Design of Hydrogen Ion Concentration Measurement System

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Abstract

This paper presents an application for measuring the concentration of hydrogen ion by using ion selective electrodes. By this research we hope to provide useful information and verify the feasibility of measuring the concentration of other ions in the same way for sensing sweat. In this research, a pH electrode is used to generate an electrical potential which reflects the concentration of hydrogen ion. A voltage shift circuit is implemented to shift the negative voltage to positive voltage so that it can be inputted to the Analog to Digital Converter of an Arduino microcontroller. By programming the microcontroller, the calibration of pH electrode can be done. The effect of temperature on the electrode can be corrected digitally. An LCD display is used to show the pH value of the testing solution. According to the testing results, when the pH values vary from 3 to 11, the range of electrode output voltage was changes from -236mV to +236mV. After shifted by the voltage shift circuit, the output voltages range from 0.764V to 1.236V.

Keywords: Hydrogen Ion concentration measurement, Ion-Selective electrode application, Microcontroller application, Circuit design.

Introduction

The accurate and fast detection of electrolyte concentration in biological fluids are very useful for medical application [1, 2]. Doctors analyze fluid samples like blood or urine, taken from the patients in order to know their physical condition. However, these kinds of fluids analysis require laboratory equipment and work, which make the analysis expensive and much more time consumption. In some cases, certain ions can reflect someone's physical condition. For instance, the concentration of sodium in someone's sweat can directly show the dehydration level of that person [3]. In that case, it is much better for us to use Ion selective electrode (ISE) to analyze the fluids instead of sending the sample to laboratory.

Basically, Ion selective electrode consists of a silver/silver chloride electrode which was covered with ion selective membrane for detecting the certain ions in solution [4]. It also has a reference electrode, which can provide a reference potential for measuring the electrical potential [5]. In this study, an Extech 601500 pH probe was used as our ISE device.

Ion selective electrode is inexpensive and easy to use, which makes it an ideal choice for our project. However, considering the electrode's output voltage slope and the mobility of

ions are vary with temperature. Temperature compensation was made using a temperature sensor and software [6].

This paper presents a device that can measure the concentration of hydrogen ion. The analog output of Ion selective electrode which reflects the concentration of hydrogen ion would be linearly shifted by a voltage shift circuit. Then the voltage is sent to the ADC of a microcontroller. The microcontroller will have a calibration process before measurement. After the calibration, the microcontroller will know the relationship between voltage and pH value. Therefore, it can calculate the pH value and display it on the Serial monitor.

Basic theory of Ion selective electrode

Ion selective electrodes are devices that can measure the ionic potential between two solutions.

The Ion selective membrane allows certain ion through the membrane to reach the measuring electrode. Then an electrical potential between the measuring electrode and reference electrode is created. The electrical potential theoretically depends on the logarithm of the specific ion activity or concentration based on Nernst equation. [9]

$$E = E^0 + \left(2.303 * \frac{RT}{nF}\right)\log(A) \quad (1)$$

Here E^0 is a constant which is a characteristic of the particular ISE measure/reference electrode pairs. R is the gas constant (8.314 joules/degree/mole). T means temperature. n is the charge on the ion. F is the faraday constant (96,500 coulombs). A is the concentration or activity of the ion.

Ion selective electrode output the voltage of $2.303 * \frac{RT}{nF}\log(A)$ part of the equation. Therefore, at room temperature (25 degree Celsius), for decade concentration change we should get approximately 59mV output voltage.

System design

In this work, the Arduino microcontroller reads voltage from the Ion selective electrode. Generally, at room temperature (25 degree Celsius), for pH that varies from 4 to 10, the output voltage of Ion selective electrode will range from -177mV to +177mV. Ideally, we should input this voltage directly to microcontroller. However, most of the microcontroller's analog to digital converter (ADC) are unipolar type. It means that they cannot read negative value directly. Thus, it is vital for us to implement a voltage shift circuit.

