

Electro-Catalytic Oxidation of Glucose on Zinc Oxide. Effect of Bacteria

Salma Zahid^{1*}, Youness Tahiri¹, Mohamed Oubaouz¹,
Oukbab Mustapha¹, Aziz Zaroual² and Abdelilah Chtaini¹

¹University Sultan Moulay Slimane, Faculty of Science and Technology, Department of
Chemistry and Environment, 23000, Beni Mellal, Morocco

²University Mohamed V, Faculty of Science, Department of Chemistry and
Environment, 10100, Rabat, Morocco

*Corresponding author: slmzahid77@gmail.com

Received 27/09/2023; accepted 15/01/2024
<https://doi.org/10.4152/pea.2025430402>

Abstract

EMD was herein applied as a glucose-oxidizing electrode catalyst. ZnO electrode showed considerable electro-catalytic activity for glucose oxidation. The effect of glucose Ct was studied by CV and SWV. The *j* increased with glucose Ct. Bacteria presence in the reaction environment showed that they tended to adhere to the Zn surface. The biofilm developed on the ZnO electrode surface did not promote glucose oxidation.

Keywords: bacteria; CV; EIS; EMD; glucose; oxidation; SEM; SWV; ZnO.

Introduction*

Recently, WHO published statistics on diabetes, stating that more than 300 million people suffer from it [1]. Diabetes affects people of all ages. It is a chronic disease that occurs when blood sugar levels are too high. It develops when the pancreas does not produce enough insulin, or the body does not react properly to the effects of insulin. Diabetes can lead to several complications like blindness, cardiac arrest, kidney failure and other serious illnesses. There are four types of diabetes: type 1, type 2, other specific types of diabetes and gestational diabetes [2-3]. Diabetes is usually detected early by measuring blood sugar levels. Blood is collected for the test on an empty stomach, followed by a meal, or after having a glucose solution. This method requires often painful injections, especially for children. These methods are faced with difficulties, such as the preparation of patients and reagents, and the need for sophisticated instruments and skilled technicians. Recently, research studies have proposed enzymatic glucose biosensors, which are generally elaborated by the combination of enzymes, such as glucose oxidase, and an electronic mediator [4-8] for determination of glycaemia level in the blood. This technique also faces certain limitations, such as the high cost of enzymatic electrodes and the very demanding physical conditions of use.

* The abbreviation list is on page 233.

Non-enzymatic electrodes were then imposed for their lower cost, and also the ease of development. They are based on catalysts for glucose oxidation, such as CuO, Ni(OH)₂ and MnO₂ [9-13]. Glucose oxidation on metals strongly depends on the nature of materials and on the crystallographic orientations of the electrodes surface [14-17].

In this work, the performance of a ZnO-based electrode for glucose oxidation was examined. The reaction kinetics was followed by CV and SWV. Several parameters were studied such as glucose Ct effect, pre-Ct time and scan speed. The effect of bacteria on the reaction efficiency was also studied.

Materials and methods

The experiments were carried out by an electrochemical measuring cell equipped with Ag-AgCl, Pt and ZnO plates (both with a surface area of 1 cm²), as reference, auxiliary/counter and working electrodes, respectively. An Orignalys type potentiostat delivered by Youssef Horani SONOYA TRADE allowed to impose E differential and to follow the response in form of j. Data processing was provided by OrigaMaster 5 software. The electrolyte was a 1 M NaCl solution. The bacteria used in this work were *Pseudomonas* (gram-negative), and the powdered glucose was of pure quality. The entire protocol used is shown in Fig. 1, step-by-step.

