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Flexible polyamide-based dental floss sensor for pH monitoring

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Abstract

Sensing of pH is of prime interest for various biomedical applications, however, sensing materials and sensor configurations are two important aspects for its monitoring. In this work, we present a novel prototype of a resistive pH sensor composed of disposable polyamide-based dental flosses which act as a sensing layer connected to the electrodes comprised of conductive silver-plated polyamide threads. Without any need for a reference electrode, the prepared dental floss-based sensor was able to detect the pH change of different buffer media of acidic, neutral, and basic nature in the form of variation in the electrical resistance. The measurements were performed using electrochemical impedance spectroscopy in the frequency range from 1 Hz to 100 kHz. With the use of dental flosses and thread-based electrode set up, the present sensor offers an easy miniaturized, flexible and promising interface for pH measurements that can be optimal for the development of implantable and wearable devices for in-vivo applications to ensure oral health and consequently systemic health.

Key works: Sensor; Dental floss; pH value; Impedance spectroscopy.

1. Introduction

Innovations in the field of stretchable materials have demonstrated a new direction to electrochemical diagnostic systems [1]. For healthcare monitoring, stretchable pH sensors based on electrochemical transduction mechanisms are of considerable interest [2]. The buffering capability of the human biological system helps in maintaining equilibrium states and balancing

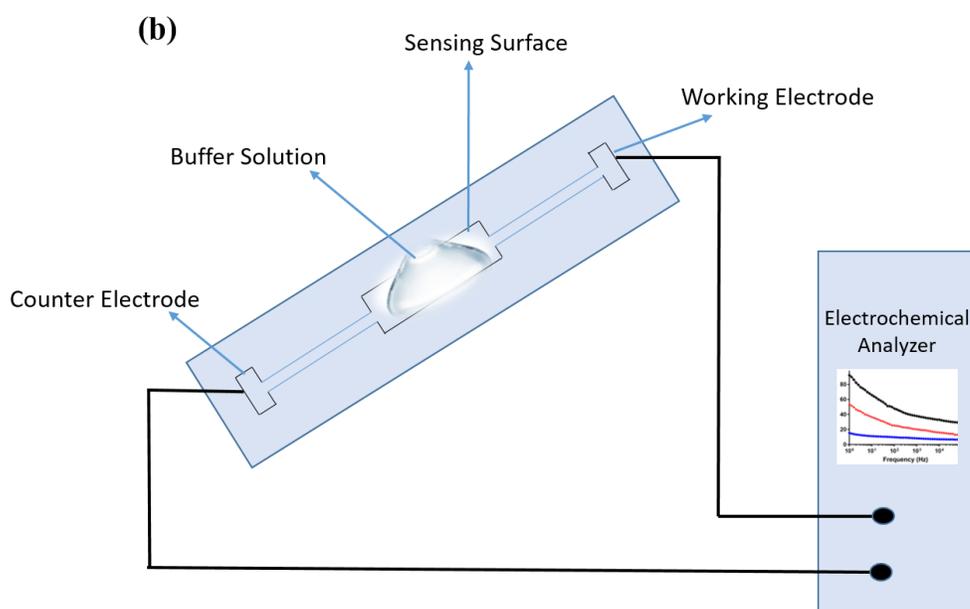
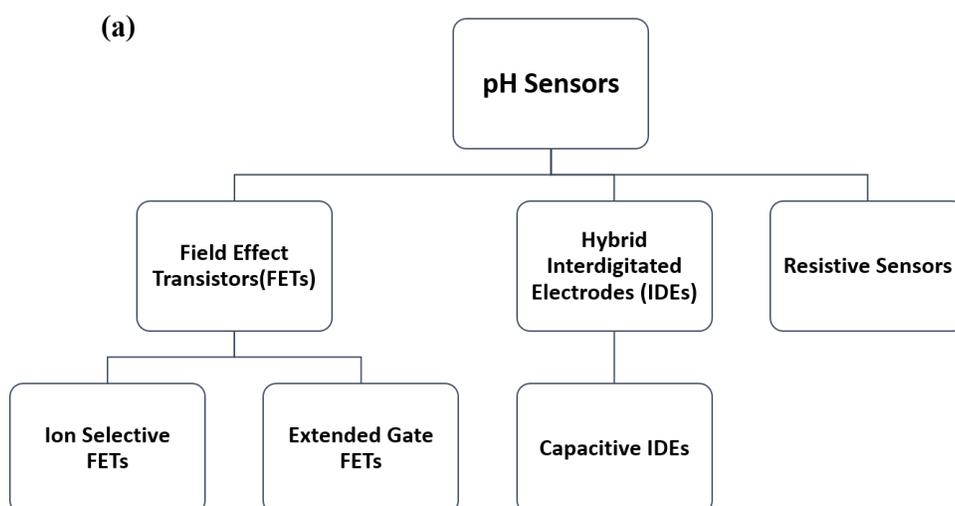
pH between different physiochemical reactions and thereby indicating possible anomalies occurring within the body [2]. Provided the significance and substantial need for pH regulation within biological systems, a surge in developing pH sensors has been noticed in past years [2]. Conventionally, electrochemical pH sensors were developed on hard substrates like glass where a hydrogen electrode was used in combination with a calomel reference electrode to measure the potential proportion to H^+ concentration in the solution. Although it is considered as one of the most accurate methods of measuring pH, frequent needs for calibration and the fragile nature of glass electrodes exclude them from being miniaturized and applied in wearable sensing systems. Electrochemical pH sensors have seen a tremendous evolution related to electrode materials from the time of glass electrodes and acidimeter to the current day interdigitated electrodes, solid state pH sensors and field effect transistor electrodes. These advances in the materials and methods of electrode fabrication, enabled precise pH measurements and opened exciting routes for developing more novel sensors.

