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A Robust Sensor for Inline pH Measurements

Nikila Nair, Akshaya A. V., Michael John Bosco, G. K. Ananthasuresh and Jose Joseph

Abstract—Conventionally, a pH sensor having a glass bulb and a liquid-based reference electrode is used for accurate, real-time pH measurement. However, glass bulb-based pH sensors suffer wear and tear in harsh operating conditions and yield erroneous readings in strong alkaline and acidic media. This necessitates the development of a robust pH sensor that renders stable performance in harsh operating conditions. This paper reports the fabrication and characterization of an all-solid-electrode pH sensor with excellent linearity in the pH range of 4 to 9 with a sub-Nernstian slope of -43.18 mV/pH. The fabrication process of the sensor is explained in detail, and the performance of the sensor is validated with extensive characterization. Furthermore, the efficacy of the sensor in practical applications is established by measuring the pH of idli batter during its fermentation process. The proposed sensor is also used to measure the pH of soil solutions, wherein the pH of soil samples showed an error of less than ± 0.15 pH when compared with a laboratory pH meter.

Index Terms—pH sensors, electrochemical pH sensing, soil pH, all-solid electrode, sub-Nernstian

I. INTRODUCTION

CONTINUOUS pH monitoring is essential for various applications such as pharmaceutical manufacturing, breweries, water treatment plants, and agriculture [1]. pH monitoring is performed with the help of a glass-based ion-selective electrode in conjunction with a reference electrode. The surface of the ion-selective electrode consists of fixed silicate groups linked with sodium ions ($\text{SiO}_2^- \text{Na}^+$). When these electrodes come in contact with an aqueous solution of unknown pH, the Na^+ ions switch places with the solvated protons (H^+) in the solution creating a 'hydrated' region near the interior and the exterior parts of the glass membrane [2]. The anion sites of these layers are covalently bound to the bulk of the glass. At the same time, the H^+ ions of the solution are mobile and can freely exchange between the testing medium and the sodium ions on the glass body. The activity of H^+ ions in the test solution differs from that of the H^+ ions in the hydrated layer, generating a potential difference between the solution and the glass membrane surface [2]. Likewise, the reference electrode is an Ag/AgCl wire submerged in a saturated solution of KCl or HCl enclosed in a glass tube. This tube has a small cavity that separates the internal solution from the test medium by a ceramic frit. Such glass-based pH sensors ideally exhibit a Nernstian behavior with fast response and high repeatability over a pH range of 1 to 14 [3]. However, these traditional sensors have certain drawbacks such as being delicate and losing sensitivity over time. The porous

nature of the ceramic frit permits free diffusion of the internal solution (KCl or HCl) into the testing medium contaminating the analyte. The diffusion may also cause clogging of the pores by AgCl complexes creating a potential instability [4]. Due to the diffusion of the internal solution, the reference electrode must be replenished periodically with KCl or HCl solution to have sufficient supply of chloride (Cl^-) ions [5]. All the limitations as mentioned above of the glass electrode-based pH sensor suggest the need for a new pH sensor that requires minimal maintenance, offers adequate performance and reduces contamination of the test medium. pH sensors with all solid electrodes mitigate most of the problems associated with the traditional sensors and provide advantages such as low maintenance, potential to miniaturize, ease of mass-production, etc. [6]. Table 1 summarizes the literature on all-solid electrode pH sensors reported in the recent past.

Metal oxides like IrO_x [7]–[9], Sb_2O_3 [10], TiO_2 [11], RuO_x [12], WO_3 [17], TaO_2 [18], and SnO_2 [19] can exhibit unique mechanical, electrical, and electrochemical properties such as robustness, stability against dissolution, and independence from cationic interference due to the formation of insoluble hydroxides on their surface when placed in the test medium [17]. These are also economical and can exhibit better performance in aggressive conditions even at miniaturized form factors [20]. Fast response and long lifetime in complex environmental conditions make metal oxides an excellent sensing material [21]. Here, Antimony (Sb) is used as the sensing electrode, as it exhibits excellent selectivity to H^+ ions and provides linear response [22]. Unlike other transition metals, Sb has less affinity towards electrons and can withstand aggressive abrasions in hostile conditions, thereby minimizing the erroneous readings incurred while participating in the redox reactions of the half cell [23], [24].

The reference electrode of the sensor should maintain a constant potential regardless of the analyte being tested. The potential of the working electrode is measured against this reference [25]. Developing a reliable solid reference electrode is crucial for creating all-solid electrochemical sensors. Patrick

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TABLE I
LITERATURE SURVEY OF ALL-SOLID-ELECTRODE PH SENSORS REPORTED FOR VARIOUS APPLICATIONS.

