Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp967-968

PS-11-13 (Late News)

Paper-based Potentiometric pH Sensor using Carbon Electrode Drawn by Pencil

Ryotaro Kawahara[1], Parikshit Sahatiya[2], Sushmee Badhulika[2] and Shigeyasu Uno[1]
[1]Department of Electrical and Electronic Engineering, Faculty of Science and Engineering, Ritsumeikan University
1-1-1 Noji-Higashi, Kusatsu, Shiga, 525-8577, Japan
Phone: +81-77-561-2625 E-mail: suno@fc.ritsumei.ac.jp
[2]Department of Electrical Engineering, Indian Institute of Technology Hyderabad, Kandi, 502285, India

Abstract

We examined the sensitivity of the paper-based pencil-drawn pH sensor by potentiometric measurement. The sensor has sufficient pH sensitivity and it changes by pencil hardness, showing feasibility as a pH sensor for environmental assessments.

1. Introduction

The pH sensing is a basic method for monitoring water quality, and an inexpensive pH sensor is required for reduction of enormous cost related to the pH monitoring in a wide area. A number of inexpensive disposable chemical sensors using paper and a pencil have been reported so far [1]. Compared to sensors using graphene or carbon nanotubes, its low cost and simplicity of manufacturing process have attracted attention. However, there are just a limited number of reports on pH sensing using such paper-based pencil-drawn sensors. In this work, we report a new type of paper-based pencil-drawn pH sensor based on potentiometric measurement (Fig.1). This is an extension of a previous pH sensor based on resistance measurement [2].

2. Theory

The Pencil-Carbon-Electrode (PCE) consists of graphite and kaolin based clay [3], and there are many oxygen-containing functional groups [2]. In the pH sensor using graphene containing the functional groups, its pH sensitivity mechanism has been proposed based on the site-binding model [4,5]. On the other hand, kaolin is similar in composition to glass, so it may be possible to apply the ion sensitive mechanism of the glass electrode based on the Eisenman equation [6]. The doping effect proposed in [2] will also play a key role in pH sensitivity. In any of these mechanisms, potential across electrode and electrolyte will be changed by pH, and it can be measured by a high input impedance electrometer. This is, in principle, a potentiometric measurement in electrochemistry, and is advantageous in S/N ratio and power consumption of sensor circuitry.

3. Experimental

We designed a structure of paper electrodes (Fig.2), where three different solution droplets can be simultaneously contacted with the Ag/AgCl electrodes (RE:Reference Electrode) and the PCE. The pattern is printed on chromatography paper (ChrPr Whatman 3001–878) with a wax printer (Xerox color Qube 8580) and annealed in an oven (AS ONE ONW–300S) (Fig.3(a) and (b)). The RE was prepared by applying Ag/AgCl ink (BAS 011464) and dried at room temperature (Fig.3(c)). The PCE was traced on ChrPr with a pencil (Staedtler Mars Lumograph 6B/2B/H)(Fig.3(d)). Finally, a cellophane tape (Nichiban) was affixed on the reverse side to prevent the outflow of solution (Fig.3(e). The KCl (100mM) as a standard solution was prepared. Phosphate-buffered-saline (100mM, pH5, 6, 7, 8, 9) as pH buffer to be measured were prepared from K_2HPO_4 and KH_2PO_4. The measurement system and the flow of the experiment are shown in Fig.4. For each measurement, the paper electrode was replaced with a new one.

4. Results and Discussion

The potential change after dropping the target solution at pH5–9 was measured with a PCE drawn by a 2B pencil. The electrode potential changed in response to the pH of the target solution (Fig.5(a)). Calibration curve showed the slope of 23.2mV/pH, and sufficient response and linearity were confirmed (Fig.5(b)). In order to investigate the sensitivity dependence on pencil hardness, PCE with 6B, 2B and H pencil were prepared. Three patterns of potential change of PCE after dropping the target solution at pH6–8 were measured. Even if the pencil hardness was changed, the pH dependent responses were obtained (Fig.6(a)-(c)). When the pencil hardness was changed to 6B, 2B and H, the coefficient of determination increased. As the G:C (Graphite:Cray) ratio varies depending on pencil hardness [7], the increase in clay content increases the functional group sensitive to H^+.

5. Conclusions

We examined the pH sensitivity of the inexpensive and disposable PCE and dependence on pencil hardness. The paper-based PCE on paper has sufficient pH sensitivity and the linearity of calibration curve changes by pencil hardness, showing feasibility as a water pH sensor for river and soil.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number 26289111.

