CODE OF YOUR ABSTRACT

OPTIMIZING E-TEXTILE PH SENSORS: A COMPARATIVE EVALUATION OF RGO-PANI AND RUO_2 MATERIALS

Nurul Fauzani Jamaluddin[2], Fatimah Ibrahim[1,2] , Aisyah Hani Zulkiflee[1], Aung Thiha[2], Bojan Petrović[3], Sanja Kojić[4], Nurul Fauzani Jamaluddin[2], Goran M Stojanović[4]
[1] Department of Biomedical Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur,
[2] Centre for Innovation in Medical Engineering (CIME), Universiti Malaya, Kuala Lumpur, Malaysia
[3] Department of Dental Medicine, Faculty of Medicine, University of Novi Sad, Novi Sad, Serbia
[4] Faculty of Technical Science, University of Novi Sad, Novi Sad, Serbia
Email: fatimah@um.edu.my

ABSTRACT

Wearable devices have emerged as a promising solution in the medical field, offering early diagnosis and effective monitoring. E-textile is a type of biosensor that can potentially be used in wearable devices for pH monitoring purposes. The purpose of this research paper is to compare the effectiveness of two different pH sensing materials: reduced graphene oxide-polyaniline (rGO-PANI) modified screen electrode and Ruthenium (IV) Oxide (RuO2) coated thread for creating e-textiles. The study evaluated the sensitivity of both sensing materials for pH detection and found that both are suitable for this purpose. However, the results show that the rGO-PANI-modified electrode is more sensitive (with a sensitivity of -54.2 mV/pH) compared to the RuO2-coated thread (with a sensitivity of -47.7 mV/pH). The findings of this study suggest that e-textile biosensors have great potential in the medical field and that their sensitivity can be further improved through material modification and optimization.

Keywords: E-textile, reduced graphene oxide-polyaniline, Ruthenium (IV) Oxide, thread sensor

INTRODUCTION

Chronic diseases are responsible for a significant proportion of global deaths, accounting for approximately 75%, and have a considerable economic impact [1]. However, wearable devices have emerged as a promising solution in the medical field, offering early diagnosis and effective monitoring. Utilising non-invasive and dynamic measurements of biomarkers found in biological fluids can provide continuous and real-time physiological insights, making it possible to track and manage chronic diseases more efficiently[2] .

A wearable device is a portable device that consists of biosensors attached to a person's body in various ways, such as through clothing, bandages, watches, glasses, contact lenses, and rings[1], [3]. These devices are designed to offer unique features that set them apart from conventional devices, including ease of use, portability, and adaptability to various environments. E-textile is one of the innovative biosensors that is designed to accurately measure various biological parameters by analyzing sweat. These textile-based bio-sensors are precisely engineered to be in close contact with the skin and provide conformable, non-invasive monitoring of vital signs and other physiological data [4]. E-textiles can monitor important biological parameters such as ECG, EMG, EEG, and sweat analysis. Sweat analysis has become increasingly important in health and performance monitoring due to its composition. One example of its significance is pH sensing through sweat, which has the potential to provide valuable insights into an individual's health and well-being.

pH is a measure of acidity or alkalinity in a solution. The pH level of sweat is closely linked to an individual's hydration status. When a person's body becomes dehydrated, the concentration of electrolytes in their sweat increases, resulting in more acidic pH levels. Monitoring sweat pH can be helpful for individuals, athletes, and healthcare professionals to determine hydration levels and take the necessary steps to maintain proper fluid balance [5]. Athletes and fitness enthusiasts can especially benefit from tracking sweat pH to optimize their training and performance. It is essential to maintain the correct pH balance in sweat to prevent issues such as muscle cramps and fatigue during physical activity.

However, there are several challenges associated with using e-textiles for pH sensing. These challenges include ensuring that the e-textile sensors remain durable and stable over time while achieving high accuracy and sensitivity in pH measurements [2], [4]. This paper aims to evaluate the performance of two different pH sensing materials: reduced graphene oxide-polyaniline (rGO-PANI) modified screen electrode and Ruthenium (IV) Oxide (RuO2) coated thread for e-textile fabrication in the future.