Different sensing mechanisms and configurations for pH sensors are now available which include interdigitated hybrid (IDEs) and capacitive electrodes, resistive electrodes, ion selective field effect transistors (ISFETs) and extended gate field effect transistors (EGFETs) [3-8] as shown in Scheme 1a. All these configurations possess unique advantages which are well suited for various in vitro and in vivo biomedical applications. ISFETs and EGFETs possess similar operational principles to the potentiometric configuration except the use of a transistor as gating structure which modulates current in place of voltage. However, impurities in the semiconducting channel and instability of the sensing materials are common problems that arise in ISFETs and modifications of sensing materials through doping are generally required to improve the sensitivity of the sensing material in EGFETs. Furthermore, EGFETs require a reference electrode which

might be costly and bulky. On the other hand, IDE configurations measure the capacitance or current without any need for a separate reference electrode, however, novel materials need to be explored for approaching maximum sensitivities and stability towards pH sensing.

Compared to other configurations, resistance-based pH sensors are an interesting alternative to ISFETs and EGFETs [2]. Resistive pH sensors are made up of highly sensitive electrode layers connected to an electrochemical analyzer which measures the resistance of the solution without requiring reference electrode [9]. Schematic configuration of a resistive pH sensors is shown in Scheme 1b. Interdigitated electrodes are also included within the configuration of resistive sensors to increase the surface area. Thin film metal oxides are proven to be useful in potentiometric pH sensors with electrode-electrolyte interfaces. Metal oxides such as iridium oxide [10, 11], carbon nanomaterials [12-14] and zinc oxide [15] are the most common nanomaterials being utilized as sensing materials. However, these nanomaterials dissolve and react with the test solution and get deposited on the electrode surface which makes them insensitive towards detecting H^+ activity.

