CPE/Zn/Polymer/Bacteria Anode for Methanol Fuel Cells

M. Oukbab[1]*, S. Loughmari[2], Y. Tahiri[1], H. Haddouchy[3], M. Oubaouz[1], S. Zahid, S. E. El Qouatli[3], A. El Bouadili[2], M. Visseux[4] and A. Chtaini[1]

[1]*Molecular Electrochemistry and Inorganic Materials Team, Faculty of Sciences and Technologies, Sultan Moulay Slimane University, Beni-Mellal, Morocco*
[2]*Laboratory of Industrial Engineering and Surface Engineering, Applied Chemistry and Environmental Sciences Team, Sultan Moulay Slimane University, Beni-Mellal, Morocco*
[3]*Physical Chemistry Environment and Material, Moulay Ismail University, Faculty of Sciences and Technologie, Boutalamine, Errachidia, Morocco*
[4]*University of Lille, CNRS, UCCS, Catalysis and Solid State Chemistry Unit, Lille, France*
*Corresponding author: mustapha.oukbab@usms.ma

Received 16/05/2024; accepted 20/11/2024
https://doi.org/10.4152/pea.2026440405

Abstract
The aim of this study was to shed light on the process of CH_3OH bacterial electrolytic oxidation, catalysed by a Zn-modified CPE, in the presence of PM polymer in a solution containing 0.3 g NaCl dissolved in 20 mL distilled water. Electrodes were fabricated by depositing Zn on a CPE using potentiostat and galvanostatic techniques. Optical morphology analysis and microscopy techniques revealed Zn efficient dispersion on C, forming well-structured and connected clusters. The study of electrode behavior using CV techniques revealed catalytic effects that improved CH_3OH oxidation results.

Keywords: CH_3OH; CV, electrodeposition; oxidation; PM Zn.

Introduction•

The efficient use of green energy is important, given the rapid depletion of fossil energy resources such as coal, oil and natural gas. Human activities, rapid economic growth and industrial development require this transition. In addition, the use of fossil energy resources as a long-term energy solution has had negative effects on the environment, mainly due to emissions of greenhouse gases and other harmful substances [1].

Carbon, O_2, hydrazine (N_2H_4/O_2), oxygen (H_2/O_2) and methane (CH_4/O_2) are just some elements used in fuel cells. A fuel cell is a device similar to a battery, which is constantly being recharged as it produces electrical energy through a low-temperature electrochemical reaction with oxygen and hydrogen. Unlike batteries, fuel cells produce energy continuously, as long as there is a continuous supply of fuel and oxygen, their main purpose being energy storage. They use an internal or external hydrogen-rich fuel reforming process [2]. The classic

•The abbreviations list is in page 320.

definition of a fuel cell is an electrochemical device capable of continuously converting chemical energy of fuel and oxidant into electrical power, using a fundamentally constant electrode-electrolyte combination [3]. Research is currently focusing on hydrogen fuel cells. Technologies are being developed to reduce the cost of expensive materials. Catalytic layers extend the life of components in fuel cell's membrane-electrode assembly. These studies are very much focused on creating procedures. Low-cost and high-volume manufacturing is also important to make fuel cell systems affordable, making them competitive with conventional technologies. In addition, effective temperature management inside the fuel cell contributes to this improvement, and it also reduces costs [4].
Fuel cell is a promising technology that generates power by directly converting chemical energy of fuel into electricity through electrochemical reactions. It is a practical application that promises a better and cleaner alternative energy source. There are several types of fuel cells, which can be characterized according to their materials, configuration, electrolytes and operating temperatures.
However, from the point of view of real applications, transients generated at the anode begin to considerably degrade the fuel cell system performance [5-6].
Fuel cells presently use CH_3OH as energy, which is flammable, easily volatile and non-renewable [7].
The first fuel cells used hydrogen as energy. Hydrogen is currently the only practical element used in the current generation of fuel cells, due to its high electrochemical reactivity compared with most common fuels from which it is derived, such as hydrocarbons [8]. There are several applications for fuel cells: laptops, mobile phones and fixed or mobile appliances [9].