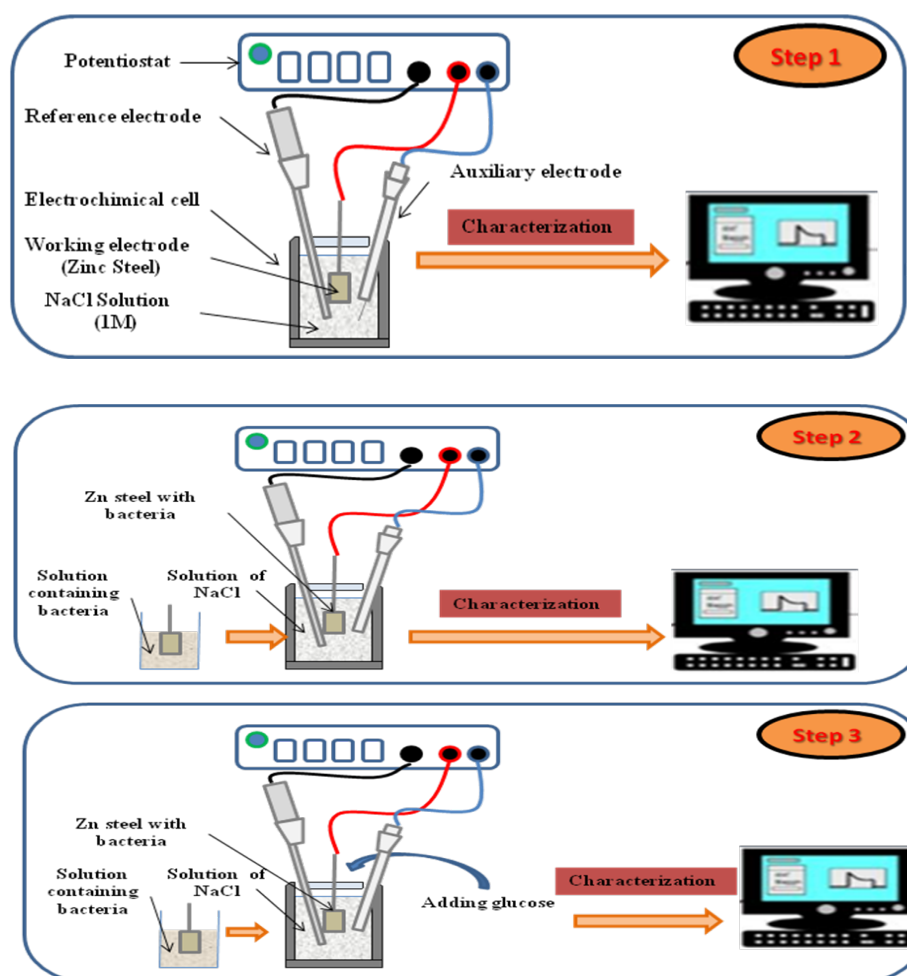


Figure 1: Working protocol step-by-step.

Results and discussion

Fig. 2 shows the SEM image taken for the ZnO electrode. The electrode surface has crystal defects, being uniform and dense. ZnO tends to passivate in a neutral medium such NaCl, forming an insoluble, adherent and protective layer.

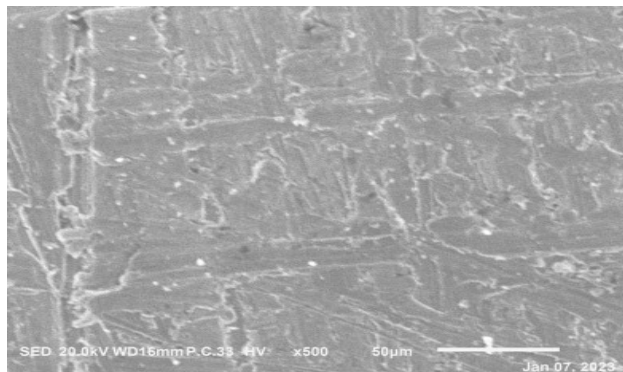


Figure 2: Photos showing ZnO electrode surface in a NaCl solution.

EO of glucose

Fig. 3 shows SWV in a 1 M NaCl solution with and without 1 M glucose, at the ZnO electrode surface. Glucose oxidation is manifested by a significant increase in j , coinciding with Zn oxidation and ZnO formation.