Thus, despite the availability of a wide range of materials with pH sensing abilities, the suitability of the electrode material depends on the configuration of pH sensing devices, sensing methodology, aimed application and sensitivity requirements. In present time, the focus for developing electrochemical pH sensing devices has inclined towards miniaturized and flexible electrode configurations that can easily be integrated and applied to wearable systems. Recently, various electrochemical stretchable pH sensors based on textile [10], flexible plastics [11] and paper [13] materials have been developed [2]. In a recent work, an electrochemical sensor constructed from dental floss was painted with carbon and Ag/AgCl ink to create two electrodes for glucose measurement [16]. Although the study was considerable, the approach was time-consuming.



Scheme 1: (a) Different types of pH sensors, (b) Schematic representation of resistance-based pH configuration.

In the present work, we report design of a resistive pH sensing interface comprising of single-use polyamide-based dental floss and conductive thread-based electrodes. Dental floss is a thin filament which is made up of mainly polyamides and extensively used for cleaning dental plaque

and food remnants from the interdental gaps. To create the resistive pH sensor prototype, polyamide core-based silver plated conductive thread was used and tied with thin filaments of dental flosses. The present configuration of pH sensor follows the principle that the sensing material (in this case dental floss) detected the change in the pH of different buffer media (acidic, neutral to basic) in the form of variation in the electrical resistance which was analyzed by impedance spectroscopy. The proposed prototype acts as a potential device for pH measurements that can be used for real time detection applications in the field of dental medicine to ensure oral health. The experimental set-up and sensor configuration has been shown in Supplementary information (SI Fig. S1).

2. Experimental

2.1 Materials and instruments

Silver plated polyamide thread HC40 (by MADEIRA, Germany) with a nominal resistance of $< 300 \Omega/\text{m}$ was chosen to create a two electrode system assigned as working and counter electrodes. One end of each electrode was connected to the electrochemical interface and the other end was tied to thin filament polyamide-based dental flosses. The distance between two electrodes was set as 3 cm. Dental flosses-namely Sensodyne and Lacalut were purchased from local pharmacy. The electrode set up was connected to PalmSense4 electrochemical analyzer and change in electrical resistance of buffer solutions of different pH values was measured using PSTrace 5.8 software using impedance spectroscopy in the frequency range from 1 Hz to 100 kHz. Sodium chloride (NaCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl, 37%) were obtained from Laboratorija doo, Novi Sad, Serbia. Milli-Q water ($>18.2 \text{ M}\Omega\text{-cm}$) was used for the preparation of solvents. Fourier transform infrared (FTIR) spectroscopy was performed in the spectrum range $400\text{-}4000 \text{ cm}^{-1}$ in Attenuated Total Reflectance mode using ALPHA (Bruker,

Germany) while contact angle measurement was carried out at Drop Shape Analyzer DSA25 (Kruss, Germany). Surface morphology of sensor was investigated by scanning electron microscopy (SEM) using TM3030 (Hitachi, Japan) at an accelerating voltage of 15 kV. Manual probe station (SUSS PM5) with Motic images plus 3.0 software was used for capturing images of prepared dental floss sensor.

2.2 Preparation of buffer solution

To prepare buffer solution, firstly, a 0.5 M stock solution of NaCl was made. Further, 0.1 M basic and acidic solutions were prepared using NaOH and HCl respectively which were used to adjust the pH of the stock and thereafter solutions of desired pH values were prepared. In the whole experiment, pH 3, pH 6 and pH 10 were used as acidic, neutral and basic buffer respectively to perform the measurements. All solutions were prepared under standard laboratory conditions.

3. Results and discussion

3.1 Structural characterization of the sensor

To examine the behavior of the constructed pH sensor, conductive silver threads comprising its electrodes and sensing layer composed of dental flosses were studied under SEM. The silver conductive coating of the polyamide cores was observed to have various imperfections throughout the fiber (Fig. 1a). Also, the subject under test here was cut halfway with standard scissors, to study the effects of everyday actions. As it can be seen, even the fiber cores that were not cut, towards the back of the image, show significant delamination of the silver layer, primarily due to the bending force of the scissor mechanism. Fig.1b and Fig. 1c show the SEM images of the Sensodyne and Lacalut dental flosses respectively. A rough but flat surface was seen in the case of Sensodyne while an uneven and long twisted channels were observed in the case of Lacalut.