Experiment

All chemicals were used without further purification, and tested for analytical purity. Solutions were prepared from doubly distilled water. CH_3OH, purchased from Sigma-Aldrich (USA), had a purity of 97%. Commercial graphite powder was supplied by Carbone (reference 9900), in Lorraine, France. Electrochemical measurements were carried out using a Voltalab potentiostat (model PGSTAT 100, produced by Ecochemie BV in Utrecht, Netherlands) via Voltalab Master 4 electrochemical system software.
The electrochemical cell was designed to operate with three working electrode,s using Zn/CPE. A saturated calomel electrode and a Pt backplate were used as reference electrodes. CPE were made by mixing paraffin oil and high-purity carbon graphite powder. CPE compound was then introduced into the electrode cavity. The electrical connection was provided by a carbon rod. *Escherichia coli* was the bacteria used in this work.

Results and discussion

Morphologic characterization of CPE and CPE/Zn

Fig. 1 shows the surface morphology of two different electrodes, CPE and CPE/Zn, prior to electrochemical measurements. The first image shows the morphology of a CPE, while the second shows the surface of a Zn metal-modified CPE, forming a well-connected Zn flower.

CPE **CPE/Zn**

Figure 1: Optical surface image of CPE and CPE/Zn.

Fig. 2 shows surface morphology of CPE/Zn and CPE/Zn/PM. The electrode surface is composed of a Zn-modified CPE in the shape of a well-connected flower. CPE/Zn/PM surface has a transparent layer, which is almost solid, due to its high viscosity. When force is applied, this surface can easily be destroyed or stained.

CPE/Zn **CPE/Zn/PM**

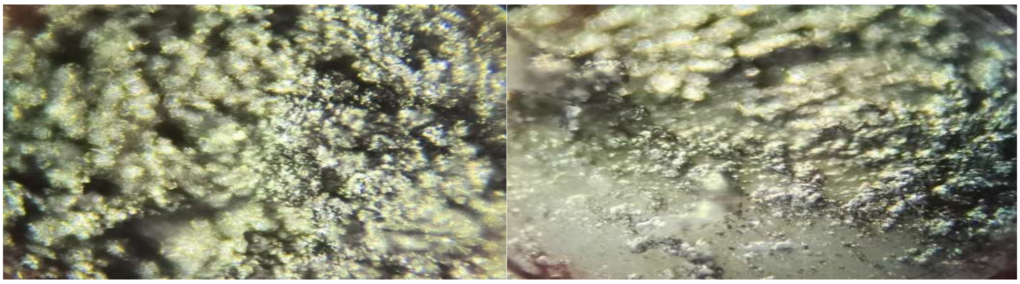
Figure 2: Optical surface image of CPE/Zn and CPE/Zn/PM.

Fig. 3 shows a comparison between the surface morphology of CPE/Zn/PM and CPE/Zn/PM/bacteria. In this context, the polymer played an essential role in protecting Zn against corrosion, thereby extending its life. The bacteria also helped to regenerate the electrode surface.

CPE/Zn/PM **CPE/Zn/PM/bacteria**

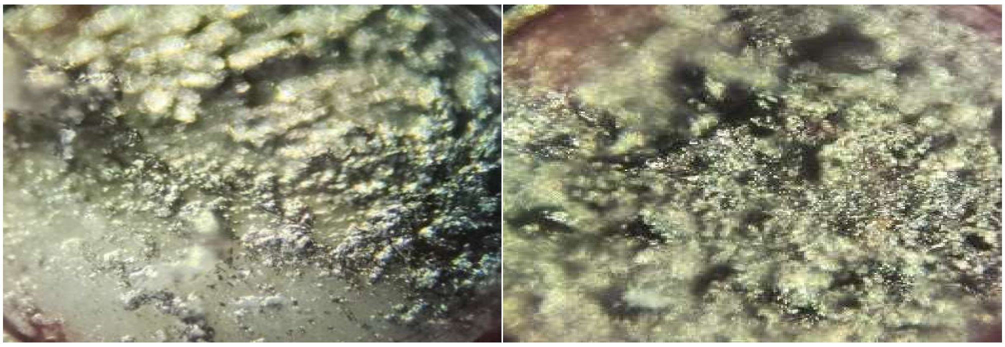
Figure 3: Optical surface image of CPE/Zn/PM and CPE/Zn/PM/bacteria.