It should be noted that considering normally Ion selective electrode has a very large resistance. Even a very low current will produce large voltage drop across those resistance. Moreover, passing current on Ion selective electrode means that the electrons are moving in the testing solution, causing additional error to the measurement. So, it's very important to shift the voltage without drawing any current.
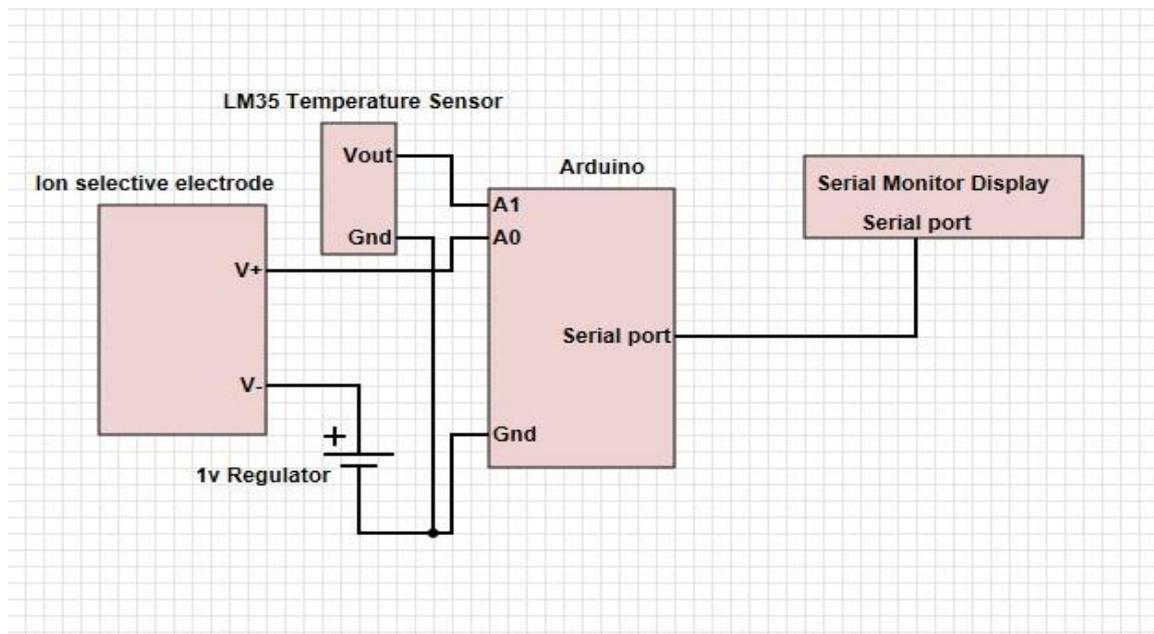
Figure 1: schematic of the hydrogen ion measurement system

The 1V power supply was connected to the negative output of the Ion selective electrode can shift the voltage without passing any current. The positive output of the Ion selective electrode is connected to the ADC of the microcontroller.

Software design

1. Calibration

The Ion selective electrode is a sensitive device. The characteristic of an Ion selective electrode will change with time due to electrode coating and aging.[6][8] Although compared with other types of Ion selective electrode, pH electrode is more stable over time. It still cannot be produced with identical characteristic.

In result, the real life Ion selective electrode does not exactly follow the Nernst equation. The difference between the theoretical value and actual value must be compensated by calibration in order to get an accurate result.

Ion selective electrode calibration is performed by measuring known, well defined solution and recording the output voltage. Generally, the calibration of electrode should be performed everyday. However, to get a more accurate result, it's better to perform a new calibration each time before measurement.

