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Simple and Economical Procedure To Assemble pH Glass Membrane Electrodes Used in Chemical Education

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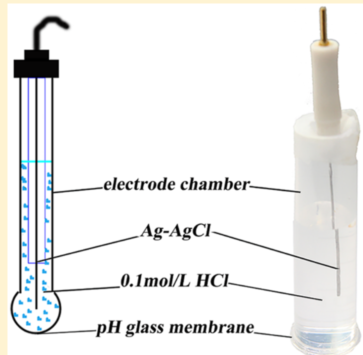
Supporting Information

ABSTRACT: The stated purpose of this paper is to provide a simple and quick method to assemble pH electrodes using readily available materials. The present assembled electrodes are comparable with commercial pH electrodes, with accuracy for pH determination in the range 2−12. Furthermore, the constructed simple pH electrodes exhibit a fast and stable response with a relatively wide linear range, meaning that these electrodes offer the promise of potential utilization in experiments. The inexpensive assembly and use of these pH glass membrane electrodes lends itself to introductory electrochemistry lab experiments at only a fraction of the cost of commercial electrodes. Under the guidance of instructors, students could make and test their own electrodes for chemical experiments. This might be helpful for students to gain a deeper understanding of the fundamentals of electrochemistry, such as the structure of ion-selective electrodes, the Nernst equation, etc.



KEYWORDS: *Laboratory Instruction, Hands-On Learning/Manipulatives, Electrochemistry, Ion Selective Electrodes, Laboratory Equipment/Apparatus, pH, First-Year Undergraduate/General*

INTRODUCTION

As the most common potentiometric device, pH glass membrane electrodes are often used in direct pH measurements, and these electrodes involve proton transfers. Because the glass membrane ion-selective electrode has been widely used for pH determination for decades,[1] the principles and their application became fundamental concepts in various areas of chemistry education, such as organic chemistry,[2] inorganic chemistry,[3] analytical chemistry,[4] physical chemistry,[5] etc. The outstanding advantage of the glass membrane ion-selective electrode is attributed to its remarkable analytical performance, which includes extremely high selectivity to hydrogen ions,[6] a wide response range, and a fast and stable response. The commercial electrode possesses a spherical film made of a special glass film with a carefully controlled composition. The potential of a glass film varies with H^+ ion concentration (more accurately, the activity) in the solution because a glass film establishes an interphase potential with the solution on both sides. The rapid equilibrium established across the glass membrane, with respect to the hydrogen ions in the inner and outer solutions, produces a potential

$$E_{(H^+/H_2)} = \frac{RT}{F} \ln a_{H^+} = \frac{RT}{F} \ln \frac{a_{H^+,\mathrm{outer}}}{a_{H^+,\mathrm{inner}}} \quad (1)$$

where R is the ideal gas constant, F is the Faraday constant, T is the temperature, and a_{H^+} is the activity of hydrogen ions. At 25 °C, when $a_{H^+,\mathrm{inner}}$ = 0.1 mol/L, RT/F = 25.69 mV, this relation becomes

$$E_{(H^+/H_2)} = \text{constant} - 59.16\ \text{mV} \times \text{pH} \quad (2)$$

Therefore, the measured potential is a linear function of pH, and an extremely wide linear range is obtained, yielding a slope of 59.1 mV/pH unit.[4,7−10]

In chemistry education, the pH measurement of solutions can be performed in introductory level experiments. However, the content of such courses generally concentrates on the operation of using commercial pH electrodes as the electrochemical sensor, which partly weakens the learning opportunities with respect to ion-selective electrodes and the Nernst equation.[11]

In recent years, many different self-made electrodes have been reported in the literature.[11−19] The preparation of these electrodes usually follows an effective and convenient method. For example, Goldcamp et al. designed an inexpensive and disposable pH electrode by the assembly of a liquid membrane.[14] However, due to the complexity of the manufacturing process of the membrane and the difficulty in obtaining the material, the method for fabricating the membrane electrode is difficult to apply on a large scale in teaching laboratories.

Considering the composition and thickness of the film of the constructed glass membrane ion-selective electrode, we used commercial coverslips as electrode films to construct a simple pH electrode and test its performance in pH measurement.

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The purpose of the present paper is to provide a simple and quick method to assemble pH electrodes to be used in chemical education.