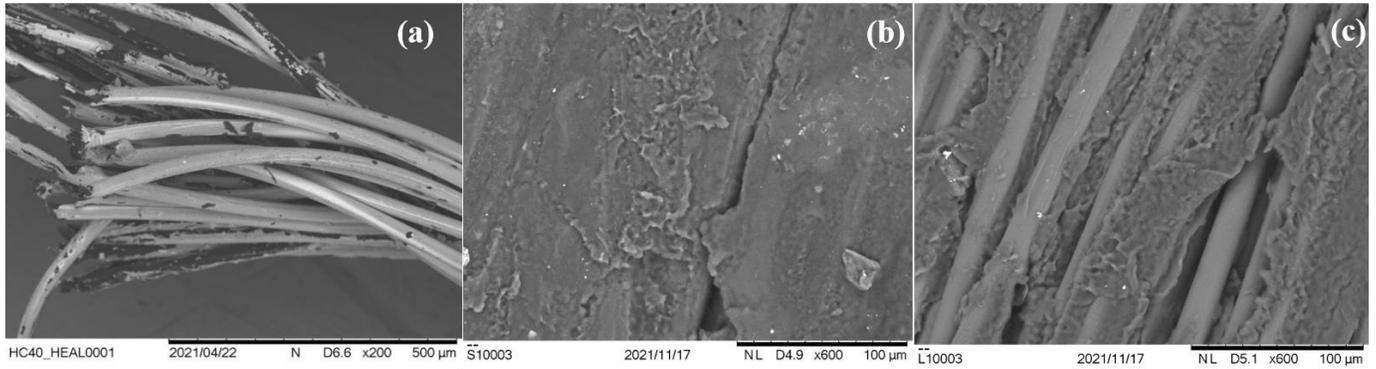


Fig. 1: SEM images of (a) silver-plated polyamide conductive thread, (b) Sensodyne and (c) Lacalut dental floss.

Functional group characterization of the dental flosses can be clearly seen by the FTIR-ATR spectra in Fig. 2a. The spectra of Sensodyne and Lacalut showed their polyamide origin with characteristic peaks at around $\sim 1630\text{ cm}^{-1}$ and $\sim 1533\text{ cm}^{-1}$ in the case of Sensodyne and $\sim 1712\text{ cm}^{-1}$ and $\sim 1511\text{ cm}^{-1}$ in the case of Lacalut corresponded to amide C=O stretching and C–N–H bending absorbance bands respectively [17].