Morphology analysis of CPE, CH_3OH, CPE/Zn/CH_3OH and CPE/Zn/PM/CH_3OH surfaces was carried out using an optical microscope after electrochemical measurements. Figs. 4 and 5 shows the extent of changes in surface morphology.



CPE/CH_3OH **CPE/Zn/CH_3OH**

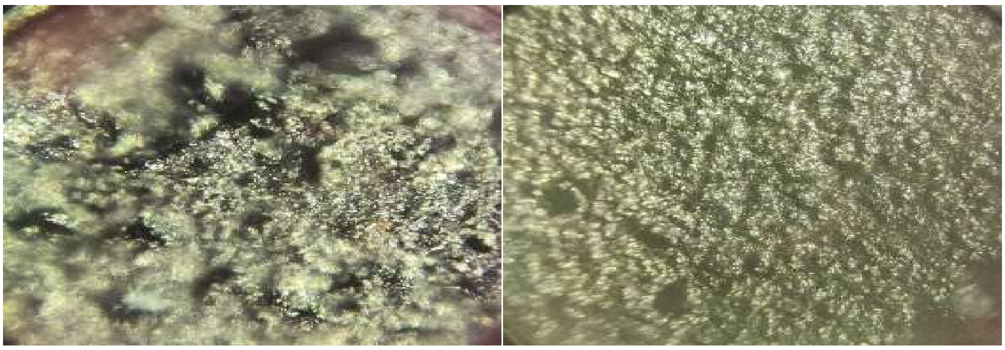
Figure 4: Optical surface image of CPE/CH_3OH and CPE/Zn/CH_3OH.



CPE/Zn/CH_3OH **CPE/Zn/PM/CH_3OH**

Figure 5: Optical image of CPE/Zn/ CH_3OH and CPE/Zn/PM/CH_3OH.

Fig. 6 shows the surface morphology of CPE/Zn/CH_3OH, which has a porous structure, allowing better adsorption of reactive species. CPE/Zn/PM and CH_3OH have an inhomogeneous film.



CPE/Zn/PM/ CH_3OH **CPE/Zn/PM/bacteria/ CH_3OH**

Figure 6: Optical image CPE/Zn/PM/CH_3OH and CPE/Zn/PM/bacteria/CH_3OH.

Fig. 7 shows the surface morphology of CPE/Zn riveted by polymer after CH_3OH reaction and CPE/Zn/PM/bacteria after CH_3OH reaction. The polymer formed a protective layer or coating around the Zn particles and carbonaceous material, allowing for a more uniform and stable surface morphology. Bacteria, played a role in transferring electrons to the electrodes and in forming biofilms to promote electrochemical reactions.

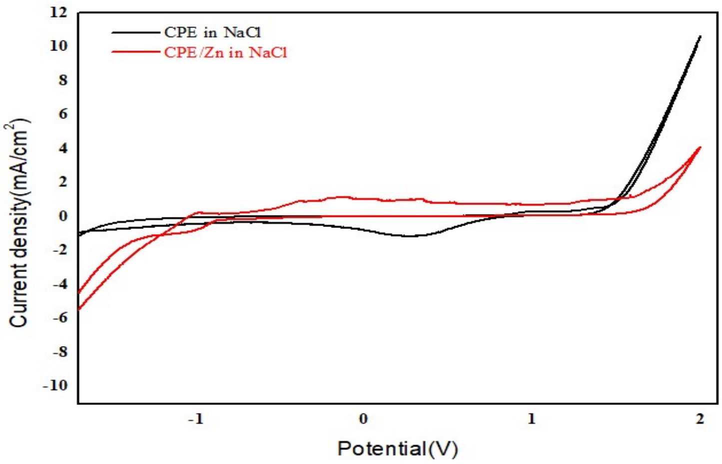


Figure 7: CV on CPE and Zn/CPE, in a 1 M NaCl solution, at 50 mV/s.