Sensing Electrode	Reference Electrode	pH range	Slope	Application	Ref
IrO_2	PEDOT:PSS	6-9	$(59 \pm 4) \mu A \text{ pH}^{-1}$	Real-time pH monitoring of wound	[7]
IrO_x	Mn/MnO_2	6.86-12.96	53 mV pH^{-1}	Monitoring pH during corrosion of cement	[8]
Ir/IrO_2	NASICON	1.68-9.18	52.1 mV pH^{-1}	Monitoring the pH under harsh conditions like deep-seawater	[9]
Sb/Sb_2O_3	$Ag/AgCl$	4.06-9.3	62.27 mV pH^{-1}	pH of soilless culture	[10]
TiO_2 nanorods		2-12	78.25 mV pH^{-1}	pH sensing membrane for extended-gate field-effect transistors	[11]
Ti/RuO_x	$Ag/AgCl$	2-10	59.04 mV pH^{-1}	Monitoring of water pH	[12]
Electrochemical modified Niobium	$Ag/AgCl$	1-13	52.1 mV pH^{-1}	Tested in various solutions	[13]
Surface-Enhanced Raman Scattering active Au/Thermoplastic polyurethane nanofiber		4-7		Flexible and wearable sweat pH monitoring	[14]
Emeraldine-PANI	Pt wire	1.3-10	66 mV dec^{-1}		[15]
Nb/Nb_2O_5	$Ag/AgCl$	2-12	41 mV pH^{-1}		[16]

et al. developed a nafion-coated $Ag/AgCl$ solid reference electrode for pH estimation [26]. Criscuolo et al. reported several polymeric membrane-based reference electrodes for pH estimation [27]. The solid reference electrode (SRE) demonstrated in this paper is fabricated by coating the $Ag/AgCl$ electrode with two layers of polymers: (i) polyvinyl chloride (PVC) saturated with finely powdered KCl and (ii) a pure PVC layer. Materials such as polyvinyl acetate (PVA), polyacrylates (PA), nafion, and poly butyral (PB) can also be used as a coating material on the reference electrode [28]. However, PVC has shown superior properties such as film-forming ability without the assistance of an external agent, high resistance to solvents, bases, and acids, and a long lifespan [29]. It has also been studied for ion-exchange membranes and the fabrication of ion-selective electrodes [30].

Herein, we report the fabrication of an all-solid-electrode pH sensor, detailing all the optimisations in material synthesis and fabrication processes. A thorough characterization protocol is embraced to study the performance of the all-solid-electrode pH sensor. To demonstrate the practical utility of the sensor, the fabricated sensor is further used to analyze the pH of idli batter and soil solution.

II. MATERIALS AND METHODS

A. Chemicals and equipment

Potassium Chloride (KCl), Polyvinyl Chloride (PVC), and Tetrahydrofuran (THF) are purchased from Merck KGaA, Bengaluru, India. Sb rod of 99.8% purity and Ag wire of 1 mm diameter are procured from Alfa Aesar, Mumbai, India. The electrochemical workstation K-Lyte, used for electrodeposition and OCP measurements is procured from Kanopy Technosolutions, Kanpur, India. Laboratory pH meter LMPH9 having an accuracy of ± 0.01 pH, which is used for calibrating the fabricated sensors is procured from Labman Scientific Instruments, Chennai, India.

B. Fabrication of the sensor

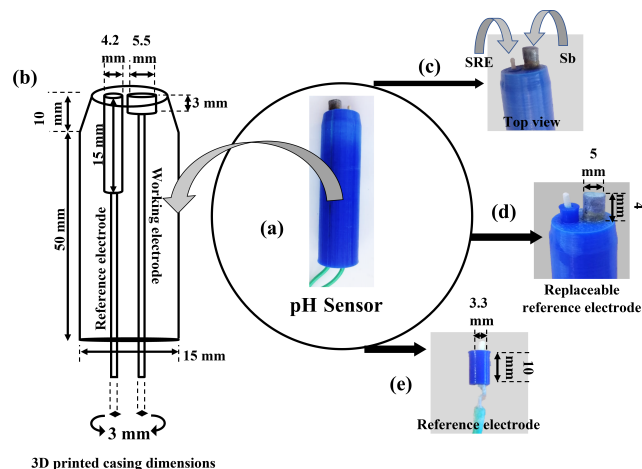


Fig. 1. Abstraction of the fabrication process of pH sensor. (a) photograph of a complete sensor with a working electrode (WE) and a solid reference electrode (SRE) (b) physical dimensions of the sensor casing (c) sensing region of the sensor (d) replaceable nature of reference electrode (e) reference electrode assembly.

