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Impact of Analyte pH on the Sensitivity of Screen-Printed Flexible Ammonium Sensor

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Abstract— This work reports the impact of analyte pH conditions on the sensitivity of the Ammonium (NH4+) sensor. The NH4+ sensor was developed by screen printing an IDE structure and subsequently modified with multiwalled carbon nanotube (MWCNT) and Zinc Oxide (ZnO) nanocomposite active layer on a fiber epoxy substrate. The sensor impedance response was studied for the varying NH4+ analyte pH levels, and device sensitivity was found to decrease with increased analyte pH concentrations (pH 4 - pH 9). The maximum impedance of the sensor operated at pH 4 was ~ 10.5% higher when performed at pH 9. The outcome demonstrates that the presented study could open new opportunities to develop highly sensitive nutrient sensors based on tuning of the analyte pH conditions. Alternately the study highlights the need for maintaining analyte pH conditions for the stable and reliable response of the flexible ammonium sensor.

Keywords— Screen-Printing; Nanocomposites, IDE; Analyte pH and Ammonium Sensor.

I. INTRODUCTION

Printed electronics is a rapidly progressing technology that utilizes innovative conducting inks and resource-efficient printing methods to advance the fabrication of various electronic devices on a wide variety of substrates[1][2][3]. Among various printing technologies, screen printing is enticing for low-cost manufacturing at scale, and it has been used for the development of a wide variety of electrochemical sensors[4][5][6]. Biocompatible and degradable active materials are fast being explored for screen printed sensors as a step forward to reduce the toxic materials and waste generated from the growing number of electronic devices[7][8]. The properties of the inks made from these materials could significantly affect the response of sensors. Accordingly, various studies on aqueous and non-aqueous printing solvents have been published in a variety of fields, including biomedical, industrial, and agriculture applications[9].

Among a wide variety of applications where screen-printed electrochemical sensors are used, the pH values of analytes are an essential factor that needs to be measured or against which the sensors need to have a stable response. For example, in agriculture applications, the pH controls the physicochemical properties of the soil and hence the availability of the nutrients to the plant. The soil pH level between 5.5 – and 7 stabilizes the macronutrients (NPK) and micronutrients (Mg, Zn, etc.)[10]. Therefore, when measuring parameters such as ammonium (NH4+), which is the primary source of Nitrogen (N) for plant growth [11], it is essential to ensure variations in pH do not influence the ammonium sensor response. But the change in soil pH conditions varies the NH4+ concentration, and it can be toxic at higher concentrations [12]. This toxic effect could inhibit the plant root and shoots growth and lead to leaf chlorosis [13]. A broad range of NH4+ sensing techniques ranging from optical to electrochemical methods has been developed using materials such as metal oxides, polymer, and carbon-based composites. Due to their ease of manufacture and unique optical, electrical, and chemical sensing characteristics, the metal-metal oxide-based active layer nanostructures have been widely employed for the electrochemical detection of NH4+ ions [15]–[17]. The target concentration mainly dominates analytical signals from such sensors. Besides the target molecule, interfering ions and process parameters such as analyte solution pH, conductivity, and temperature could also contribute to the sensor signal. In a dynamic background, these parameters could contribute heavily to signal variability, and there is a need to evaluate their role. Very limited work has been carried out to investigate the reliability of analyte pH conditions.

In this context, in this work, we investigate the impact of analyte pH conditions on the sensitivity of the NH4+ sensor. The NH4+ sensor was developed by screen printing an IDE structure on a fiber epoxy substrate. The IDE structure was subsequently modified with a multiwall carbon nanotube (MWCNT) and zinc oxide (ZnO) nanocomposite active layer. ZnO is an attractive material as it is biocompatible, easy to synthesize, and abundantly available [18][19]. It is one of the amphoteric materials and, therefore, can create oriented dipoles or surface bonds by adsorbing ions in pH analyte solution [20]. The combination of MWCNT and ZnO has been demonstrated to reduce the resistance of the sensing material, and the metal oxide has an impact on the sensing properties. Furthermore, we have
also investigated the sensor impedance response by varying NH$_4^+$ analyte concentrations under optimal frequency conditions.

This paper is organized as follows: Section II describes the experimental arrangement for sensor fabrication. Section III describes the results, and the key outcomes of the study are summarized in Section IV.

II. SENSOR FABRICATION

The fiber epoxy substrate and Copper (Cu) ink used to fabricate the sensor were commercially obtained (Finar, India). The IDE structure was screen printed on the fiber epoxy sheet layer. The design has been developed and examined using the CIRCAD software tool (finger length: 11 mm, electrode width, and space: 0.5 mm). After the screen printing process, the IDE layers were dried at 80°C for 30 minutes. The screen-printed IDEs (Fig. 1) consist of 18 fingers, providing a total sensing area of 18 x 15 mm$^2$ for the NH$_4^+$ analytes [6]. The MWCNT/ZnO nanocomposites were prepared by the chemical reflux method. Nitric acid (HNO$_3$) was used to functionalize MWCNT for 8 hours at 110°C. Further, F-MWCNT powder was treated with Zn(NO$_3$)$_2$.6H$_2$O to synthesize ZnO. The binding agent (0.01 M Hexamine) and NaOH were added to the homogenous nanocomposite solutions, refluxing at 120°C for 3 hours before drying for 10 hours at 80°C. Obtained nanocomposite was further mixed in Dimethyl sulfoxide (DMSO) and drop-casted over the screen-printed IDEs. The surface orientation of the MWCNT/ZnO active layer was investigated using field emission scanning electron microscopy (FeSEM), and the results are shown in Fig. 1. The crystal phase and orientation of nanocomposites were investigated using an X-ray diffractometer (XRD). The device impedance response was evaluated with an Agilent 4294A precision impedance analyzer instrument.

III. RESULTS AND DISCUSSION

A. Morphological Characterisation

From the FeSEM image, the presence of ZnO nanoflowers (NF) was found over the uniformly distributed F-MWCNT. The X-ray diffraction (XRD) studies for ZnO, F-MWCNT, F-MWCNT/ZnO samples were performed to investigate the crystalline nature of the particles, and the pattern shows maximum intensity for the peak positioned at 2θ=36.56° for ZnO along the (101) plane, with no other impurity-related peak.

B. Electrical Characterisation

The impedance response of the fabricated device was studied to determine sensitivity with varying analyte pH levels. The performance of the sensor was investigated using standard NH$_4^+$ solutions (1–100 mM) at various pH levels. The experiment results shown in Fig. 2 show that the pH of the NH$_4^+$ testing samples influences the response of impedance magnitude. The maximum impedance of the sensor operated at pH 4 was ~10.5% higher when operated at pH 9. The device sensitivity to NH$_4^+$ was found to decrease as the pH of the analyte increased from acid to alkaline. The rate of change of impedance was fastest at pH 4, and the increase in impedance was most gradual at pH 7 and 9. These findings confirm that the dense allocation of hydrogen ions (H$^+$) in an acidic analyte medium is critical for NH$_4^+$ sensor sensitivity.

IV. CONCLUSION

In summary, this work reports the impact of analyte pH conditions on the sensitivity of the NH$_4^+$ sensor. The NH$_4^+$ sensor was developed by screen printing an IDE structure, subsequently modified with multiwalled carbon nanotube (MWCNT) and zinc oxide (ZnO) nanocomposite active layer on a fiber epoxy substrate. The sensor impedance response was studied for the varying NH$_4^+$ analyte pH levels, and device sensitivity was found to decrease with increased analyte pH concentrations (pH 4 - pH 9). The presented study could open new opportunities to develop highly sensitive and stable nutrient sensors.

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