EXPERIMENTAL SECTION

Chemicals, Equipment, and Materials

All chemicals were of analytical grade and were obtained commercially. All aqueous solutions were prepared with deionized water. Hydrochloric acid was provided by Chengdu Kelon Co. Potassium hydroxide was provided by Sinopharm Chemical Reagent Co., Ltd. pH standards, the saturated calomel electrode (SCE), and the Ag|AgCl electrode were obtained from Shanghai INESA Scientific Instrument Co., Ltd., or prepared according to the procedures in the literature.[20] The super glue was purchased from Shanghai M&G Stationery Inc. To measure the potential, a pH−mV meter (Shanghai INESA Scientific Instrument Co., Ltd.) was used. Three brands of coverslips used to construct the pH electrode were purchased from Shanghai Lingcheng Biotechnology Co., Ltd., in China, Beijing Beier Bioengineering Co., Ltd., in China and AmScope Map & Directions of the PS25-BSC12-72P100S22 in the United States (the photograph is shown in Figure S2).

Preparation of the pH Glass Membrane Electrode

The glass films used to construct the pH electrode are commercial coverslips with thicknesses in the range 0.12−0.17 mm. Before assembly, the coverslips were soaked in deionized water for at least 24 h to activate the glass films in advance. The procedure of the pH electrode construction is described as follows: (a) The activated coverslips are dried with lens wiping paper and linked to one end of the PVC tube using super glue, and the time for fixation is ca. 3−5 min. (b) After checking for fixation and leaking, a 0.1 mol/L HCl solution was injected into the PVC body, and the Ag|AgCl electrode was inserted into the tube. (c) The constructed electrode and a saturated calomel electrode (SCE) were connected to the pH meter with a shielded wire to form a complete test circuit. The overall flowchart for constructing the pH electrode is shown in Figure 1.

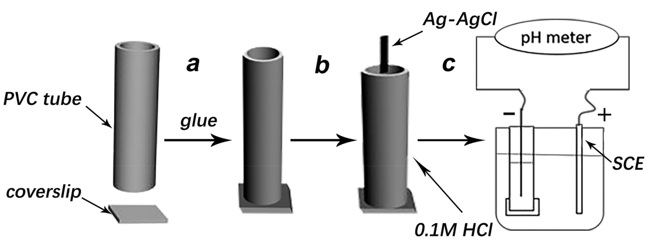

Figure 1. Flowchart for constructing the pH electrode.

HAZARDS

Hydrochloric acid is a strong acid that can cause severe burns. Sodium hydroxide is a strong base that is corrosive and can cause severe burns. These acids and bases are harmful and should be handled with care. It is suggested to flush skin with plenty of water for at least 15 min if exposed. Other equipment and usage procedures for the glass membrane ion-selective electrode preparation do not pose any significant hazards or safety risks.

RESULTS AND DISCUSSION

First, we prepared and tested these pH electrodes using coverslips with differing thicknesses to measure the influence of the origination of coverslips. The pH electrodes (one commercial electrode and one constructed electrode) were calibrated with buffer solutions of pH 4.01 and 9.18. The pH of the solution was determined from pH 7.00, and the pH of the solution was adjusted by adding dilute HCl and dilute KOH: three sweeps from pH 0 to 14 were averaged. As shown in Figure 2, four electrodes prepared by the above method exhibit high accuracy when used in combination with the reference electrode, such as SCE, compared with the commercial pH electrode. Notably, the response and linearity of the electrodes with respect to pH determination were desired within the range from 2 to 12. The above results indicate that the present electrodes constructed of usual commercial coverslips could work in a relatively wide pH range.

Next, the Nernstian response of these electrodes to the pH values was also measured, and the results are plotted in Figure 3. The slopes of Nernstian response are summarized in Table 1. As shown in Figure 3 and Table 1, four coverslip pH electrodes exhibited a strong linear response in the pH range 2−12 at room temperature. The calculated Nernstian response of these electrodes varies from 47.8 to 56.1 mV/pH (vs theoretical value of 59.1 mV/pH unit) when the thickness of the coverslip changes from 0.17 to 0.12 mm. Interestingly, this shows that the thicker coverslip generates the lower Nernstian response in Table 1. Among these electrodes, the glass film thickness of 0.12 mm represents the slope of 56.1 mV/pH unit, and that of 0.17 mm generates the slope of 47.8 mV/pH unit. This phenomenon could be used as an educational focus to show the reason why calibration for every electrode is necessary and why 50 μm glass film is typical in the commercial pH electrode (i.e., with ideal Nernstian response and sufficient mechanical strength).[9,10]

Furthermore, ion-selectivity was studied in the work because ion-selectivity is a key parameter for pH electrodes. The selectivity preference of the membrane for an interfering cation relative to H^+ was determined by the separate solution method.[21] When $C_{H^+} = 1.0 \times 10^{-6}$ mol/L, the potential selectivity coefficient $K_{i,j}$ (i is H^+, j is the interfering ion) of the electrode to common ions (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}) was determined under the medium condition of pH = 6. It is evident that most of the interfering ions showed selectivity coefficients below 10^{-2}, indicating that these ions slightly interfere with the determination of H^+ and that the electrode has a moderate selectivity for hydrogen ions (Table 2).