Sensor casing and its dimensions are shown in Fig. 1(a) and Fig. 1(b), respectively. The casing is printed using Flashforge Adventurer-4 3D printer. Fig. 1(c) depicts the placement of electrodes in the sensor and Fig. 1(d) specifies the dimension of the working electrode projecting from the sensor casing. The reference electrode is placed in another casing as shown in Fig. 1(e) so that it can be easily detached from the sensor.

C. Optimization of $Ag/AgCl$ electrode

Silver (Ag) wires of diameter 1 mm and length 15 mm are abraded with P400 emery paper and cleaned with deionized (DI) water. These samples are electrodeposited using the three-electrode system of the electrochemical workstation in 1 M

KCl for 50 s, 100 s, 200 s, 300 s, 400 s, and 500 s, as shown in Fig. 2(a). To figure out the optimal deposition time that yields a stable $AgCl$ coating, the open circuit potential (OCP) between the electrodeposited $Ag/AgCl$ samples and a commercial reference electrode ($Ag/AgCl$) is evaluated in 1 M KCl . Fig. 2(b) shows the physical condition of the $Ag/AgCl$ samples after repeated testing. The $Ag/AgCl$ sample deposited for 300 s remained intact even after several cycles of OCP measurements. Fig. 2(c) shows the SEM micrograph of the $Ag/AgCl$ electrode deposited for 300 s and it clearly delineates the clusters of $AgCl$ particles formed over the Ag wire. The inset of Fig. 2(c) shows the image of the $Ag/AgCl$ electrode used for SEM analysis and the same electrode at 500 μm scale. From the elemental mapping of the electrode surface (Fig. 2(d)), it is evident that both Ag and Cl are present in much higher concentration than the other elements, confirming the formation of $AgCl$ on the surface of the Ag wire. To figure out the appropriate KCl concentration that can be used for $AgCl$ deposition, KCl of molarities 1 M, 2 M, 3 M, and 4 M were used for the optimization of $AgCl$ deposition. Fig. 2(e) shows the OCP measured for each of these $Ag/AgCl$ samples with respect to a standard $Ag/AgCl$ reference electrode. It is observed that $AgCl$ deposited using 1M KCl yielded minimum potential difference with the standard $Ag/AgCl$ reference electrode and therefore, 1M KCl is used henceforth for the electrodeposition process. Hereon, the $AgCl$ -coated Ag wire is referred to as REF0.

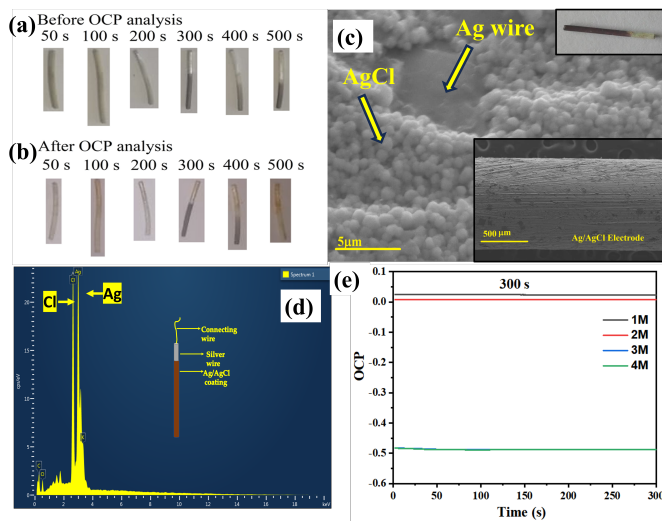


Fig. 2. (a) Ag wire electrodeposited using 1 M KCl for 50 s, 100 s, 200 s, 300 s, 400 s, and 500 s. (b) $Ag/AgCl$ samples after OCP analysis in 1 M KCl . (c) SEM image of REF0 at 5 μm scale. Inset are the SEM image of REF0 at 500 μm scale and the sample image. (d) Elemental mapping of Ag and Cl on the surface of REF0. (e) OCP study of the electrode deposited using different molarities of KCl tested for 300 s in 1 M KCl .