EXPERIMENTAL

Fabrication of rGO-PANI biosensor

The synthesis of rGO-PANI followed the method employed by Thu et al. (2018). Initially, a graphene oxide solution with a concentration of 1 mg/ml was prepared by mixing 1 ml of a 4 mg/ml graphene oxide aqueous dispersion with 3 ml of deionized water. Subsequently, the graphene oxide solution underwent sonication to achieve a homogeneous mixture. To eliminate dissolved oxygen and other impurities in the GO solution, a nitrogen purging method was implemented, utilizing nitrogen gas. The carbon-coated electrode was then immersed in this solution.

Next, the GO-modified electrode underwent reduction via the cyclic voltammetry (CV) technique. The potential range applied for the reduction of the thread was between 0.2 V and -1.2 V. Following reduction, the thread was thoroughly rinsed, dried, and thereby prepared as the conductive modified electrode with rGO.

Subsequently, a solution was prepared by combining 0.1M aniline with 30 ml of 0.5M sulfuric acid. To obtain the desired 30 ml of 0.5M sulfuric acid, 15 ml of 1M sulfuric acid was mixed with 15 ml of deionised water. Next, 0.2621 ml of the 0.1M aniline solution was added to the 30 ml of 0.5M sulfuric acid. The resulting mixture was then placed on a magnetic hotplate stirrer, and a stir bar was immersed to provide simultaneous stirring and heating.

Fabrication Process of RuO_2 Biosensor

The fabrication process of the RuO_2-coated thread followed the methodology described by [6]. Initially, 0.0104g of ruthenium trichloride hydrate ($RuCl_3$. nH_2O) was dissolved in deionized water, resulting in a 10 ml solution with a concentration of 5 ml $RuCl_3$. Subsequently, the dropwise addition of a 5 ml NaOH solution was carried out until the precipitation of solid $RuOH_3$ precursor occurred. The obtained precursor was isolated through centrifugation and then suspended in deionized water. The resulting suspension was evenly spread onto the thread, allowed to dry at room temperature, and subsequently subjected to an oven temperature of 350 ℃ for a duration of 3 hours. As a result, the RuO_2-coated thread was successfully formed.

Consequently, 1 ml of 25% glutaraldehyde solution and 4 ml of DI water were mixed and placed in microcentrifuge tubes. The RuO_2 deposited threads were dipped in the diluted glutaraldehyde solution and then heated to 50 ℃ in the oven for 30 minutes.

Evaluation Method

The evaluation of the rGO-PANI and RuO2-based pH sensors involved designing pH solutions ranging from pH 5 to 9 and dropping them onto the electrodes. The potential was obtained using the zero current potentiometry method, and the assessment was repeated for each pH solution. The sensitivity and pH range were evaluated in this study.

RESULTS AND DISCUSSION

Figure 1 shows the conductive modified rGO-PANI electrode and RuO_2 thread sensor fabricated in this study.

Figure 1. The fabricated conductive modified rGO-PANI electrode and RuO_2 thread sensor

Vollamomogram of rGO-PANI Modified Electrode

The voltammogram of rGO electrode fabrication using the cyclic voltammetry (CV) technique is shown in Figure 2. The synthesis of the rGO-PANI composite involved chemically polymerising aniline monomers onto the surface of rGO sheets. The fabrication process of rGO comprised cyclically varying the potential between -0.2 and 1.2 V, with a scan rate of 50

mV/s, in a solution containing 1 mg/ml of graphene oxide solution for a total of 20 cycles. Analysis of the CV data obtained during the fabrication process revealed distinct redox peaks, signifying the successful reduction of graphene oxide to rGO. The voltammogram of rGO displayed a clearly defined redox peak at a reduction potential of -0.5 V, aligning with the expected behaviour of rGO. This result shows that the CV method employed on a carbon thread proved effective in the fabrication of rGO from graphene oxide.