It should be emphasized that the coverslip pH electrodes have some limitations in practical pH determination when combined with a pH meter. According to the Nernstian equation, the slope of the pH value versus the voltage change is 59.1 mV/pH unit at 25 °C, but the best slope of all constructed electrodes reaches just 56.1 mV/pH unit, which might be caused by the larger internal resistance of the coverslip compared to the glass film of commercial pH electrodes.

On the other hand, the change in voltage with the pH change is linear, which agrees with the overall course of the Nernst equation. The response time of the electrode potential in reaching equilibrium stability is less than 2 min over the entire concentration range. These electrodes are excellent with

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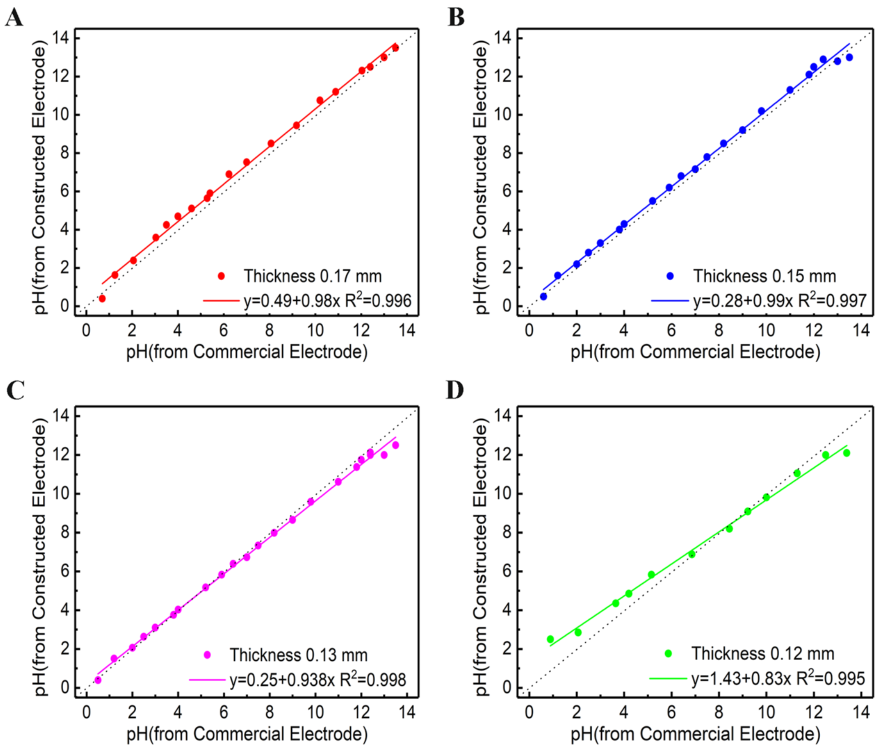

Figure 2. Comparison of pH values measured simultaneously using a commercial pH electrode (x-axis) and a constructed pH electrode (y-axis). The thickness of each coverslip is (A) 0.17 mm, (B) 0.15 mm, (C) 0.13 mm, and (D) 0.12 mm, respectively; the dashed line represents the theoretical $x = y$ relationship for the same response.