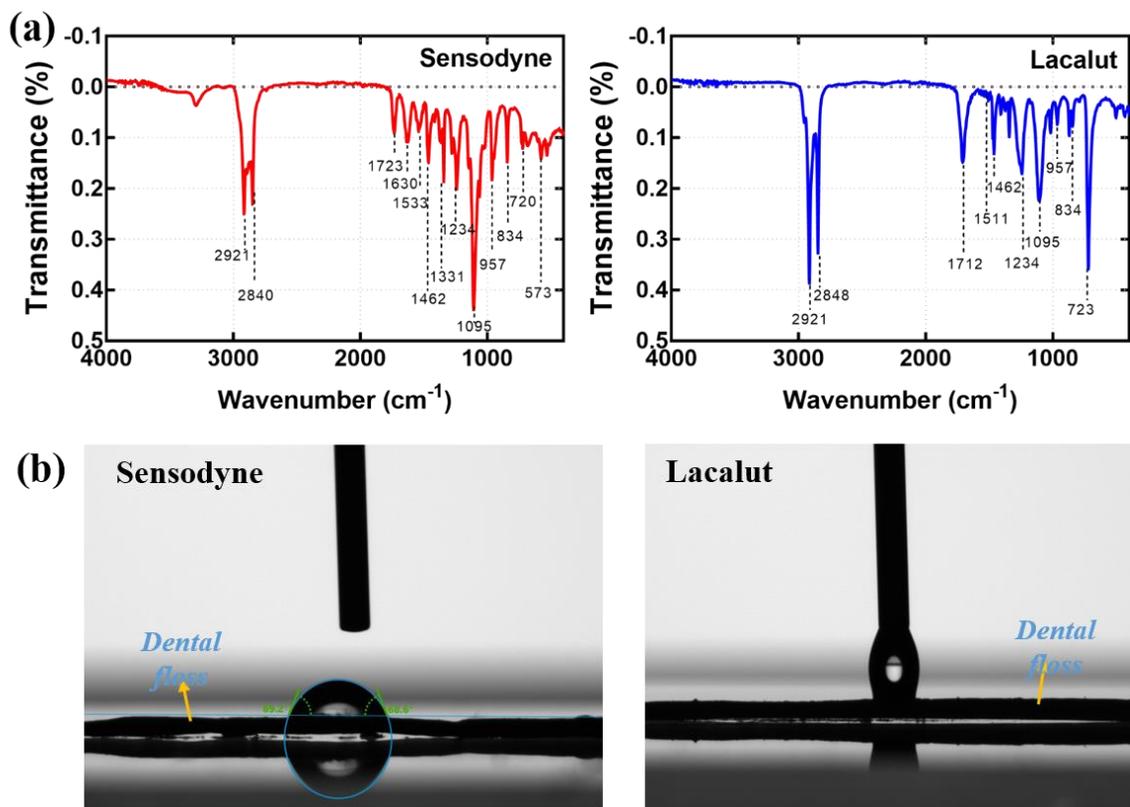


Fig. 2: (a) FTIR spectra and (b) contact angle measurement of dental flosses.

Contact angle measurements were carried out using pH 6 buffer to determine the surface adhesive properties of the dental flosses (Fig. 2b). Measurement of contact angle is one of the common methods to determine the wettability of a surface and defined as an angle which a liquid makes with a solid surface. Thus, wetting is determined by measuring the contact angle. Under ideal measuring conditions, a larger wetting tendency is denoted by a smaller contact angle which is usually smaller than 90° whereas a non-wetting liquid creates a contact angle between 90° and 180° . In principle, this angle is measured by (i) the surface properties of both the solid and the liquid and (ii) by the interaction and repulsion forces between the liquid and the solid. These interactions are mainly described by adhesive and cohesive forces which are in essence intermolecular forces. The balance between the cohesive forces of similar molecules such as between the liquid molecules are hydrogen bonds and Van der Waals forces while the adhesive

forces between dissimilar molecules such as between the liquid and solid molecules are explained by mechanical and electrostatic forces which determine the contact angle created between the solid and liquid interface [18]. In the present study, the contact angle of Sensodyne was found to be 66.89° which represented the mean value of five consecutive measurements with a standard deviation of 2.74% while Lacalut dental floss indicated poor wetting characteristics. This difference in the surface adhesive properties of the two dental flosses could be ascribed to the difference in the free surface energy which can further be related to the difference in the surface morphologies [17].

3.2 Impedance studies of sensor towards pH analysis

The resting pH of our mouth is around ~ 6.3 and saliva has a normal pH range about $\sim 6-7$ [12], however, intake of different kinds of food and beverages changes the salivary pH. In order to study the change in pH, the dental floss sensors were connected to the electrochemical interface and Bode plots of the measured impedance were produced taking acidic, neutral and basic buffer solutions as shown in Fig. 3. During an electrochemical reaction, the ionic diffusion occurs at the electrode surface when the pH solution interacts with the surface of the WE. This process leads to the formation of an electrical double layer and can be observed mainly as straight line in the low-frequency region of the Bode plot. Further, the generated charge moves towards the conductive layer of the electrode leading to reactance which can be observed in the high frequency region leading to the drop of the curve. Thus, the resistance in the high frequency region is related to the mobile ions of the pH solutions which can be observed in the Bode plot above 1 kHz (Fig. 3a-b) or in other words it can be said that the pH sensitivity can be observed at a frequency of about 1 kHz in the whole spectrum range. Moving further from this frequency point, the resistance becomes constant as ion movement does not follow the field changes. Thus in the high frequency