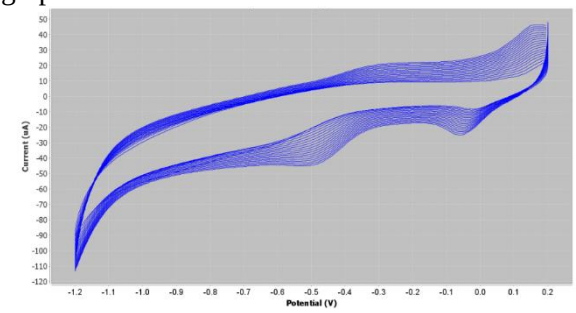

Figure 2. Voltammogram of rGO electrode fabrication using the cyclic voltammetry (CV) technique

While, Figure 3. presents the cyclic voltammogram achieved through the systematic variation of the potential applied to the working electrode, ranging from -0.2 V to 0.9 V, with a scan rate of 50 mV/s.

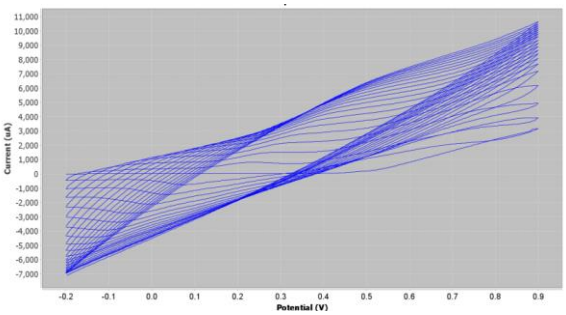

Figure 3. Voltammogram of electrodeposition of aniline on rGO-coated screen printed electrode

The experiment was conducted in a solution comprising 0.1 M aniline and 0.5 M sulfuric acid. The obtained voltammogram exhibited distinctive peaks, appearing at approximately 0.1 V and 0.8 V, representing the reduction and oxidation processes of polyaniline (PANI) respectively. The peak at 0.1 V corresponds to the reduction of PANI, transforming it from its emeraldine salt state to leucoemeraldine form. Conversely, the peak at 0.8 V corresponds to the oxidation of leucoemeraldine form back to the emeraldine salt state. Additionally, the voltammogram depicted a minor peak around 0.6 V, indicating the occurrence of PANI doping.

The fabricated voltammogram of PANI on rGO carbon thread using cyclic voltammetry method provides important information on the electrochemical behavior of PANI. The rGO carbon thread provides a stable platform for the deposition of PANI, and the cyclic voltammetry method allows for precise control of the electrochemical polymerization process.

rGO-PANI and RuO2-Based Sensors Assessment

Figure 4 and Figure 5 illustrate the response characteristics of these materials in relation to pH variations, specifically concerning the rGO-PANI modified electrode and the RuO_2-coated carbon thread. Open circuit potentiometry is a measurement technique determining the potential difference between two electrodes without any current flow. In this technique, when the sensor contacts a pH solution, a potential difference arises at the pH-sensitive electrode due to the hydrogen ion concentration difference with the reference electrode. This potential difference is measured without current flowing through the sensor.

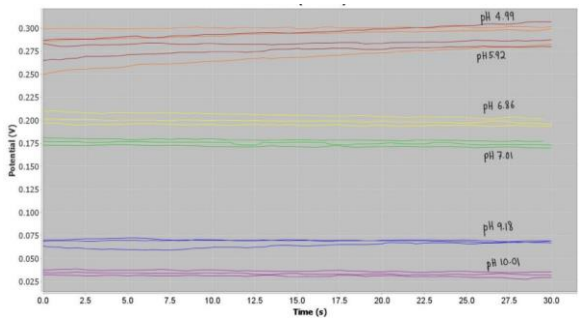

Figure 4. Open circuit potentiometry of rGO-PANI modified screen-printed electrode

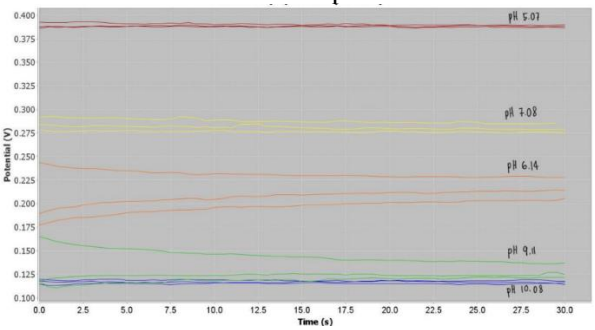

Figure 5. Open circuit potentiometry of RuO_2-coated carbon thread.