The following CV (Fig. 8) were recorded on two electrodes: CPE and CPE/Zn in an electrolytic medium containing a NaCl solution.

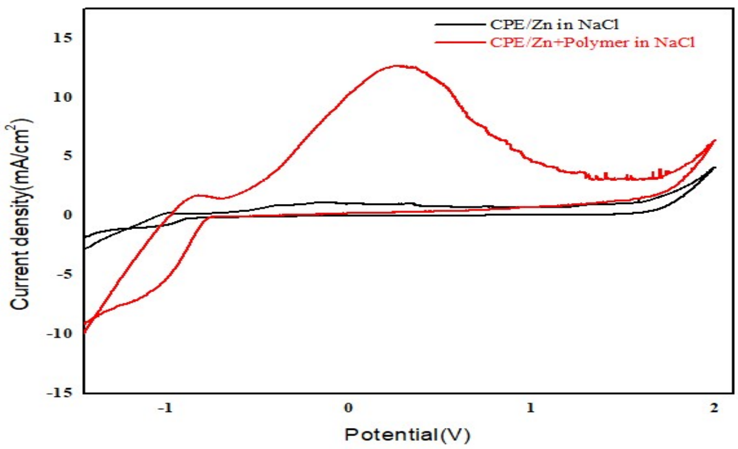


Figure 8: CV on Zn/CPE and Zn/CPE/PM electrode, in a 1 M NaCl solution.

The following CV (Fig. 9) was recorded on Zn-modified CPE (CPE/Zn) and Zn-modified CPE/PM, in an electrolytic medium containing a NaCl solution. The CV for CPE/Zn shows a well-defined cycle attributed to polymer oxidation, while CPE/Zn/PM CV shows a distinct peak in the anodic sweep direction, at about 0.3 V. It can be concluded that the polymer played an essential role in protecting Zn from corrosion, thereby extending its life. The bacteria also help to regenerate the electrode surface. The polymer acted as an electron-conducting matrix, promoting electrochemical reactions between Zn, PM and the bacteria.

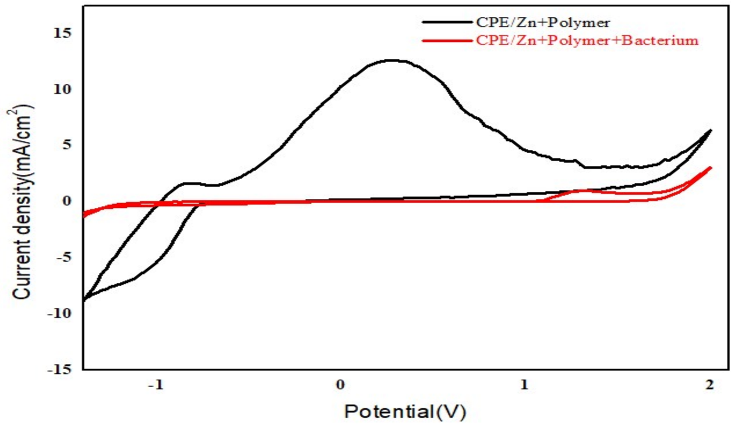


Figure 9: CV on Zn/CPE/PM electrode and Zn/CPE/PM/bacteria electrode, in a 1 M NaCl solution, at 50 mV/s.

These two CV (Fig. 10) were recorded on CPE/Zn/PM and CPE/Zn/PM/bacteria, in an electrolytic medium consisting of a NaCl solution. The bacteria addition causes a peak to disappear. This phenomenon can be interpreted as the formation of bacterial biofilms on the electrodes surfaces, which can modify the electrode surface's properties and influence chemical reactions that take place in there.