D. Fabrication and characterization of the reference electrode

The $Ag/AgCl$ reference electrode must maintain a constant potential even when used for prolonged duration. To achieve

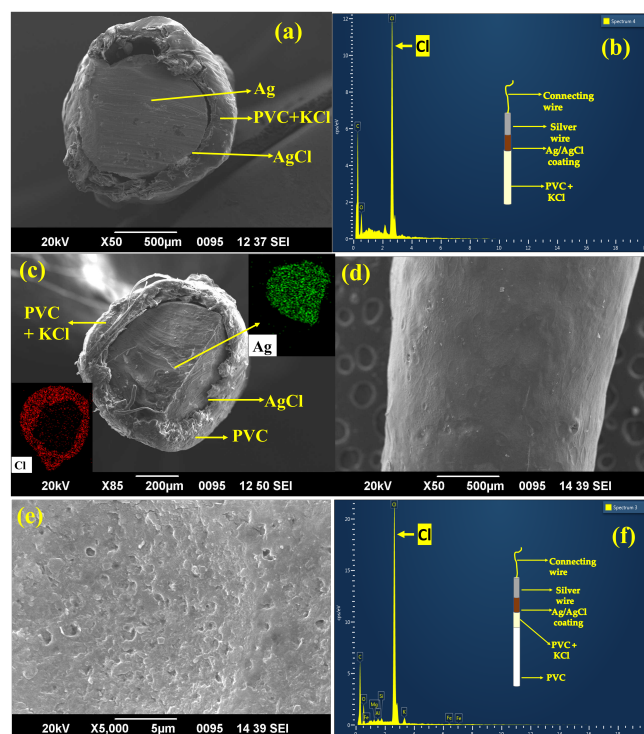


Fig. 3. (a) Cross-sectional SEM analysis of REF1 (b) elemental mapping of REF1 surface. Inset is the pictorial representation of REF1 composition. (c) cross-sectional SEM analysis of REF2. Inset shows the EDAX area mapping for Ag and Cl at the cross-section. SEM images of REF2 surface at (d) 50X and (e) 5000X magnification and (f) elemental mapping of REF2 surface. Inset is the pictorial representation of REF2 composition.

this, a constant supply of Cl^- ions is needed. To accomplish this, the $Ag/AgCl$ wire is coated with KCl -saturated PVC. The process begins by dissolving PVC in tetrahydrofuran (THF), followed by the addition of finely powdered KCl to the PVC solution. This mixture is manually coated over $AgCl$ coated Ag wire and is allowed to dry for 5 h at room temperature. Fig. 3(a) shows the cross-section of the $Ag/AgCl$ reference electrode coated with KCl -saturated PVC, referred to as REF1 hereon. Fig. 3(b) shows the elemental mapping (EDAX) of the REF1 surface and it shows that the electrode surface is highly populated with Cl^- ions helping the SRE maintain a constant potential [31]. The inset of Fig. 3(b) is the schematic representation of the REF1 electrode.

The OCP of the sensor using REF1 as the reference and Sb as the sensing electrode is studied for two consecutive days in three standard buffer solutions as shown in Fig. 4(a). A standard calibration protocol is embraced for this purpose. According to ASTM (American Society for Testing and Materials) standards and U.S. EPA (U.S. Environmental Protection Agency) guidelines, pH sensor calibration can be performed using either a two-point or a three point calibration with standard buffer solutions [32]. A three-point calibration is adopted in this study. Three standard buffer solutions are prepared for this purpose. Four tests were conducted in each solution to obtain the error bar, and the test is repeated for two days. A variation in the OCP is detected when the same solution was measured on these two days. The probable cause

of this drift is that when the test solution interacts with the reference electrode, the fine granules of KCl dispersed in PVC begin to dissolve, thereby causing a decrease in Cl^- concentration within the $Ag/AgCl$ electrode [33]. Leaching of Cl^- ions into the analyte will deteriorate the performance of the reference electrode. To control the rate of leaching, the reference electrode (REF1) is coated with another layer of PVC that is not saturated with KCl . The reference electrode coated with the second layer of PVC will hereon be referred to as REF2. Fig. 3(c) shows the cross-sectional SEM image of REF2. The inset of the figure shows the cross-sectional area mapping for Ag and Cl elements. Fig. 3(d) and (e) depict the surface of REF2 at 50X and 5000X magnifications, respectively. The SEM analysis clearly indicates that the surface of the electrode is porous, allowing for effective electric contact with the analyte through ion exchange. Fig. 3(f) shows the elemental mapping of the REF2 surface, the inset of which indicates the final composition of the fabricated reference electrode, REF2. When the sensor with REF2 as the reference electrode and Sb as the sensing electrode is tested for two consecutive days in buffer solutions, the sensor potential almost overlaps as shown in Fig. 4(b), indicating the repetitive nature of the sensor. This also confirms that the reference electrode maintained its constant potential after coating with PVC.