In this design, two-point software calibration is used. The calibration software's flowchart is shown in figure 2. After the calibration we can get a slope used to calculate the unknown pH value of our unknown solution.
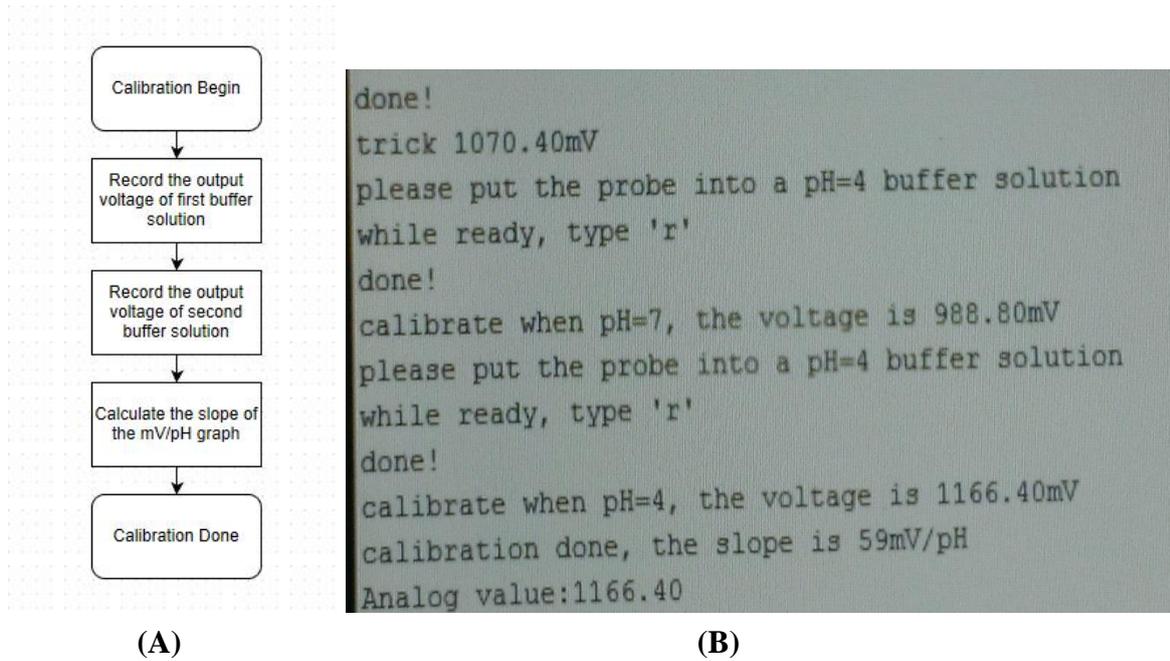
```
done!
trick 1070.40mV
please put the probe into a pH=4 buffer solution
while ready, type 'r'
done!
calibrate when pH=7, the voltage is 988.80mV
please put the probe into a pH=4 buffer solution
while ready, type 'r'
done!
calibrate when pH=4, the voltage is 1166.40mV
calibration done, the slope is 59mV/pH
Analog value:1166.40
```

         (A)   (B)

Figure 2: (A) Flow chart of the calibration software.　(B) Calibration process.

2. Temperature compensation

After the calibration, Ion selective electrode is expected to work properly. However, if the environment temperature changes after the calibration, it will cause error to the measurement. Generally, this kind of error is minimized by doing measurement right after the calibration to avoid significant temperature changes. However, considering our future work is to design a human dehydration level monitoring system, we cannot expect our device works in a laboratory's environment. Therefore, it's important to design a temperature compensation system. This can be done by adding a temperature sensor to microcontroller and designing temperature compensation software.

A LM35 temperature sensor is connected to the microcontroller. This sensor will record the temperature value when system doing calibration. It will also periodically record the temperature value after the calibration. The microcontroller will compare the two temperature values and fix the calibration result.

According to Nernst equation (1), the slope of mV/pH line at room temperature (25 degree Celsius, which is 298 Kelvin) should be

$$2.303 * \frac{RT}{nF} = \frac{2.303*8.314*298}{96500} = 0.059V/pH$$

When temperature rises to 29 degree Celsius after calibration, the theoretical slope will change to

$$2.303 * \frac{RT}{nF} = 2.303 * 8.314 * \frac{302}{96500} = 0.060V/pH$$

So each Celsius degree difference will result in a 0.25mV/pH calibration slope difference. The microcontroller can modify the calibration slope by the temperature difference between calibration temperature and measurement temperature. If the original calibration slope is 59mV/pH, when temperature rises 1 degree Celsius, microcontroller will

change the calibration slope to 59.25mV/pH. The temperature error without compensation shows in Table 1.

By doing this the temperature error can be eliminated.