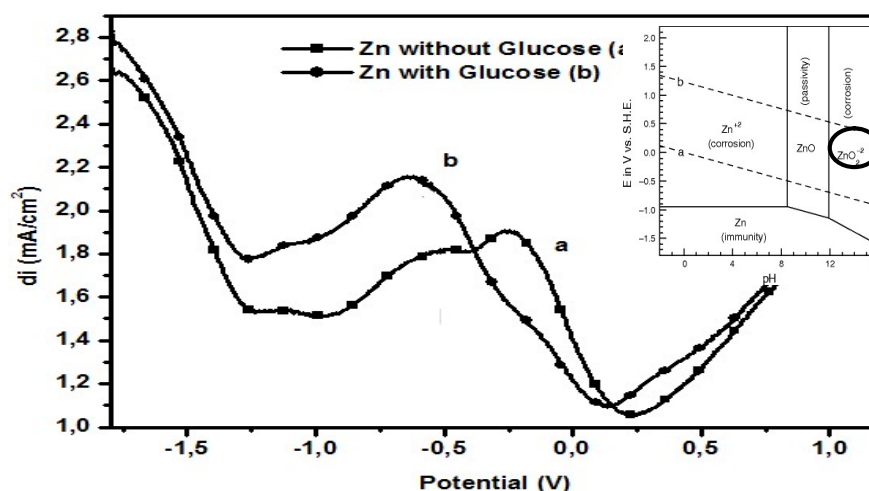
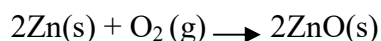


Figure 3: SWV recorded at ZnO electrode, in 1 M NaCl -(a) without; and -(b) with glucose and bacteria.

ZnO formation

ZnO is typically formed through Zn reaction with O_2 . In this reaction, Zn reacts with O_2 to produce ZnO as a solid. The balanced chemical equation for the ZnO formation is:



This oxidation is illustrated in Fig. 3, curve (a), from -0.75 to -0.5 V, which was confirmed by Pourbaix diagram, at the figure top. In curve (b), an intense peak

appears in the same E range, corresponding to glucose oxidation, which coincided with ZnO formation.

EO of glucose in bacteria presence

Glucose oxidation on the ZnO surface, in bacteria presence, was manifested by the appearance of two redox peaks in the CV, of which j linearly increased with glucose Ct (Fig. 4).

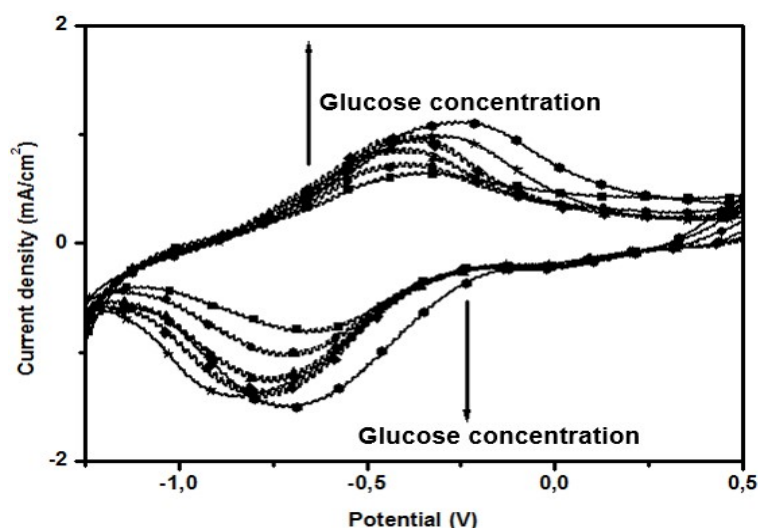


Figure 4: CV recorded at ZnO electrode, in a 1 M NaCl solution containing different glucose Ct, at a SR of 100 mV/s.

The effect of glucose Ct on the ZnO electrode performance was also determined by SWV (Fig. 5). One finds that glucose oxidation is manifested by a peak, of which j linearly increased with glucose Ct.