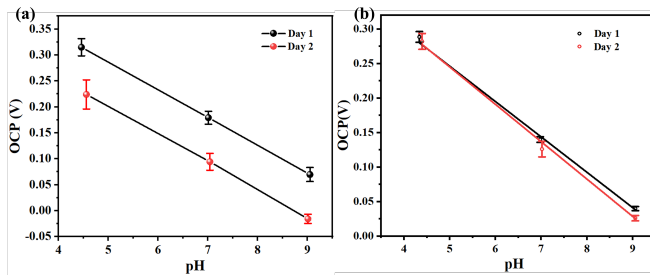
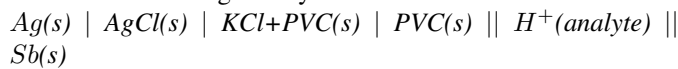


Fig. 4. Response of the sensor using Sb as the sensing electrode and (a) REF1 and (b) REF2 as the reference electrode tested for two consecutive days in three buffer solutions.

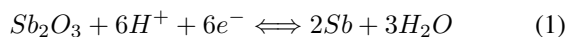
A general chemical structure of the fabricated pH sensor with REF2 can be given by:



where, '||' represents the physical separation between chemical species and the electrodes, and '|' represents the separation between different layers in the reference electrode.

E. Sensor calibration

As the fabricated pH sensor is immersed in the test solution, H^+ ions in the analyte interact with the Sb electrode creating an ionic charge at its surface [34]. The following reaction occurs at the surface of the sensing electrode [35].



Meanwhile, the reference electrode remains passive to the test solution generating a potential difference between the sensing

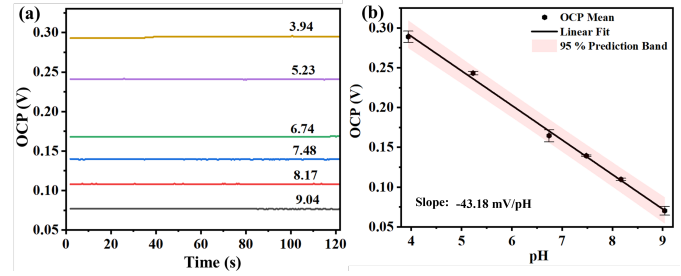


Fig. 5. (a) OCP recorded by the sensor when measured in solutions of different pH, and (b) the linear response of the fabricated pH sensor when tested in the pH range of 3.94 to 9.04

and the reference electrodes. This difference is related to the pH of the solution by the Nernst equation given by [36]

$$E = E_0 - 2.303 \frac{RT}{nF} * pH \quad (2)$$

where E is the measured potential of the cell, E_0 is the standard potential, R is the gas constant, T is the temperature in Kelvin, n is the number of electrons transferred, and F is the Faraday's constant. As per the Nernst equation, the sensitivity of a pH sensor at room temperature is expected to be -59 mV/pH. However, the actual value of the sensitivity could be sub-Nernstian or super-Nernstian depending on the fabrication aspects and the electron exchange at the sensing electrode [37]. The fabricated pH sensor is initially examined in solutions of different pH prepared by diluting the standard buffer solutions with KOH . The pH of these solutions is predetermined using the laboratory pH meter, Labman LMPH9. OCPs across the sensing and the reference electrodes are captured on the electrochemical workstation and repeated several times to fetch the error values.

The OCP measurement between the Sb electrode and the REF2 can provide insight into the electrochemical characteristics of the pH sensor. Fig. 5(a) depicts one of the four OCP measurements taken by the sensor when tested in buffer solutions having pH 3.94, 5.23, 6.74, 7.48, 8.17, and 9.04 for 120 s. The potential difference between the two electrodes remained constant for the specified time in each case. Fig. 5(b) shows the calibration graph for the fabricated pH sensor. It indicates a linear relation between the pH of the solutions and the OCP recorded by the sensor. Also, the OCP value decreases as the pH increases which is in accordance with the Nernstian equation [38]. The slope of the calibration graph gives the sensitivity of the pH sensor and it is found to exhibit a sub-Nernstian value of -43.18 mV/pH ($R^2=0.99$). Here, the standard electrode potential is evaluated by extrapolating the graph to the y-axis.

$$E = 460mV - (43.18mV/pH) * pH \quad (3)$$

The repeatability of the fabricated pH sensor is investigated by measuring the OCP during a titrated cycle from acid to base and vice versa (Fig. 6(a)). It takes an average of 60 s for the fabricated sensor to attain stability when the pH of the solution changes drastically, excluding the time taken for removing, cleaning, and re-inserting the sensor. The sensor showed a