All sensors have a positive potential at low pH levels, which denotes their tendency to attract electrons. The potential of the sensors decreases

as the pH rises. At acidic pH levels, PANI commonly exists in its protonated state called emeraldine salt. During this state, the PANI demonstrates a positive electrical potential due to the existence of positively charged protons linked to the nitrogen atoms within the polymer chain. As the pH rises, the proton concentration diminishes, causing PANI to undergo deprotonation and convert into its emeraldine base form. In this form, PANI loses its positive charge, leading to a reduction in its electrical potential.

At high pH levels, the PANI is expected to be fully deprotonated, and the potential of the rGO-PANI sensor should turn negative. However, the potential of rGO-PANI sensor did not turn negative, and there can be certain factors that may influence or limit the extent of the potential shift. One of the contributing elements could be partial deprotonation, which might occur when the pH of the PANI is high and prevent it from totally deprotonating, resulting in a partial rather than full change in the negative potential. The PANI molecule's equilibrium or deprotonation kinetics may be constrained in this way. In addition, the potential response may be influenced by how the rGO-PANI surface interacts with the buffer solution or other species found in the solution. These surface interactions may hinder fully realising the negative potential shift at high pH levels. As a result, the sensitivity of the rGO-PANI sensor is -54.2 mV/pH in this study.

While for RuO2-coated thread, at low pH values, the potential was positive, similar to the rGO-PANI coated carbon electrode, indicating an electron-attracting behavior. However, as the pH increases, the potential becomes more positive, demonstrating an enhanced affinity for electrons with increasing pH. The result also shows that the final sensitivity RuO_2 sensor obtained from the graph trendline is -47.7 mV/pH, which is lower than the rGO-PANI sensor.

CONCLUSION

This paper demonstrates that both rGO-PANI-modified electrodes and RuO_2 thread sensing can be used to detect pH. Although the RuO2 sensor demonstrated a lower sensitivity compared to the rGO-PANI sensor, further evaluation needs to be conducted such as stability and response time to ensure the suitability of RuO_2 coated thread suitable for wearable e-textile pH sensing.

Acknowledgement

This project has received funding from Universiti Malaya Partnership Grant RK006- 2021, the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 872370 and 854194, and Universiti Malaya Impact Oriented Interdisciplinary Research Grant IIRG002A-2022HWB.

References

[1] S. M. A. Iqbal, I. Mahgoub, E. Du, M. A. Leavitt, and W. Asghar, "Advances in healthcare wearable devices," *npj Flexible Electronics*, vol. 5, no. 1. Nature Research, Dec. 01, 2021. doi: 10.1038/s41528-021-00107-x.

[2] Y. Shi, Z. Zhang, Q. Huang, Y. Lin, and Z. Zheng, "Wearable sweat biosensors on textiles for health monitoring," *Journal of Semiconductors*, vol. 44, no. 2. Institute of Physics, Feb. 01, 2023. doi: 10.1088/1674-4926/44/2/021601.

[3] K. Du, R. Lin, L. Yin, J. S. Ho, J. Wang, and C. T. Lim, "iScience Electronic textiles for energy, sensing, and communication", doi: 10.1016/j.isci.

[4] M. Hirman, J. Navratil, M. Radouchova, J. Stulik, and R. Soukup, "Influence of Sweat on Joint and Sensor Reliability of E-Textiles," *Energies (Basel)*, vol. 15, no. 2, Jan. 2022, doi: 10.3390/en15020506.

[5] D. Liu *et al.*, "Wearable Microfluidic Sweat Chip for Detection of Sweat Glucose and pH in Long-Distance Running Exercise," *Biosensors (Basel)*, vol. 13, no. 2, Feb. 2023, doi: 10.3390/bios13020157.

[6] E. Tanumihardja, W. Olthuis, and A. van den Berg, "Ruthenium oxide nanorods as potentiometric ph sensor for organs-on-chip purposes," *Sensors (Switzerland)*, vol. 18, no. 9, Sep. 2018, doi: 10.3390/s18092901.