References

[1] E. Bernalte *et al., Biosensors* 6(3) (2016) 45.
[2] S. Kanaparthi *et al., RSC Adv* 6 (2016) 95574.
[3] N. Kurra *et al., Phys. Chem. Chem. Phys* 15 (2013) 8367.
[4] Il-Yung Sohn *el al., Biosensors and Bioelectronics* 45 (2013) 70.
[5] Ir.P. Bergveld Em. *IEEE Sensor Conference Toronto* (2003) 26.
[6] G. Eisenman. *Glass Electrodes for Hydrogen and Other Cations*.
[7] M. Costa Sousa *et al., Computer graphics forum* 19(1) (2000) 27.

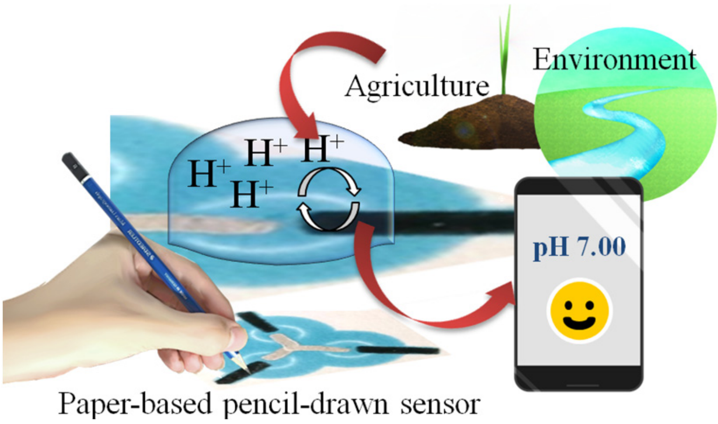

Fig.1 Concept of this research.

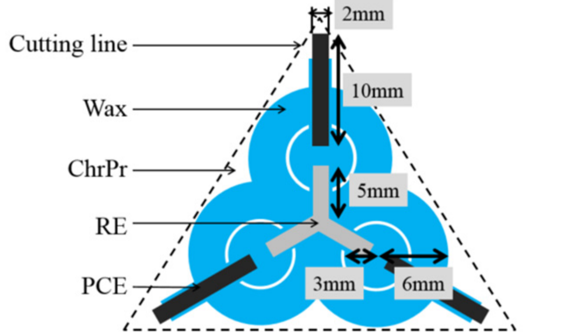

Fig.2 Schematic diagram of paper electrode structure.
ChrPr : Chromatography Paper, RE : Reference Electrode,
PCE : Pencil Carbon Electrode.

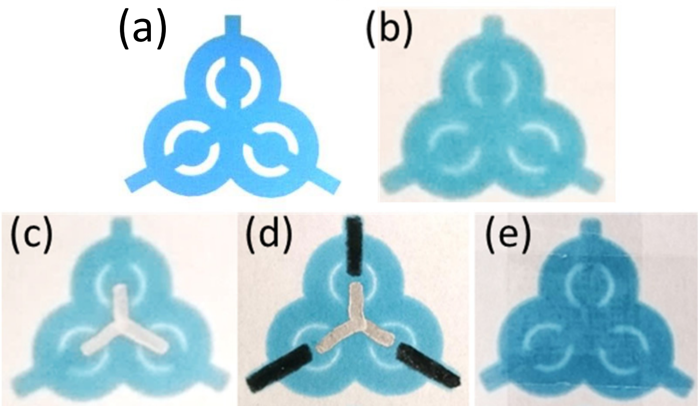

Fig.3 Photograph of procedure for making paper electrode.
(a) Wax printing, (b) wax annealing, (c) RE fabrication,
(d) PCE fabrication, (e) paste the cellophane tape on the back side.

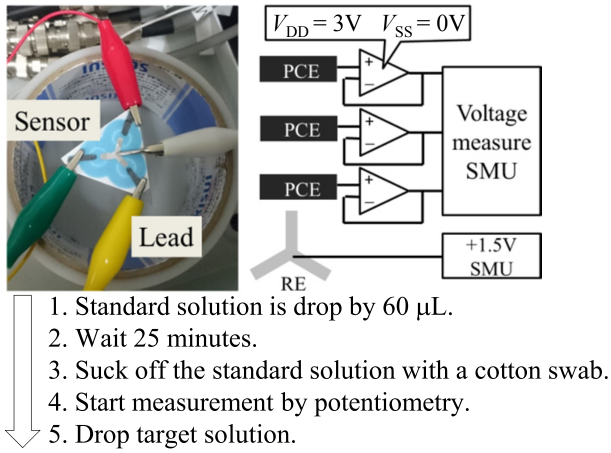

Fig.4 Experimental system and experimental procedure.