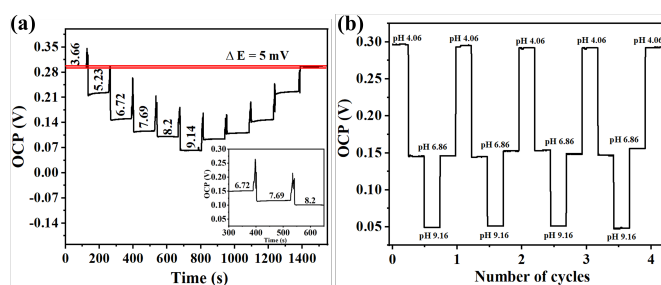


Fig. 6. (a) Characterization of the repeatability aspect of the sensor by pH titration process. Inset the temporal response of the pH sensor when changed from pH 6.72 to 8.2, (b) OCP variation of the sensor when tested in solutions of pH 4.06, 6.86, and 9.16, respectively.

hysteresis of approximately 5 mV when taken through the titration process. The sharp spikes observed in the graph between any two pH readings correspond to the noise captured by the sensor while shifting it from one solution to the other. Inset of Fig. 6(a) shows the temporal response of the pH sensor when changing from pH 6.72 to 8.2.

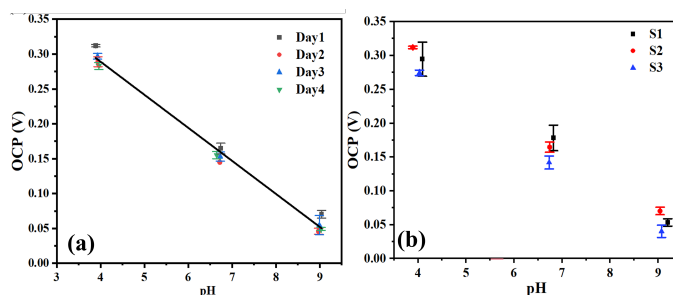


Fig. 7. (a) Reproducibility of the sensor output when tested for four consecutive days (b) Response of three different sensors S1, S2 and S3 when tested in buffer solutions

An ideal pH sensor should yield repeatable readings while cycling between extreme pH values in its specified range. Fig. 6 (b) shows the OCP readings of the sensor when tested repeatedly in solutions of pH 4.06, 6.86, and 9.16 for four consecutive cycles. The OCP remains almost constant even after repeated experimentation, proving the consistency and repeatability of the pH sensor. Fig. 7 (a) shows the sensor response when tested for four consecutive days. The sensor showed consistent results across four days with variation less than ± 0.15 pH. Fig. 7(b) indicates the response of three sensors (S1, S2, and S3) fabricated using the same fabrication procedure, when tested in buffer solutions of pH 4.06, 6.86, and 9.16. S1, S2 and S3 showed a sensitivity of about -48 mV/pH, -47.5 mV/pH and -46.5 mV/pH, respectively. The sensor sensitivity differed by about 1 mV/pH which is attributed to the change in the thickness of the polymer coating during the fabrication process and also to the amount of *KCl* granules embedded in the polymer matrix coated over each electrode.

Fig. 8(a) shows the stability analysis of the pH sensor when immersed in a solution of pH 5.6 for 17 h. The maximum deviation in the potential of the fabricated pH sensor is found to be 66 nV/s over 17 h with a maximum change in OCP less than 15 mV. This can be attributed to the change in

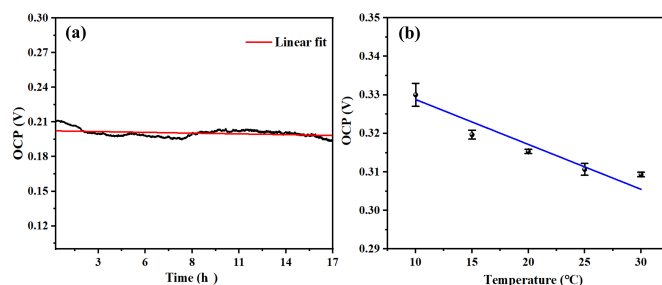


Fig. 8. (a) Stability analysis of the sensor when tested in pH 5.6 for 17 h, (b) influence of solution temperature on the OCP recorded by the sensor

the room temperature. To better understand the influence of temperature on the sensor response, the sensor was tested in a solution heated at different temperatures. Fig. 8(b) shows the effect of solution temperature on the OCP yielded by the fabricated pH sensor. The sensor was tested for temperature in the range of 10°C to 30°C. As the temperature of the analyte is increased, the OCP recorded by the sensor decreased, which is in agreement with the Nernst equation.

F. Applications

The practical utility of the pH sensor is established by measuring the pH of idli batter (a slurry of ground rice and lentils soaked in water) during its fermentation process and the pH of different soil solutions.