region, the resistance only depends on the dipole elongation of the buffer solution. Therefore, it is seen that the resistance of the sensor is strongly related to the distance between the electrodes.

10 μ L of the solution were carefully dropped on the area of dental floss connected to the conductive thread-based electrodes. It is clear from the graph that our prepared sensor was sensitive enough to register a change in electrical resistance of the solutions with changing pH. The resistance increased as pH increased which could be ascribed to the increase of OH⁻ in the solution [3, 9]. Moreover, H⁺ and OH⁻ ions interacted with the sensing layer of thin filament dental floss and led to the variation in electrical resistance with an increase in pH and measured as a function of frequency. The linear correlation between the resistance and different pH conditions was plotted for both dental floss sensors showing relative resistance change at a frequency of 1 kHz. The results showed a trend of increasing resistance with the change in the buffer medium from acidic to neutral and finally to basic pH values which matched well with the previously reported resistive pH sensors [3, 9]. The findings demonstrated high sensitivities of our prepared sensor towards pH change with a linear coefficient (R^2) of 0.9963 and 0.9437 in case of Sensodyne and Lacalut sensors respectively. It can be observed that by increasing the pH from 3 to 10, electrical resistance values also increased from 8.18 k Ω to 37.83 k Ω for Sensodyne and from 19.11 k Ω to 76.73 k Ω for Lacalut. The reason for this high resistance variation of Lacalut sensor could be attributed to its rough structure and poor surface adhesive properties which inhibited the interaction of H⁺ and OH⁻ ions of the buffer solution with the sensing layer.