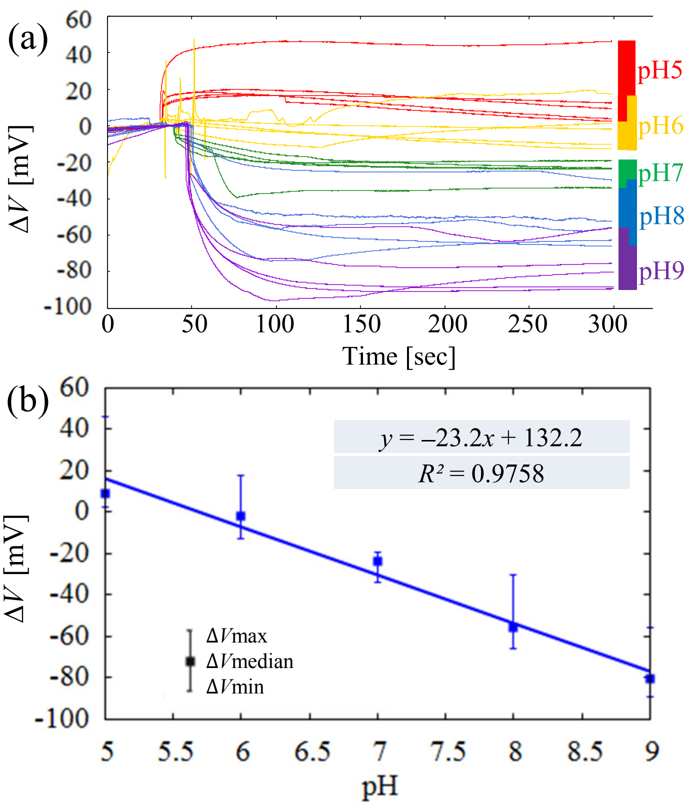

Fig.5 (a) The pH response, (b) calibration curve of pencil in 2B (300 sec). The ΔV is the potential change from the value when sample solution is dropped.

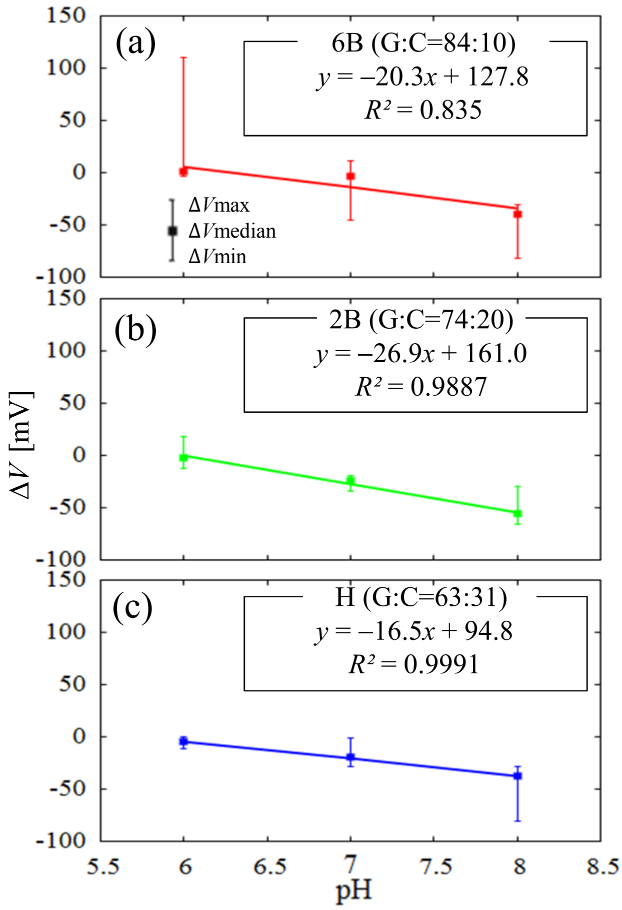

Fig.6 Calibration curve for pencil hardness (300 sec).
(a) 6B pencil, (b) 2B pencil, (c) H Pencil.