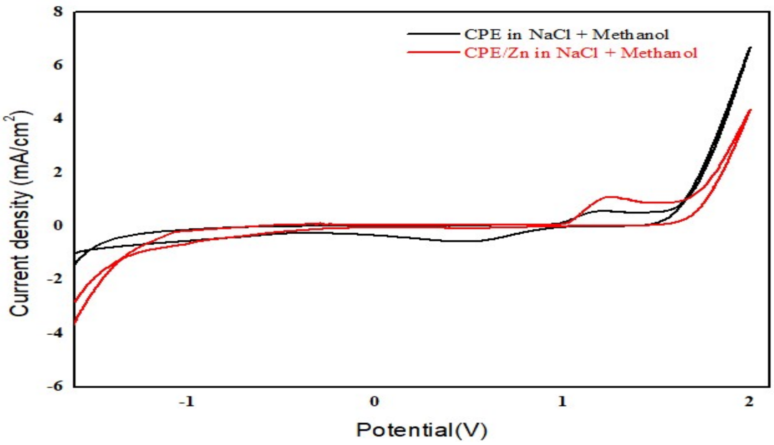


Figure 10: CV on CPE/CH_3OH and CPE/Zn/CH_3OH, in 1 M NaCl, at 50 mV/s.

These two CV were recorded on CPE and CPE/Zn in an electrolyte solution containing NaCl and CH_3OH. In the presence of CH_3OH, the CV recorded on CPE/Zn shows a peak in the anodic sweep direction, at around 1.2 V, corresponding to CH_3OH oxidation. The absence of a reduction peak in the cathodic sweep direction is characteristic of CH_3OH irreversible oxidation, which appeared, on CPE, in the form of two redox peaks: one in the anodic sweep direction at around 1.2 V, and the other at 0.8 V.

The polymer presence on the CPE/Zn surface made no difference in CH_3OH oxidation, since its peak was always present. The peaks observed around -1 V were attributed to the polymer reversible oxidation (Fig. 11).

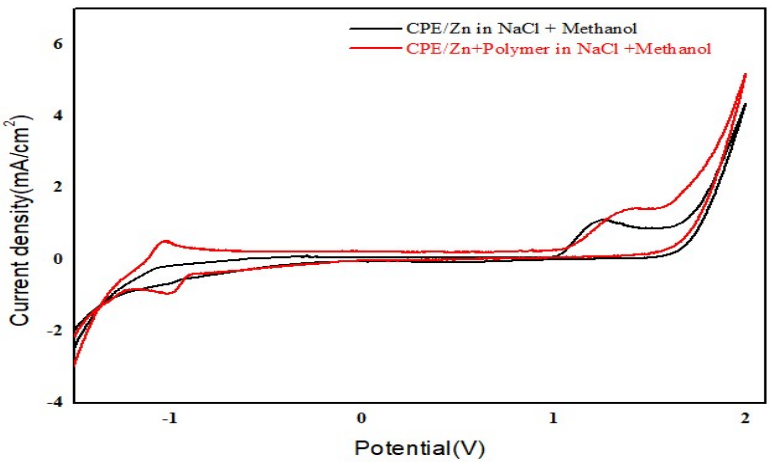


Figure 11: CV on CPE/Zn/CH_3OH and CPE/Zn/PM/CH_3OH, in a 1 M NaCl solution, at 50 mV/s.

In the presence of bacteria, the CV shows a well-defined CH_3OH oxidation peak, at around 1.2 V. Redox peaks (-1 V) attributed to polymer redox probably disappeared due to the formation of a biofilm on the electrode surface, which blocked redox sites (Fig. 12).