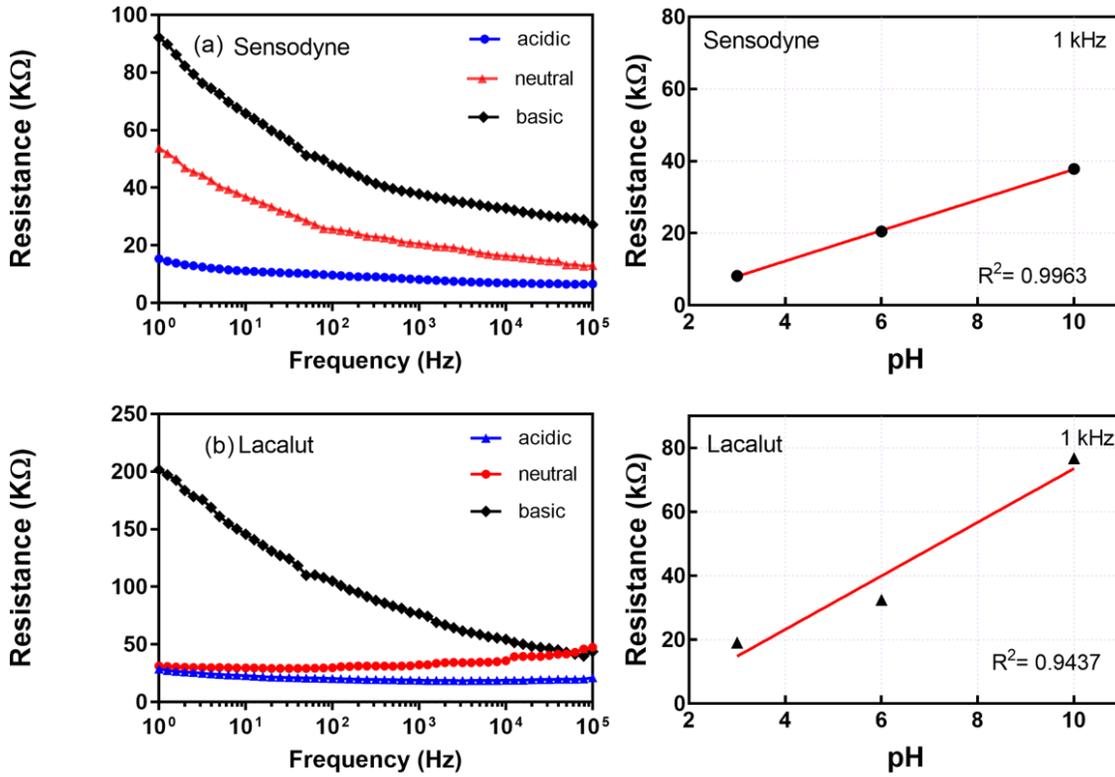


Fig. 3: Change in electrical resistance of acidic, neutral and basic buffer solutions as a function of frequency and correlation between electrical resistance and variation in pH for (a) Sensodyne and (b) Lacalut-based sensors.

Performance of our prepared dental floss sensor is summarized with other previously reported pH sensors based on various flexible platforms. The literature study are found to be in well agreement with our present work detecting pH change using different methods (Table 1) [9-15, 19-21].

Table 1: Different flexible electrodes and sensing materials as pH sensors.

Electrode/Substrate	pH Sensitive Layer	pH Range	Method	Correlation Factor	Reference
Indium tin oxide	Oxide groups	3-8	EIS	0.994	9
Fabric (Argenmesh, Ripstop, Stainless steel)	Electrodeposited IrO ₂	4-8	EIS	0.98-0.997	10
Graphite/kapton	Electrodeposited IrO ₂	3-8	Potentiometry	0.992	11
Interdigitated Gold	Graphene oxide/polyaniline	2-9	Potentiometry	0.998	12
Paper/polyvinyl alcohol	Carbon ink	2.8-8.6	EIS	0.994	13
Single walled carbon nanotubes	Poly-1 amino anthracene	2.20-11.82	Potentiometry	0.993	14
Glass	Zinc oxide nanorods	4-7	-	-	15
Gold wire	Polyvinyl alcohol/polyacrylic acid hydrogel	6-9.1	EIS	-	19
Cellulose-polyester blend fabric	Graphite paste/prussian blue	6-9	Potentiometry, EIS	0.989	20
Polydimethylsiloxane	Graphite/polyurathane	5-9.5	Potentiometry	-	21
Silver plated polyamide thread	Dental floss	3-10	EIS	0.996, 0.943	Present work

To further justify the use of the prepared dental floss sensor, the effect of temperature on the sensor was evaluated towards pH monitoring. For this, change in resistance of neutral buffer (pH 6) was analyzed using dental floss-based sensors as a function of frequency at an elevated temperature of 50°C. Fig. 4 shows the bode plot obtained for Sensodyne and Lacalut-based sensors which revealed high resistance of buffer solution at 50°C. The reason for this behavior can be attributed to the strong dependency of temperature on pH measurements. In principle, a change in temperature led to a change in viscosity as well as movement of ions in the solution. This impacted the pH sensing performance of the sensing material due to the change in its temperature coefficient which further affects measurement speed [2]. The imbalance and thermal variation at the sensing

interface resulted in high resistance at elevated temperature. The behavior manifested the capabilities of our dental floss sensor towards pH measurements with change in temperature conditions.