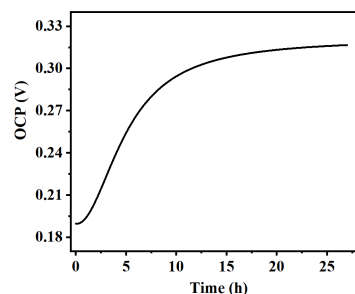


Fig. 9. Change in open circuit potential of the pH sensor while measuring the pH of the idli batter during fermentation.

1) *Measuring the pH of idli batter*: For testing purposes, 18 g of non-fermented, refrigerated idli batter was mixed with 10 ml of DI water to adjust its consistency and also to allow free movement of the ions. The pH of the idli batter is reported to vary from 6.1 to 4.1 over 24 h analysis [39]. This change in pH is confirmed with the help of the laboratory pH meter. The change in OCP recorded by the all-solid-electrode pH meter is plotted in Fig. 9. As the fermentation process starts, the OCP of the sensor increases and becomes stable after complete fermentation which is equivalent to the reduction of pH as the batter ferments. This demonstrates the utility of the fabricated pH sensor in the food processing industry.

2) *Measuring the pH of soil solutions* : Fig. 10(a) shows five different soils of pH 4.31, 5.04, 5.57, 5.85, and 6.57 collected from different parts of India. These soils are sieved,

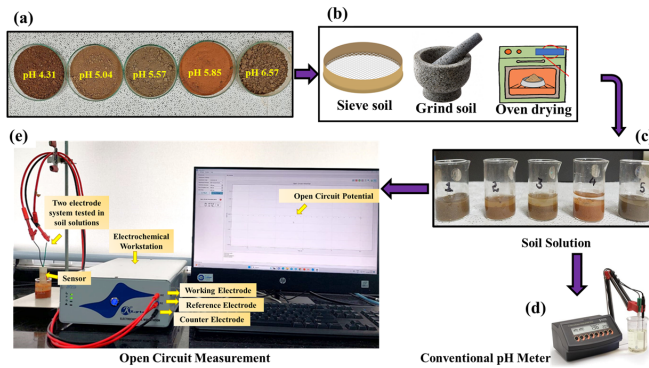


Fig. 10. Soil pH analysis method: (a) Soil samples of different pH collected from different parts of India (b) sieved, ground, and dried in an oven (c) soil solutions prepared in a 2:1 ratio (d) pH of the solutions are tested using conventional pH meter (e) OCP of the soil solution tested using the electrochemical workstation.

ground, and oven-dried as shown in Fig. 10(b). The pH of these processed soils is tested using the laboratory pH meter following the standard protocol by preparing soil solution as shown in Fig. 10(c) and (d). For OCP measurements, the soil solution is stirred for a few seconds initially, and then the fabricated pH sensor is placed in the soil solution. The electrodes are connected to the electrochemical workstation as shown in Fig. 10(e). The measurements were taken after 15 min to ensure the sensor attained stability with the soil solution.

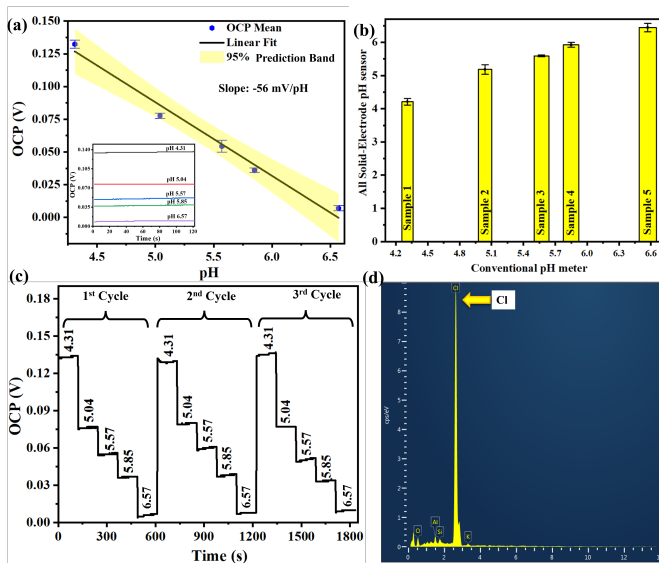


Fig. 11. (a) Potential of the fabricated sensor when tested in soil solutions with 95% prediction band, inset shows the OCP reading measured using the fabricated sensor (b) Graph showing the pH of the soil solution estimated using the conventional pH meter and the fabricated all solid electrode pH sensor with the error bar (c) Repeated analysis of the soil solution using the fabricated sensor (d) Elemental mapping of the reference electrode after repeated testing