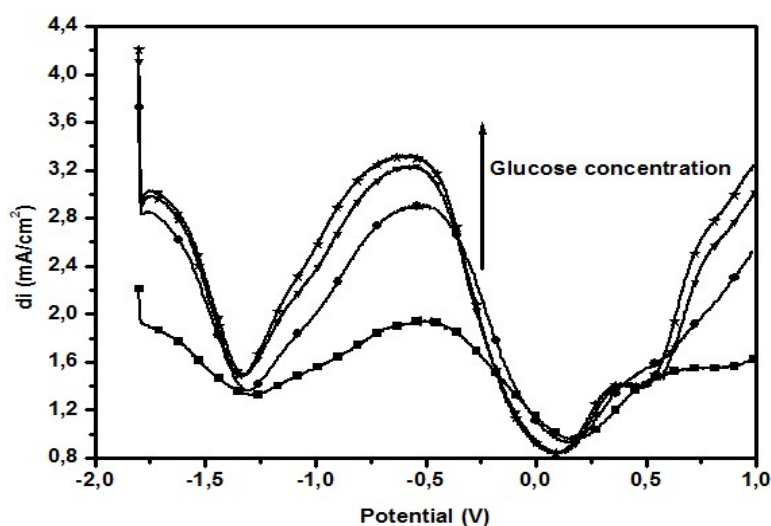


Figure 5: SWV recorded at ZnO electrode, in a 1 M NaCl solution with different glucose Ct.

EIS patterns were recorded on the ZnO electrode surface. These diagrams have

the form of high frequency half circles followed by a Warburg line. The half-loops diameter decreased with the glucose Ct, which corresponds to a decrease in the resistance to electrons transfer (Fig. 6).

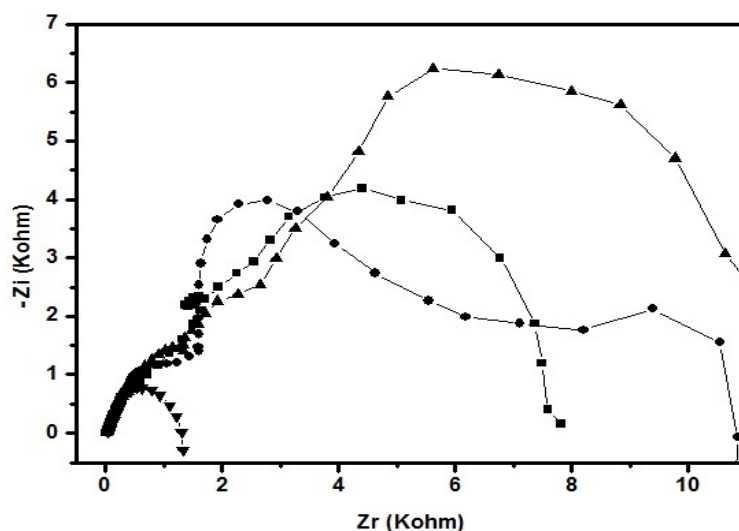


Figure 6: EIS recorded at ZnO electrode in a 1 M solution NaCl with different glucose Ct.

In CV, SR effect on glucose oxidation on the ZnO surface was studied (Fig. 7). One found that j of redox peaks increased with scan speed. Anodic peak shifted towards anode E and cathodic peak shifted towards more cathode E, which corresponds to reversibility loss at high scan speeds.

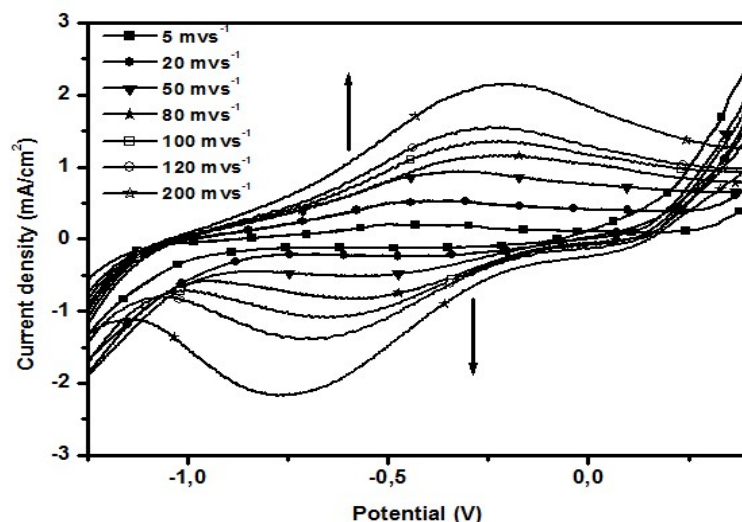


Figure 7: CV recorded at ZnO electrode in a 1 M NaCl solution with glucose, at different SR values.