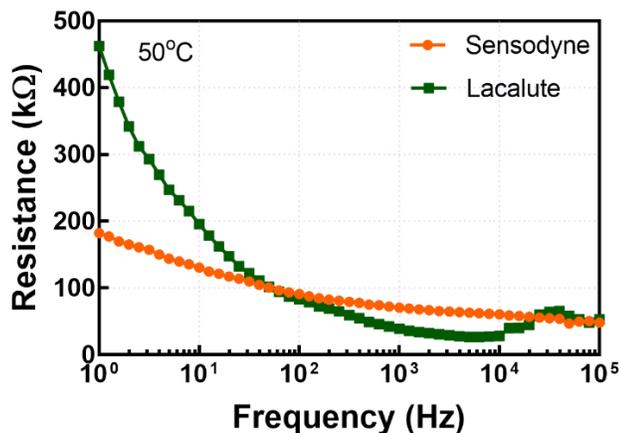


Fig. 4: Bode plot of Sensodyne and Lacalut-based dental floss sensors at elevated temperature.

Furthermore, intraday reproducibility studies of the prepared dental floss sensors were performed under similar conditions over the span of 72 h using pH 6 (10 μ L). Three independently prepared sensors (Fig. 5) were utilized for this purpose and analyzed towards impedance measurements at 1 kHz. The results showed good repeatability of the sensor where each data point represents mean of three consecutive measurement.

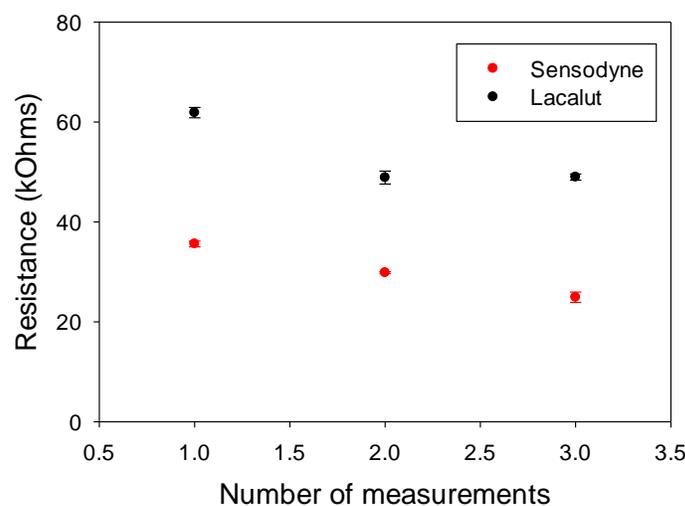


Fig. 5: Reproducibility studies of dental floss sensors towards modulus impedance using neutral pH 6 at 1 kHz.

4. Future perspectives

Despite advantages offered by resistive pH sensors such as a wide availability of sensing materials and small size of the device, replication of similar response of sensing material on each individual electrode remains a challenge. Thus, electrode-to-electrode variability, poor selectivity to H^+ and selection of suitable sensing material with high sensitivity are some crucial challenges in developing resistive pH sensors. Possible actions that need to be taken into account can be controlling fabrication process variations, doping sensing material and functionalizing electrode surface with coatings selective to H^+ . Moreover, significant work must be done for the development of a miniaturized, low cost, flexible and implantable sensor which can offer the opportunity to monitor real-time pH levels anywhere in the human body. In addition, exploitation of newer sensing materials and techniques and addressing the key challenges which affect the reliability, reproducibility and repeatability of pH measurements are necessary steps to create high performance pH sensors. Finally, sensitivity, accuracy, and precision requirements of pH sensors

for biomedical applications are highly recommended that can provide the opportunity for noninvasive measurements.

5. Conclusion

We developed a pH sensitive resistive sensor comprising of single-use dental floss as sensing layer and conductive silver thread-based working and counter electrodes. The pH change of the buffer solutions was successfully analyzed in the form of change in electrical resistance which was in found in linear correlation. Our straight-forward manufactured dental floss-based pH sensor represented a cost-effective, flexible and miniaturized sensing platform which was sensitive to pH variation. However, electrode to electrode performance variability and increasing sensitivity of the sensing material towards H^+ ions still remain a challenge.

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