Temperature difference	Calibration slope	Potential when pH = 4	Measured pH	Error rate
0 Celsius degree	59mV/pH	177mV	4.0	0%
1 Celsius degree	59.3mV/pH	178mV	3.98	0.5%
2 Celsius degree	59.5mV/pH	179mV	3.96	1%
3 Celsius degree	59.8mV/pH	180mV	3.95	1.25%

Table 1: temperature error without compensation

3. pH measurement

After calibration is done, the system is ready for pH measurement. When putting the measurement electrode into an unknown solution, microcontroller can read the electrode's output voltage and calculate the pH value using equation (2) and display the pH value and output voltage on the serial monitor.

pH value = 7.0 - (received voltage - voltage when pH equals 7)/calibration slope   (2)
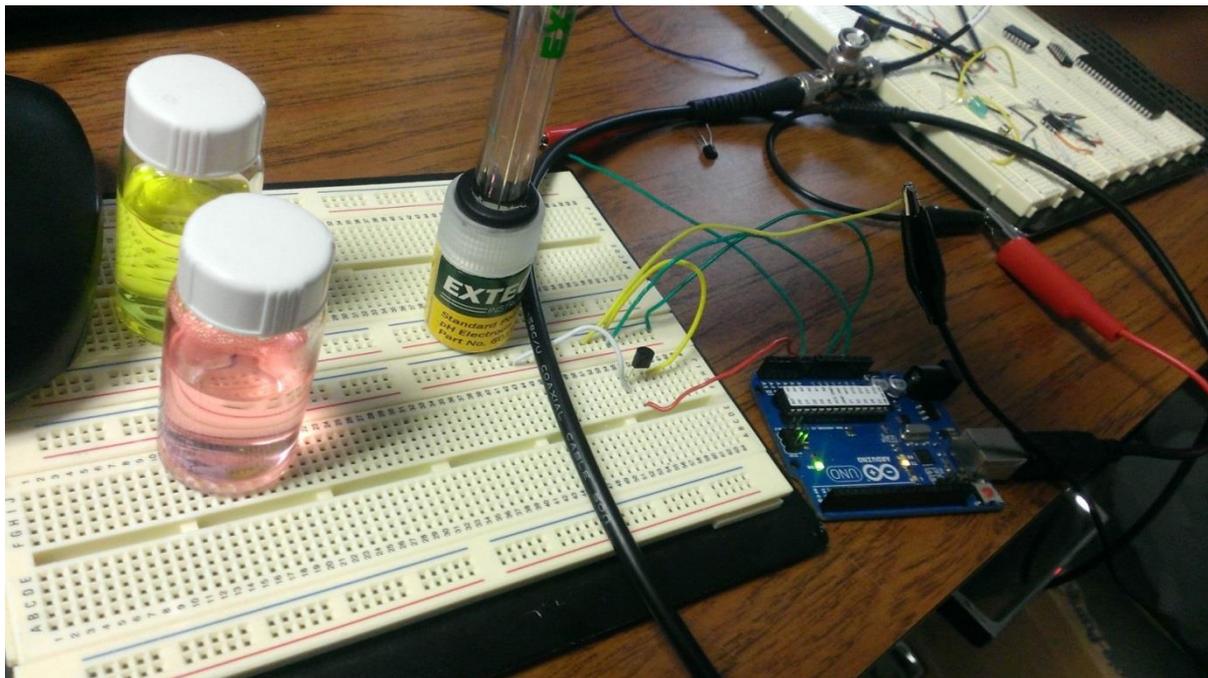
Results

For the first draft of the paper, we tested our system by some solutions with pH = 4, 6, 8, 10. These solutions are well prepared by the Chemistry Department of Central Michigan University. The results are pretty good. The accuracy and speed of this system is satisfying. As it shown in Figure 4, the measured results were almost matched the theoretical results. It shows that the system's performance is good enough for the sweat sensing project.