Fig. 8 shows the SEM image recorded for the ZnO surface in bacteria presence. One observes the damage on the ZnO surface caused by bacteria, which adhered to the surface and formed a connected biofilm.

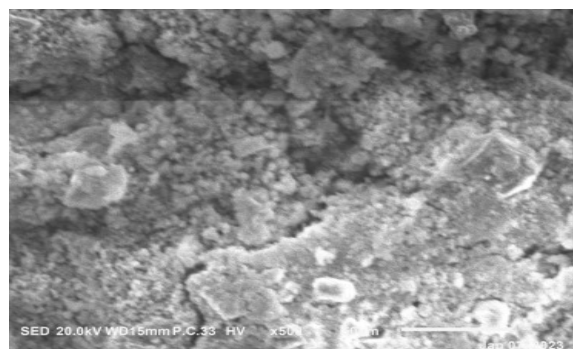
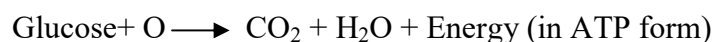


Figure 8: Photo of the ZnO electrode surface in a NaCl solution.

Bacteria mechanism of action on glucose oxidation

Aerobic bacteria use a process, called cellular respiration, to oxidize glucose and extract energy in the form of ATP [18-21]. The cellular respiration consists of several stages: glycolysis, Kreps cycle (or citric acid cycle) and electron transport chain. The overall reaction of aerobic respiration is:



There is another pathway where glucose is oxidized to gluconate, at membrane level, by the enzyme gluconate dehydrogenate, as shown in Fig. 9.

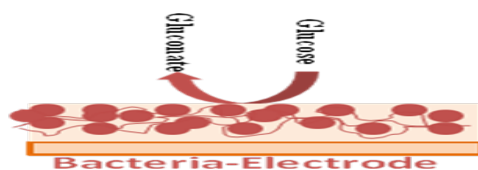


Figure 9: Image showing glucose oxidation to gluconate.

Glucose oxidation on the ZnO electrode surface in bacteria presence was studied by CV and SWV. Fig. 10 shows CV of glucose oxidation, recorded in bacteria presence and absence.

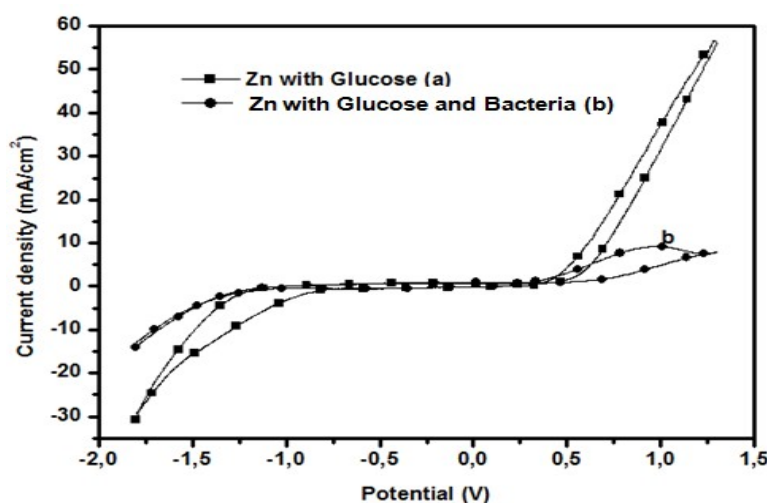


Figure 10: CV recorded at ZnO electrode in 1 M NaCl with glucose **-(a)** without and **-(b)** with bacteria.

In bacteria presence, glucose oxidation goes through stages. The first step was manifested by a considerable drop in j of glucose oxidation. Bacteria in the solution tended to adhere to the electrode surface and form an insulating biofilm. This phenomenon was confirmed by SWV (Fig. 11).

