus of a separate study. However, unlike the too many procedures described in the literature for the preparation of tin oxide transparent coatings, our method seems to have obvious advantages in terms of simplicity and cost.

The response time of the sensor

Regardless of the conductivity of the oxide film, the response of the pH sensor was found to be very long

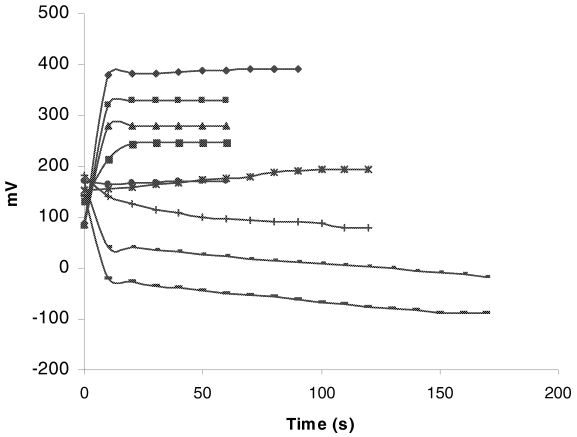

Fig. 2. Response time of the pH sensor at different pH values. Upper curve at pH=0.3 and lower one for pH=11.0.

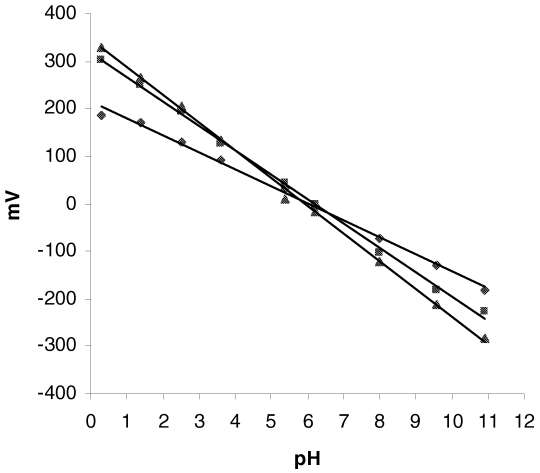

Fig. 3. Effect of temperature on slope of the pH sensor at 15 °C (♦), 60 °C (■), and 80 °C (▲).

(up to 30 min) and was dependent on the pH of the solution. The steady sate response was difficult to achieve in a reasonable time even after preconditioning the sensor in an acid, a base or a fluoride solution of different concentrations and exposure time. This drawback was surprisingly overcome by depositing a thin layer of colloidal graphite on the top of the conductive oxide layer. Response time, in the range of few seconds was achieved, which rendered the sensor highly practical. Fig. 2 shows some of the response time curves obtained using the graphite-coated sensor.

Effect of temperature on the response characteristics

The sensor response was evaluated at different temperatures as shown in Fig. 3. At lower tempera-

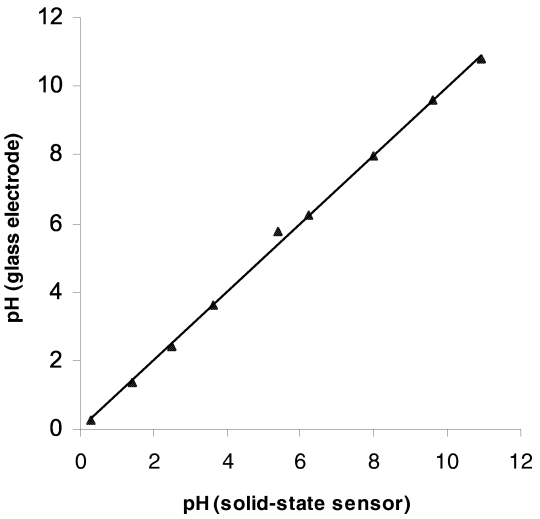

Fig. 4. Correlation between the conventional glass pH electrode and the solid-state pH sensor.

tures, like 15 °C, the slope of the sensor was about 35.9 mV/decade and the sensor would be used for pH measurements in the range from 2 – 11. However, when the test solutions were adjusted to 60 °C, the slope significantly increased to 51.3 mV/ decade and the usable pH range was extended to 0.3 – 11. When the temperature was increased to 80 °C, the slope increased to 58.3 mV/decade and the usable pH range was also extended throughout the whole range tested.

When the slopes of the calibration graphs were compared to the Nernstian response at the temperatures used, it was observed that the slope of the sensor approaches Nernstian response at higher temperatures. This would suggest a potential application of the sensor for pH measurements of hot solutions for which the conventional sensors are completely incompatible.

The square of the correlation coefficient for pH measurements using the solid-state sensor, at different temperatures, as compared to pH values obtained by a conventional pH electrode (Hanna Instruments HI 1131 pH combination electrode) was found to increase as the temperature was increased where r^2 values for measurements at 15 °C, 60 °C, and 80 °Cwere 0.996, 0.998, and 0.999, respectively. This also indicates that better results could be obtained at higher temperatures. Overall, it can be easily recognized that excellent correlation between the results obtained by the solid-sate pH sensor and the conventional glass pH electrode could be achieved (Fig. 4).

