Fabrication and Testing of a Miniaturised Water Quality Monitoring pH and Conductivity Sensors

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ABSTRACT

Development of cost-effective, durable and sensitive on-line water quality monitoring sensors that can be installed across the water distribution network has attracted attentions to increase the frequency of monitoring and hence reduce the risk of accidental or deliberate contaminations. This paper presents micro-sensors fabricated and implemented in a serpentine channel for the measurement of pH and conductivity, two important water quality parameters. The sensors are fabricated using hydrogel coated gold electrodes. The performance of these sensors was tested in both still (static) and flowing (dynamic) water. The serpentine channel, numerically optimized, provides a constant flow and constant outlet pressure condition for dynamic experiments. The results show that for flow rates less than 30 mL/min the values obtained in the dynamic experiments are similar to those measured in the static condition. Tests conducted for evaluating the sensors lifetime show no change in the performance even after one month.

Keywords: pH, conductivity, water quality monitoring sensor, hydrogel

1 INTRODUCTION

To prevent any outbreak, drinking water quality has to be at a proper level. Different water quality parameters such as turbidity, pH, conductivity, temperature and chlorine content, are determined to have a measure of drinking water quality. In most of the cases, water sample is collected and tested in laboratories using complex techniques. Compared to online sensors, these complex techniques require skilled personnel and thereby reduce the sampling frequency which consequently increases the probability of disease outbreak. Online water quality monitoring and early warning systems are becoming a necessity for large water distribution systems (WDS) [1] to prevent accidental [2] or deliberate contamination. Thus, the implementation of nearly real time water quality monitoring sensors across WDS is necessary to minimize disease outbreak. This paper studies the development of such sensors with the above properties for the measurement of pH and conductivity.

A long response time in measuring the change in pH can be an indication for biofilm development [3]; whereas the reverse could be due to leaching and nitrification [4]. In addition, pH of water has an impact on the degree of corrosion of metals [5] as well as disinfection efficiency [6]. Different pH sensors working based on a variety of principles have been developed. Potentiometric pH sensors are the most common sensors consisting of two electrodes: a reference electrode (fabricated from an inert metal, usually made from Ag/AgCl), and a working electrode (constructed from Pt or Au) having a pH-sensitive polymer layer deposited on it [13, 14]. The other groups of pH sensors which can be used as real time miniaturized integrated sensors are fabricated using a hydrogel polymer. An example includes the transducers consist of bending plates relating the change in the hydrogel volume to an electrical signal [7, 8, 9]. In such sensors, the hydrogel is placed between a rigid grate permeable to water. The swelling of hydrogel deflects the plate which in turn changes the resistance of a piezo-resistive bridge. Bashir et al. [10], Hilt et al., [11] and Zhang et al. [12] developed a transducer element with an optical read-out to record the changes in the volume of the hydrogel coated on a silicon substrate.

Another important water quality parameter is water conductivity which changes with the concentration of inorganic dissolved solids. High conductivity indicates the amount of ionic salts in water and can be an important indication of ionic salt contamination. The range of conductivity of drinking water is usually between 0.005 – 0.05 S/m. However, there is no guideline since conductivity varies depending on the amount of non-toxic salts present.

There are two major categories of conductivity measurement sensors: i) electrode based (contacting sensors), and ii) toroidal (inductive sensors). Electrode sensors can vary from having two to four electrodes [15, 16]. The sensor developed by Lee et al. [16] can be used for fresh water. The main advantages associated with this sensor are its wide measurement range, low cost, sensitivity to contact resistance, and linearity. The advantage of the toroidal conductivity sensor is that the input and output circuitry do not have to come in contact with the water, which reduces the probability of fouling. However, electrical interference and signal loss can occur for toroidal conductivity sensors.