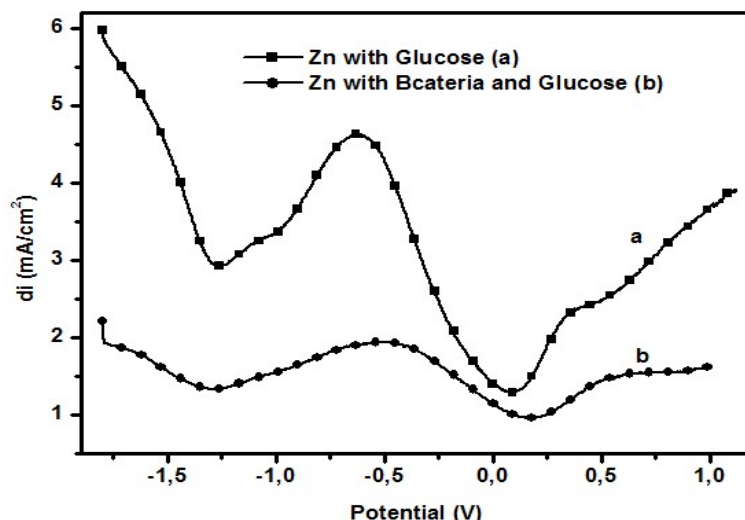


Figure 11: SWV recorded at ZnO electrode, in 1 M NaCl with glucose -(a), without and -(b) with bacteria.

Biofilm development

Bacterial biofilms are generally defined as aggregates of bacterial cells attached to a surface and embedded in a polymeric matrix. Bacteria can adhere to both biotic and abiotic surfaces. The different stages in the formation and dispersion of bacterial biofilm are: adhesion, growth, maturation and dispersion.

In a second step, one witnesses the sudden triggering of glucose oxidation, which is illustrated by Figs. 12 and 13, showing the effect of the scanning cycles number on glucose oxidation in bacteria presence. It is seen that j increased according to the cycles number.

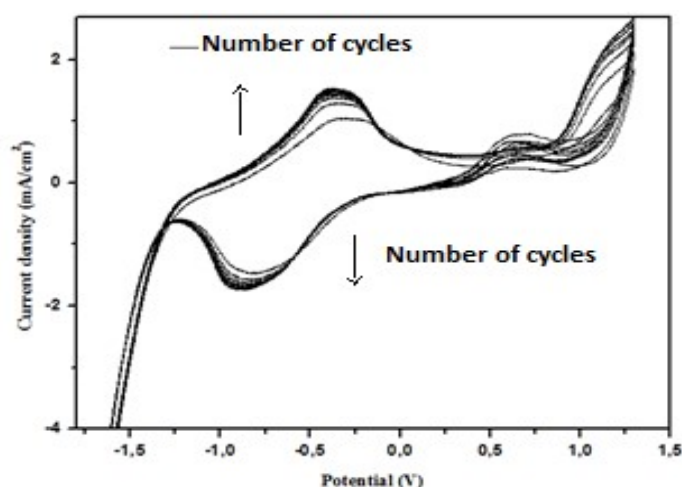


Figure 12: CV recorded at ZnO electrode in a 1 M NaCl solution with glucose and bacteria. Effect of cycle's number.

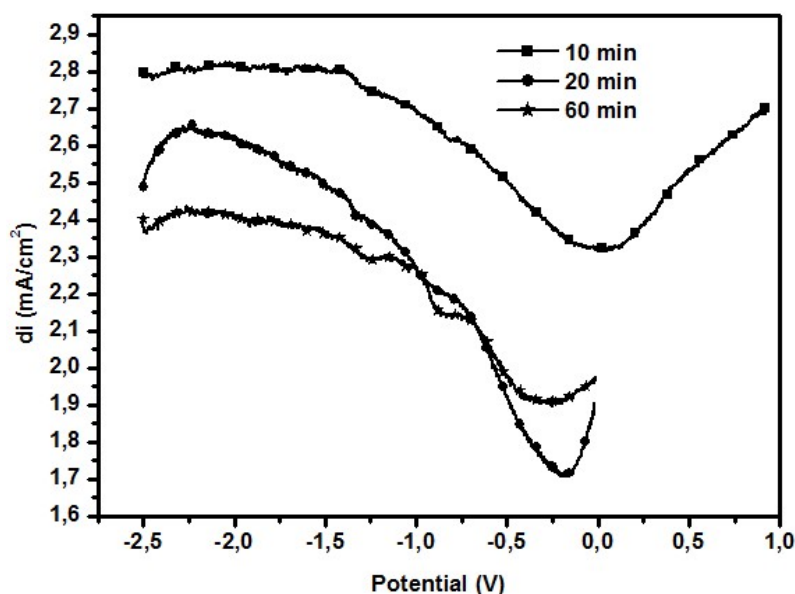


Figure 13: SWV recorded at ZnO electrode in a 1 M NaCl solution with glucose and bacteria.