Tested solution pH	Measured pH	Error rate	Electrode's voltage
4.00	4.09	2.3%	1152.00mV
6.00	5.98	0.3%	1044.27mV
8.00	8.00	0%	929.13mV
10.00	9.87	1.3%	822.54mV

Table 2: the measurement results

(A)

(B)

Figure 3: (A) Measured pH value shows on Serial Monitor. (B) Photograph of the pH measurement system with LM35 temperature sensor.
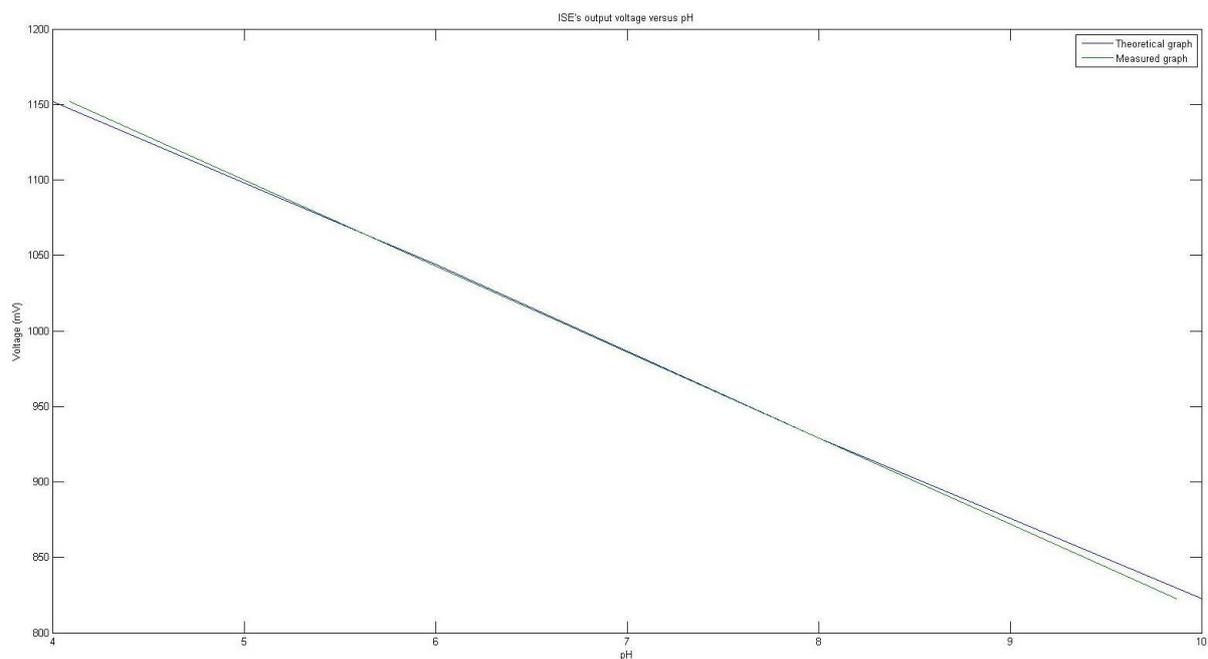
Figure 4: The ISE's output voltage versus pH, the green line was measured graph and the blue line was theoretical graph.

Future work

So far the characteristic of Ion selective electrode has already been studied. For the Next step we are going to fabricate our own device for our sweat sensing project. Sodium ion selective electrode will be used. Unlike pH electrode, sodium electrodes are not entirely ion-specific and can permit the passage of some of the other ions which may be present in the solution, causing ionic interference. So we will work on eliminating the ionic interference in the future. Also, the calibration slope of sodium electrode will be much different with pH probe. We still need to study on the sodium electrode.

Relevance with engineering education

This project was done as a prophase research aiming to provide information for our sweat sensing project. The project required us to combine the knowledge of Engineering and Chemistry, which provided us a crucial experience of multidisciplinary subject. As a fresh student research group, we learned how to use our knowledge to solve real life problems. Also, we learned the approach of dealing with cross-subject problems.

Conclusion

Using Ion selective electrode interface with microcontroller will be a good way to measure the ion concentration. By using the same design with sodium ion selective electrode, the research team can get an order of magnitude concentration or even more accurate concentration. This will provide them with the opportunity to detect the dehydration level via

measuring the sweat. The temperature compensation system of the design can provide a more accurate measurement result. It will be a very good choice utilizing ion selective electrode in the sweat sensing project.

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