In this study, we developed and studied the pH sensor working based on the change in the electrical property of a hydrogel polymer. Hydrogel swells or deswells depending on the pH of water. The electrical properties of the hydrogel that changes during the swelling/deswelling process are its conductivity and capacitance. There are several hydrogel-based sensors [17, 18, 19] developed for the measurement of different properties of the fluid of interest. Relevant to this study are the two sensors developed by Sheppard et al. [20] and Gill et al. [21] for the measurement of conductivity and pH, respectively. Sheppard et al. [20] introduced a conductometric sensor based on the change in the conductivity of a hydrogel layer coated on an interdigitated electrode array. Measuring at different frequencies ranging from 100 Hz to 100 kHz, they showed that the electrode impedance was primarily resistive. In essence, swelling of hydrogel increases its conductivity which consequently decreases its resistance. For measuring pH, Gill et al. [21] developed a hydrogel based pH sensor using Poly vinyl butaryl (PVB) and poly aniline emerald salt (PANI ES) doped with poly pyrole (pPy).

The main objective of this paper is to develop cost effective, accurate and sensitive pH and conductivity following the principles explained before [20, 21] for online drinking water quality.

2   SENSOR FABRICATION

For both the pH and conductivity sensors interdigitated electrodes were prepared by etching gold plated glass slides. Figure 1 shows the dimensions of the electrodes. The gold coated glass slide was spun coated with photoresist, covered with the mask and exposed to UV light for 8 seconds. The exposed portion of the photoresist was removed using the Microposit MF-319 developer. The gold and chromium film on the glass slide was etched consecutively by gold and chromium etchant. Copper wires were connected to the connection pads. The connection pads and bare part of the wires were covered with PDMS to prevent water coming directly in contact with the electrodes.

The same design was used for the measurement of both pH and conductivity. The only difference is that for the pH sensor the interdigitated electrodes were covered with hydrogel. The hydrogel was prepared from polyaniline emeraldine salt (PANI ES), polypyrole PPy in a solution form (5 wt.% in water), polyvinyl butyral (PVB) (see the details in [22]). 0.25 gm ppy was mixed with 10 wt% of PVB and 20 wt% ppy. The mixture was placed into an oven at $80^{o}C$ for 24 hours. Ethyleneglycolmonobutyalether was added to dissolve the prepared dried mixture which was spun coated on top of the interdigitated electrode. The chip was then placed in the oven at $50^{o}C$ for 24 hours to evaporate the solvent. After solvent evaporation copper wires were connected to the connection pads with conductive glue. The connection pad and bare copper wires were covered with PDMS coating.

3   EXPERIMENT

Figure 2 shows the experimental setup. A potentiostat (VersaSTAT-4, manufactured by Princeton Applied Research) was used to determine the electrical properties of the sensor. Water was supplied by a syringe pump. The maximum flow rate that could be provided by the pump was 30 mL/min. Water was supplied at 0, 3 and 30 mL/min to test the effect of the flow rate on the sensors. The experiments at the zero flow rate (i.e., the static test) were conducted by placing the sensor in a 20 mL of the solution. For connecting the sensors to the water pump an interface was fabricated so that the sensors do not get damaged. Three pH or conductivity sensors were placed simultaneously in the groove of the interface to determine the response at different flow rates. For the dynamic tests (flowing conditions) the sensor was placed in a serpentine channel which was designed and optimized using numerical simulation (the details of the channel are discussed elsewhere [22]).

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4   RESULTS

Figure 3 shows the resistance of two pH sensors as a function of pH measured during the static condition. To study hysteresis, tests were conducted forward (increasing pH) and backward (decreasing pH). Both sensors show small hysteresis and similar pattern over the range of pH tested. However, there is a slight difference between the measurements of the two sensors. This difference is due to the difference in the thickness of the hydrogel coated on the electrodes. However, once each sensor is calibrated against control solutions the sensor will provide accurate and reproducible measurements.