Conclusion

Electrochemical properties of ZnO electrode for glucose determination and catalytic electrochemical oxidation mechanism were examined and discussed in bacteria absence and presence. Glucose oxidation on the Zn electrode surface coincided with ZnO formation. CV recorded at the ZnO electrode surface showed two redox peaks, of which j increased with the glucose Ct. This shows that the ZnO electrode is very well suited for glucose detection in blood. Bacteria presence in the reaction environment showed that glucose oxidation went through two stages: in the first one, bacteria developed an insulating biofilm which did not show activity for glucose oxidation of; and the second one was characterized by an increase in oxidation j and, subsequently, an improvement in the electrode activity.

This kind of electrodes has various zinc applications, and they can be used in glucose biosensors, which are crucial in diabetes management. These biosensors detect glucose level by measuring its oxidation on the electrode's surface. This provides a rapid and accurate method for monitoring blood glucose levels. In addition, these electrodes can be used in medical research, food industry quality control and environmental monitoring.

Avenues for future research include: enhancing the electrode selectivity to minimize interference from other substances in complex samples and improving its sensitivity to detect lower Ct of glucose; exploring the possibility of detecting multiple analytes simultaneously for a more comprehensive health monitoring system; investigating the development of biodegradable sensors, to reduce environmental impact and provide a sustainable solution; and integrating ZnO electrodes with other emerging technologies, to create innovative and efficient biosensor platforms, such as nanotechnology or 3D printing.

Authors' contributions

Salma Zahid: is the corresponding author; did the experimental protocol; reviewed and edited the original draft of the manuscript; did the modifications asked by the referees and the editor. **Youness Tahiri, Mohamed Oubaouz, Mustapha Oukbab, Aziz Zaroual:** contributed to the project supervision, experimental investigation and conceptualization. **Abdelilah Chtaini:** acted as supervising professor; elaborated the experimental protocol; wrote the initial draft of the manuscript.

Abbreviations

Ag-AgCl: silver-silver chloride
ATP: adenosine triphosphate
Ct: concentration
CuO: copper (II) oxide
CV: Cyclic Voltammetry
E: potential
EIS: Electrochemical Impedance Spectroscopy
EMD: Electrolytic Manganese Dioxide
EO: Electro Oxidation
j: current density
MnO₂: manganese (IV) oxide
NaCl: sodium chloride
Ni(OH)₂: nickel hydroxide (II)
O₂: oxygen
Pt: platinum
Redox: reduction/oxidation reaction
SEM: Scanning Electron Microscopy
SR: scan rate
SWV: Square Wave Voltammetry
WHO: World Health Organization
Zn: zinc
ZnO: zinc oxide

References

1. Gakidou E, Mallinger L, Abbott-Klafter J et al. Management of diabetes and associated cardiovascular risk factors in seven countries: a comparison of data from national health examination surveys. *Bull World Health Organ.* 2011;89(3):172-83. <https://doi.org/10.2471/BLT.10.080820>
2. Tatoń J, Czech A, Bernas M. *Edukacjaterapeutyczna, samokontrolaglikemiii.* Eds. PZWL, Warsaw, Poland, 2008, 339-429.
3. World Health Organization. *Global Strategy on Diet, Physical Activity and Health.* WHO Library Cataloguing-in-Publication Data; World Health Organization: Geneva, Switzerland, 2004:1-18.
4. Clark LC, Lyons C. electrode systems for continuous monitoring in cardiovascular surgery. *Annals New York Acad Sci.* 1962;102:29-45. <https://doi.org/10.1111/j.1749-6632.1962.tb13623.x>
5. Updike S, Hicks G. The Enzyme Electrode. *Nature.* 1967;214:986-988. <https://doi.org/10.1038/214986a0>