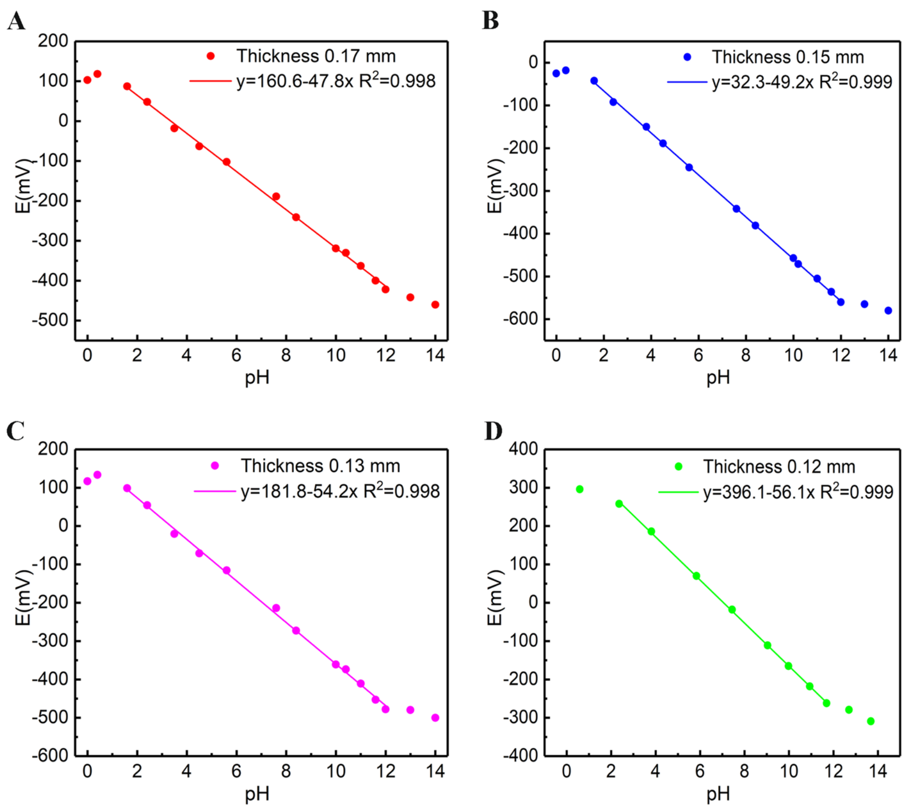

Figure 3. Effect of different coverslip thickness on pH electrode efficiency. Part A is the voltage of the glass membrane ion-selective electrode assembled when the coverslip thickness is 0.17 mm, and parts B–D are the voltages of the glass membrane ion-selective electrode assembled when the coverslip thicknesses are 0.15, 0.13, and 0.12 mm, respectively.

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Table 1. Effect of Different Coverslip Thickness on Nernstian Response Efficiency in the pH Range 2−12

Electrode[a]	Coverslip Thickness (mm)	Slope (mV/pH)
A	0.17	−47.8
B	0.15	−49.2
C	0.13	−54.2
D	0.12	−56.1

[a]Constructed sample electrodes; see Figures 2 and 3.

Table 2. Selective Coefficients of Various Interfering Cations for the H^+-Selective Membrane Electrode

Interference Ion	Coefficient Determined[a]
Na^+	1.21×10^{-3}
K^+	3.36×10^{-3}
Ca^{2+}	1.49×10^{-2}
Mg^{2+}	3.38×10^{-2}
Cu^{2+}	3.95×10^{-2}

[a]Calculated using the coefficient $K_{i,j}$ (where i is H^+ and j is the interfering ion) of the electrode under the medium condition of pH = 6.

respect to reproducibility and duration of pH measurement. These electrodes also demonstrate linear response in agreement with the Nernstian equation after one month in storage. Constructing this simple coverslip electrode may be an interesting experience for students. Throughout the experiment, the students take pride in the fact that they constructed their own glass membrane ion-selective electrodes. In addition, it might be easier for students to understand the principle of the glass membrane ion-selective electrodes and deeply comprehend the physical meaning of the Nernst equation. Therefore, a preliminary experimental procedural is designed on the basis of the present assembled electrodes in experimental teaching. This laboratory experiment is performed in an introductory chemistry course by five undergraduate students. The teaching effect was assessed before and after completion of the laboratory experiment by the student questionnaire. Through this experiment, students are able to replicate results that are equivalent to those obtained on a pH glass membrane electrode, and they get valuable insight into the principle of the glass membrane ion-selective electrodes and Nernst principles. A detailed experimental procedure for the students using the proposed setup and the student questionnaire are provided in the SI.

CONCLUSION

We successfully constructed pH electrodes quickly and efficiently with coverslips, and their performance is comparable to that of commercial electrodes. The coverslip glass membrane electrode has a strong linear response in solutions of different acidity, which conforms to the qualitative relationship of the Nernst equation. The results indicated the superiority of the constructed electrode in terms of linear range, response behavior, and detection limit. The constructed electrode could be used in a classroom experiment, research projects, or demonstrations. Building the pH electrode in class could provide students with a valuable introduction to electrochemistry or alternatively add fun to routine pH measurement experiments. Overall, this laboratory experiment reinforces the teaching of electrochemical properties in general chemistry and ensures practical experience with basic pH measurement techniques.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00254.

Influence of the intrinsic properties of the instrument on the pH electrode and experimental raw data (PDF, DOCX)

Student handout (PDF, DOCX)

Student questionnaire (PDF, DOCX)

Student lab report (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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