Figure 4 shows the effect of the flow rate (i.e., the dynamic condition) on the response of the pH sensor. It is evident that the flow rate has no effect on the response. To determine the lifetime of the sensor, the sensor was submerged in a buffer solution for 24 hours and the response was recorded. Then the sensor was placed into another buffer solution (with a different pH) for another 24 hours and response of the sensor was recorded. This procedure was conducted for more than 30 days. Figure 5 shows the effect of the exposure time on the sensor. The same sensor was placed in different pH solutions and it could detect the change in the pH value regardless of the exposure time.

Figure 6 shows the calibration curve for the conductivity sensors. The response is nonlinear for a wide range of conductivity. The conductivity of drinking water is usually between 0.05 mS/cm to 0.5 mS/ cm. For this range the response of the sensor is relatively linear as shown in

figure 6. The repeatability of each of the sensor is very high (less than 0.001 kΩ) although there is a difference in the response of the two sensors. This difference is due to the fact that it is impossible to make two sensors with an identical PDMS loading on the connections pad and wires. However, once each sensor is calibrated against control solutions, it produces reproducible results.

Figure 7 shows the effect of the flow rate on the response of the conductivity sensor. The sensor was tested for the static condition, and two dynamic conditions (flow rates of 3 mL/min and 30 mL/min). The response of the sensor is the same and reproducible for different flow rates. In other words, the effect of the flow rate on the response of the conductivity sensor is negligible.

The lifetime of the conductivity sensor was also measured by placing the sensor in solutions with different conductivity for 30 days. The tests were conducted at the static condition. The results show that regardless the exposure time the response of the sensor is the same.
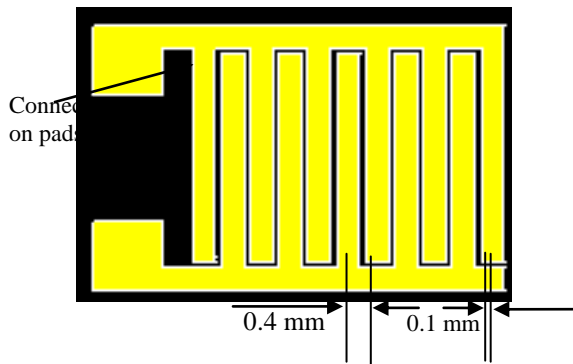

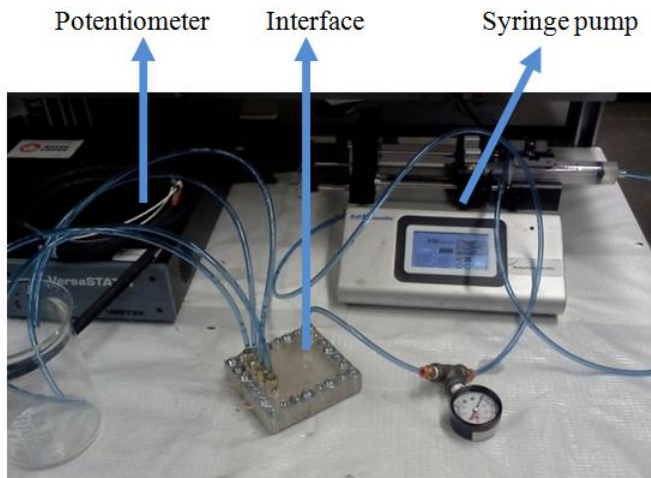Figure 1: Dimension of pH and conductivity sensors

Figure 2 (a) Experimental setup for sensor testing with different flow rates. (b) The schematic of the interface consisting of an optimized serpentine channel
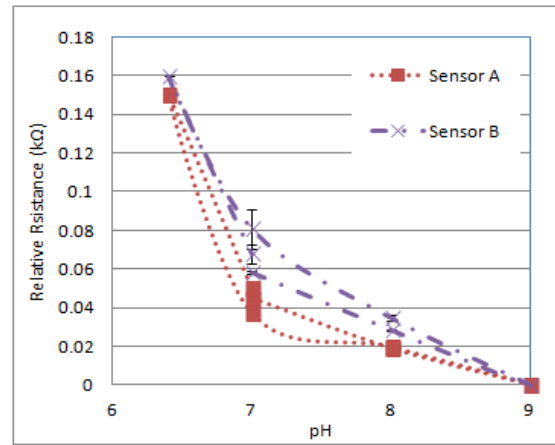