6. Williams DL, Doig AR, Korosi A. Electrochemical-enzymatic analysis of blood glucose and lactate. *Analytic Chem.* 1970;(42)10:118-121. <https://doi.org/10.1021/ac60283a032>
7. Guilbault GG, Lubrano GJ. An enzyme electrode for the amperometric determination of glucose. *Analyt Chim Acta.* 1973;(64)3:439-455.
8. Toghiani KE, Richard CG. Electrochemical Non-Enzymatic Glucose Sensors: A Perspective and an Evaluation. *Int J Electrochem Sci.* 2010;(5)9:1246-1301. [https://doi.org/10.1016/S1452-3981\(23\)15359-4](https://doi.org/10.1016/S1452-3981(23)15359-4)
9. Park S, Boo H, Chung TD. Electrochemical non-enzymatic glucose sensors. *Analyt Chim Acta.* 2006;556.1:46-57. <https://doi.org/10.1016/j.aca.2005.05.080>
10. Zhang X, Wang GF, Zhang W et al. Fixure-reduce method for the synthesis of Cu₂O/MWCNTs nanocomposites and its application as enzyme-free glucose sensor. *Biosensor Bioelectron.* 2009;24:3395. <https://doi.org/10.1016/j.bios.2009.04.031>
11. Male KB, Hrapovic S, Liu YL et al. Electrochemical detection of carbohydrates using copper nanoparticles and carbon nanotubes. *Analyt Chim Acta.* 2004;516:35-41. <https://doi.org/10.1016/j.aca.2004.03.075>
12. Zheng L, Zhang JQ, Song JF. Ni (II)–quercetin complex modified multiwall carbon nanotube ionic liquid paste electrode and its electrocatalytic activity toward the oxidation of glucose. *Electrochim Acta.* 2009;54.19:4559-4565. <https://doi.org/10.1016/j.electacta.2009.03.047>
13. Wang Y, Bai W, Nie F et al. A Non-Enzymatic Glucose Sensor Based on Ni/MnO₂ Nanocomposite Modified Glassy Carbon Electrode. *Electroanalysis.* 2015;(27)10:2399-240527. <https://doi.org/10.1002/elan.201500049>
14. Vassilyev YB, Khazova OA, Nikolaeva NN. Kinetics and mechanism of glucose electro oxidation on different electrode-catalysts: Part II. Effect of the nature of the electrode and the electrooxidation mechanism. *J Electroanal Chem Interfac Electrochem.* 1985;(196)1:127-144. [https://doi.org/10.1016/0022-0728\(85\)85085-3](https://doi.org/10.1016/0022-0728(85)85085-3)
15. Hsiao MW, Adzic RR, Yeager EB. The effects of adsorbed anions on the oxidation of D-glucose on gold single crystal electrodes. *Electrochim Acta.* 1992;(37)2:357-363. [https://doi.org/10.1016/0013-4686\(92\)85024-F](https://doi.org/10.1016/0013-4686(92)85024-F)
16. Najih R, Dehbi S, Chtaini A et al. Natural phosphate modified iron electrodes for the anode of the glucose fuel cell. *Res Rev Eletrochem.* 2012;3(3):115-121. ISSN: 0974 – 7540.
17. Chtaini A, El Mhammedi A, Najih A et al. Electro catalytic Oxidation of Glucose on Natural Phosphate Modified Iron Electrode. *Bull Catal Soc India.* 2009;8:11-15.
18. Alberts B, Johnson A, Lewis J et al. *Molecular Biology of the Cell.* 4th edition. New York: Garland Science; 2002.
19. Latour X, Lemanceau P. Métabolisme carboné et énergétique des *Pseudomonas* spp fluorescents saprophytes à oxydase positive. *Agronomie.* 1997;(17)9-10:427-443. <https://doi.org/10.1051/AGRO:19970901>
20. Tremblay YD, Hathroubi S, Jacques M et al. Les biofilms bactériens: leur importance en santé animale et en santé publique. *Canad J Vet Res.* 2014;(78)2:110-116.