To check the dependence of the sensor response on the history of the sensor, the potential was measured after equilibration of the solid-state sensor in 0.1 M HCl followed by washing with distilled water and re-measuring the potential in a 0.4 M aqueous KCl. The same procedure was repeated for a 0.1 M NaOH solution, followed by washing and measuring the potential in the KCl solution. The potential difference of the solid state sensor after this cycle was always within 2 mV. This indicates that the sensor does not show what is called a memory effect, which implies excellent performance and potential applications.

Acknowledgement

This work was accomplished through a grant from the Deanery of Scientific Research in the Islamic University of Gaza.

[1] R. Yuan, R.-Q. Yu, Talanta **8**, 1255 (1993).
[2] R. W. Cattrall, I. C. Hamilton, Ion Sel. Electrode Rev. **6**, 125 (1984).
[3] A. Michalska, A. Hulanicki, A. Lewenstam, Microchem. J. **75**, 59 (1997).
[4] A. Michalska, A. Hulanicki, A. Lewenstam, Analyst **119**, 2417 (1994).
[5] S. Alegret, A. Florido, Analyst **116**, 473 (1991).
[6] R. Y. Xie, D. D. Christian, Anal. Chem. **52**, 1806 (1980).
[7] R. W. Cattrall, D. M. Drew, I. C. Hamilton, Anal. Chim. Acta **76**, 169 (1975).
[8] R. W. Cattrall, D. M. Drew, Anal. Chim. Acta **77**, 9 (1975).
[9] A. Tamura, K. Kimura, T. Shono, Anal. Chem. **54**, 1224 (1982).
[10] A. Hulanicki, R. Lewandowski, M. Maj, Anal. Chim. Acta **69**, 409 (1974).
[11] M. Trojanowics, Z. Augustowska, W. Matuszewski, A. Hulanicki, Talanta **29**, 113 (1982).
[12] H. James, G. Carmack, H. Freiser, Anal. Chem. **44**, 856 (1972).
[13] D. Erne, D. Ammann, W. Simon, Chimia **33**, 88 (1979).
[14] D. Erne, K. V. Schenker, D. Ammann, E. Pretsch, W. Simon, Chimia **35**, 178 (1981).
[15] P. Schulthes, Y. Shijo, H. Pham, E. Pretsch, D. Ammann, W. Simon, Anal. Chim. Acta. **131**, 111 (1981).
[16] P. Anker, D. Ammann, W. Simon, Microchim. Acta **1**, 237 (1983).
[17] P. Chao, D. Ammann, U. Oesch, W. Simon, F. Lang, Pflugers Arch. **411**, 216 (1988).

[18] U. Oesch, Z. Brzozka, A. Xu, W. Simon, Med. Biol. Eng. Comput. **25**, 414 (1987).
[19] U. Oesch, Z. Brzozka, A. Xu, B. Rusterholz, G. Suter, V. Pham, D. Ammann, E. Petresch, W. Simon, Anal. Chem. **58**, 2285 (1986).
[20] H. L. Wu, R.-Q. Yu, Talanta **34**, 577 (1987).
[21] E. Lindner, V. V. Cosofret, R. P. Buck, R. P. Kusy, J. Q. Whitley, J. Electroanal. Chem. **327**, 137 (1992).
[22] J. Chojnacki, J. F. Biernat, J. Electroanal. Chem. **277**, 159 (1990).
[23] E. Lindner, V. V. Cosofret, R. P. Buck, Talanta **40**, 957 (1993).
[24] V. V. Cosofret, T. M. Nahir, E. Lindner, R. P. Buck, J. Electroanal. Chem. **327**, 137 (1992).
[25] V. V. Cosofret, E. Lindner, R. P. Buck, R. P. Kusy, J. Q. Whitley, J. Electroanal. Chem. **345**, 169 (1993).
[26] S. C. Ma, N. A. Chaniotakis, M. E. Meyrhoff, Anal. Chem. **60**, 2293 (1988).
[27] W. S. Han, M. Y. Park, K. C. Chung, D. H. Cho, T. K. Hong, Anal. Sci. **16**, 1145 (2000).
[28] H. K. Liao, J. C. Chou, W. Y. Chung, T. P. Sun, S. K. Hsiung, Sens. Actuat. B **65**, 23 (2000).
[29] J. C. Chou, Y. F. Wang, Sens. Actuat. B **86**, 58 (2002).
[30] L. T. Yin, J. C. Chou, W. Y. Chung, T. P. Sun, K. P. Hsiung, S. K. Hsiung, Sens. Actuat. B **76**, 187 (2001).
[31] E. Shanthi, A. Banerjee, K. Chopra, Thin Solid Films **88**, 93 (1982).
[32] M. Fantini, I. Torriani, Thin Solid Films **138**, 255 (1986).
[33] J. Dutta, J. Perrin, T. Emeraud, J. Laurent, A. J. Smith, J. Mat. Sci. **30**, 53 (1995).
[34] A. Czapla, E. Kusior, M. Bucko, Thin Solid Films **182**, 15 (1989).
[35] A. Saxena, R. Thangaraj, S. Singh, O. Agnihorti, Thin Solid Films **131**, 121 (1985).
[36] T. Maruyama, K. Tabata, J. Appl. Phys. 4282 (1990).