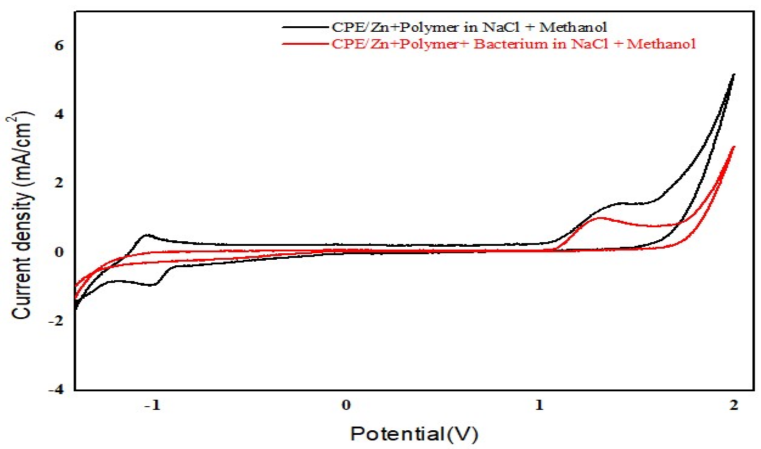


Figure 12: CV on CPE/Zn/PM in NaCl/CH_3OH and CPE/Zn/PM/bacteria/CH_3OH, in a 1 M NaCl solution, at 50 mV/s.

Conclusion

This work shows the importance of various fuel cells, which are devices that produce energy from electrochemical reactions. This fuel cell technology has valuable applications in the field of sustainable energy. One can say that, in the years to come, the evolution of fuel cells could constitute a second generation of energy.

Current research into electrochemistry, and fuel cells in particular, is paving the way for a cleaner, more efficient energy transition. Among the benefits of the energy generated by fuel cells is a significant reduction in greenhouse gases that are harmful to the planet. Fuel cells can be used in vehicles. For example, hydrogen-powered cars help to combat climate change by reducing air pollution.

Authors' contributions

M. Oukbab: conceptualization; experimental investigation; data analysis; original draft preparation, and writing; review and editing. **S. Loughmari**: conceptualization. **Y. Tahiri**: experimental investigation. **H. Haddouchy**: experimental investigation**. M. Oubaouz**: conceptualization. **S. Zahid**: conceptualization. **S. E. El Qouatli**: data analysis. **A. EL Bouadili**: conceptualization. **M. Visseux**: conceptualization. **A. Chtaini:** conceptualization; methodology; original draft preparation and writing; review and editing; supervision.

Abbreviations

C: carbon
CH_3OH: methanol
CPE: carbon paste electrode
CV: cyclic voltammogram
NaCl: sodium chloride
PM: 1,4-cis polymyrcene
Redox: reduction and oxidation reactions
Zn: zinc

References

1. Höök M, Tang X. Depletion of fossil fuels and anthropogenic climate change- A review. Ener Pol. 2013;52:797-809. https://doi.org/10.1016/j.enpol.2012.10.046
2. Kabeyi MJB, Olanrewaju O. Fuel Cells Design, Operations and Applications. IEOM Society International. Proceedings of the 5th African International Conference on Industrial Engineering and Operations Management, Lusaka, Zambia. 2023:4-6. http://doi.org/10.46254/AP04.20230270
3. Kordesch K, Simader G. Fuel Cells and their applications. 2006. ISBN: 978-3-527-60653-5
4. U.S. Department of Energy. Energy efficiency and renewable energies. https://www.energy.gov/sites/prod/files/2015/11/f27/fcto_fuel_cells_fact_sheet.pdf
5. Hu L, Hong BK, Oh JG et al. Robust Operation of Fuel Cell Systems in Subfreezing Conditions: A Material-Based Solution to Achieve Better Anode Durability. ACS Appl Ener Mater. 2019;2:7152. https://doi.org/10.1021/acsaem.9b01108
6. Yamashita Y, Itami S, Takano J et al. Degradation Mechanisms of Carbon Supports under Hydrogen Passivation Startup and Shutdown Process for PEFCs. J Electrochem Soc. 2017;164:F181. http://doi.org/10.1149/2.0101704jes

7. Wang T, Chutia A, Brett DJL, Shearing PR, He G, Chai G, Parkin IP. Palladium alloys used as electrocatalysts for the oxygen reduction reaction. Energy Environ Sci. 2021;14:2639-2669. http://doi.org/10.1039/D0EE03915B
8. Dehbi S, Massai H, Chtaini A. Phosphate-modified copper electrodes for methanol fuel cells. Port Electrochim Acta. 2010;28(4):241-252. http://doi.org/10.4152/pea.201004241
9. Najih R, Dehbi S, Chtaini A et al. Natural phosphate-modified iron electrodes for glucose fuel cell anodes. Res Rev Electrochem. 2012;3(3):115-121.