Fig. 11 (a) shows the linear relation between the OCP measured using the electrochemical workstation (as shown in Fig. 10 (c)) and the pH of the soil solution measured using the laboratory pH meter. The inset of Fig. 11 (a) shows the

constant OCP readings obtained for 120s. The graph also shows the 95% prediction band of the measured potentials. The slope of the graph is calculated to be -56 mV/pH which is nearer to the ideal Nernstian slope. The Nernst equation (equation 2) when tested in soil solution modifies as shown below

$$E = 369\text{mV} - (56\text{mV/pH}) * \text{pH} \quad (4)$$

TABLE II

PH OF THE SAMPLES TESTED WITH THE CONVENTIONAL PH METER AND THE FABRICATED PH SENSOR

Sample	Conventional meter	Fabricated pH sensor	Deviation
Sample 1	4.31	4.21	0.1
Sample 2	5.04	5.18	-0.14
Sample 3	5.57	5.59	-0.03
Sample 4	5.85	5.92	-0.07
Sample 5	6.57	6.44	0.13

Table II shows the pH of the five different soil solutions when tested using the laboratory pH meter and the all-solid electrode pH sensor. The fabricated all-solid electrode pH sensor shows a maximum deviation of $\pm 0.15 \text{ pH}$, which is admissible for agricultural applications. Fig. 11 (b) shows the graph between the pH measured using the conventional pH meter and the fabricated pH sensor. Fig. 11 (c) shows the repeatability of the sensor when tested in soil solutions for three consecutive cycles. The variation in voltage output is noted to be minimal. However, prolonged use of the fabricated sensor for several weeks in harsh environments like soil solutions may lead to the soiling of the reference electrode and also cause excessive depletion of Cl^- ions in the reference electrode. This is confirmed by performing an EDAX analysis on the reference electrode as shown in Fig. 11(d). After several days of testing in soil solution, the depletion of Cl^- ions may result in a potential change of the reference electrode, thereby impacting the pH measurement. This can be mitigated by calibrating the sensors at regular intervals. The proposed sensor is designed to allow for easy replacement of the reference electrode, effectively treating it as a consumable component of the pH sensor. Table III compares the all-solid-electrode pH sensor reported, with the present work.

III. CONCLUSION

This paper presents the fabrication and characterization of a pH sensor that can be used for inline measurements in industries such as food processing, pharmaceuticals, paint manufacturing, etc. The fabricated sensor is devoid of fragile components, making it a robust sensor that can be used for agricultural purposes as well. The longevity and repeatability of the sensor were characterized by testing the sensor for 17 h in a solution of pH 5.6. A maximum drift of 66 nV/s is observed during continuous analysis, showing its potential for inline use. The sensor has demonstrated its applicability for both fermentation analysis of the idli batter and soil pH analysis. The soil pH analysis showed that the fabricated electrode had an error of less than $\pm 0.15 \text{ pH}$ compared to the conventional pH meter.

TABLE III
COMPARISON OF ALL-SOLID-ELECTRODE PH SENSORS REPORTED FOR VARIOUS APPLICATIONS.

Working Electrode	Reference Electrode	Application	pH range	Remarks	Ref
Al_2O_3 ceramic substrate/ Sb/Sb_2O_3 modified with Nafion solution	$Ag/AgCl$ modified with Nafion solution	Soil-less cultivation	3 - 11	• Sensor should be stored in 6.88 buffer solution • Standard deviation $\leq 2mV$ • Hysteresis of about 1.63 mV on repeated tests	[35]
Carbon paste modified by alizarin	$Ag/AgCl$ ink	Soil pH	3.6 - 9.05	• Pretreatment of soil with 1M KCl or $CaCl_2$ • Relative error less than 5% . Error less than ± 0.2 pH	[40]
Sb	$Ag/AgCl$ coated with saturated KCl Araldite	Soil pH	3 - 8	• Reference electrode is not renewable	[41]
Pt disk electrode/Poly(3-cyclohexyl thiophene)	$Ag/AgCl$	To detect urea concentration		• Durability is 3 months when stored at $4^\circ C$ under dry conditions.	[42]
Thin sputter deposited RuO_2	Polyvinyl butyral- SiO_2	Breweries	2 - 12	• Accuracy of ± 0.2 pH. • Sensor stored in buffer solution.	[43]
Sb	$Ag/AgCl-KCl$ saturated PVC—PVC	Soil pH sensor	4 - 9	• Error less than ± 0.15 pH • Replaceable reference electrode • Requires minimal maintenance.	This work

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