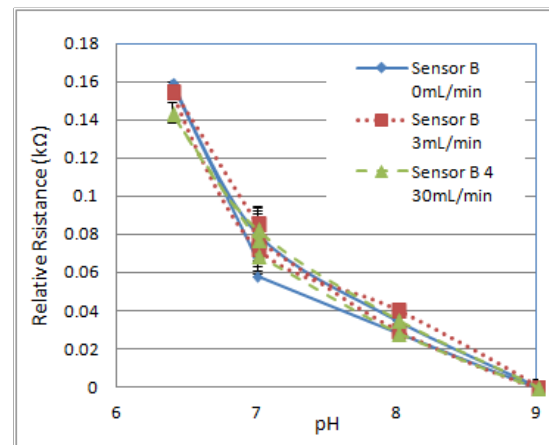Figure 3 Calibration curve for two pH sensors

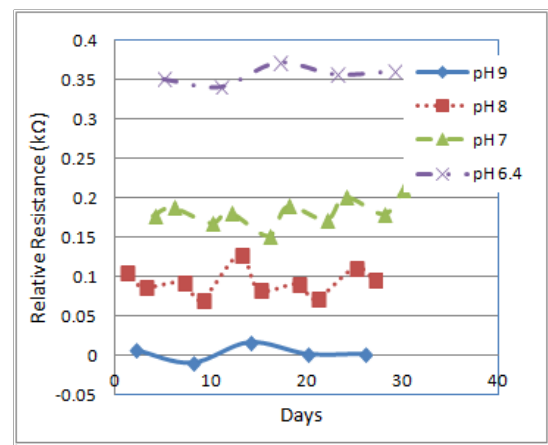Figure 4 Effect of the flow rate on the response of the pH sensor

Figure 5 Effect of exposure time on the response of the pH sensor
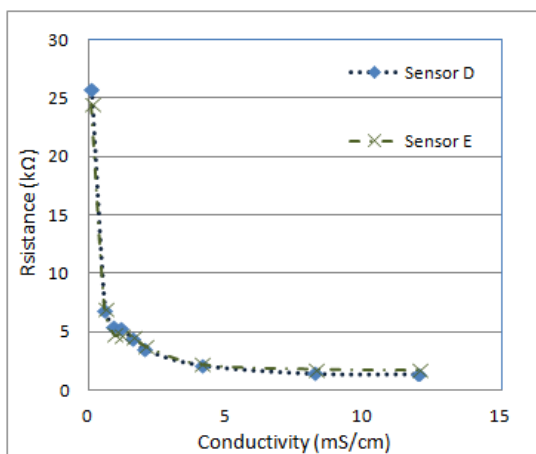
Figure 6 Calibration curve for conductivity measurement for the range of (a) 0.5 to 2mS/cm and (b) 0.02 to 12 mS/cm
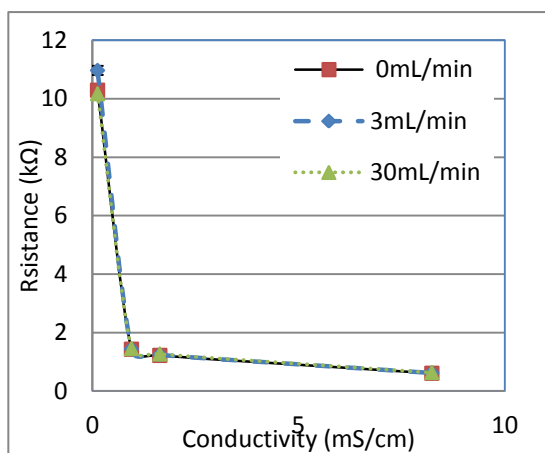

Figure 7 Effect of the flow rate on the response of the conductivity sensor

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