

Power generation by means of a prototype microcell using bioethanol as fuel and clinoptilolite-type zeolite

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Abstract: Currently, technological alternatives are being sought for the substitution of fossil fuels for different reasons. One of the most relevant is the protection of the environment, to have an improvement in this aspect, the generation of energy through clean sources is sought. The PEMFC (Proton Exchange Membrane Fuel Cell) type fuel cells are an excellent alternative for the generation of clean energy because the residues of the fuel cell are mainly water and heat. In the present work, clinoptilolite zeolite was used to produce clean energy by a fuel cell using bioethanol as fuel. Zeolite showed promising results when used in combination with carbon and hydrogel as a solid electrolyte. The material was characterized by scanning electron microscopy and x-ray electron microscopy. The result showed a maximum power of 0.00589241 mW in a surface of 900 mm², which is considered a positive result. The catalyst is functional to produce energy by an electrooxidation reaction using bioethanol in a fuel cell at a low cost compared to traditionally platinum-based catalysts.

Keywords: Bioethanol; renewable; fuel cell; electroreaction.

Introduction

Today we are looking for an alternative to fossil fuels for different reasons, one of the most relevant is the protection of the environment, to have an improvement in this aspect, the generation of energy through clean sources is sought.

Fuel cell type PEMFC (Proton Exchange Membrane Fuel Cell) is an excellent alternative for clean energy generation because the waste from the fuel cell is mainly water and heat. Although the PEMFC-type fuel cell represents a solution to global pollution, there is always a persistent drawback, which is the high cost, because the Nafion membrane is a high-cost inorganic compound that must be previously treated to be used in any fuel cell. In addition, the platinum-based catalysts used have a high cost in the market- (Hou *et al.*, 2019).

Nowadays, the development of fuel cells has focused on the automotive industry because they allow the reduction of pollutants emitted into the environment. One of the possibilities for the decrease in fuel cell costs is the investigation of new materials in the MEA (membrane-electrode assembly) as well as in sustainable and economic catalysts that make said reduction possible. One of the most studied fuels in fuel cells is hydrogen, however, ethanol as fuel allows us to reduce costs and risks due to the easy handling of this both in its production and storage.

Zeolites become an excellent candidate for a wide range of applications such as adsorbents and ion exchange, also zeolites have been the subject of research as catalysts and molecular sieves. This is due the uniform zeolitic arrangements that make them have unique characteristics such as high thermal stability, mechanical stability, high specific surface area, tunable acidity, shape selectivity, and corrosion resistance. (Limlamthong & Yip, 2019). Among the 40 natural zeolites, according to the Structures Commission of the International Zeolite Association, clinoptilolite (HEU) stands out, along with other zeolites, for its accessibility, availability, low cost, quantity, and purity (Ackley *et al.*, 2003). This zeolite is the most common species around the world and is present in various sedimentary deposits in Mexico (Krushensky *et al.*, 1987).

Clinoptilolite is an inert and non-toxic material that can be used in agrochemical, pharmaceutically, and biochemically industries because it has very good for sorption and ion exchange. It also is used for the absorption of some contaminants such as dioxide of carbon and additive to animal feed (M. Reháková *et al.*, 2004).

In this work, the design and manufacture of a direct ethanol fuel cell that uses bioethanol as fuel will be developed, as well as an economic catalyst with a good capacity to carry out electrooxidation and electroreduction reactions for its future use in mobile devices.

Materials and Methods

The materials that were used in the present work were: clinoptilolite-type zeolite, from Atzinco, Puebla, Mexico, H₂O₂ (J.T. Baker, 30%), lignite carbon and hydrogel as reagents, as well as Nafion 115 (DuPont) membrane as a solid electrolyte, bioethanol (obtained by residual biomass, 89%). Solidworks as design software.

Chemical characterization

The zeolite was chemically identified by X-ray in a diffractometer BRUKER D8 DISCOVER, furthermore, the morphology and composition were determined by Scanning Electron Microscopy (SEM) in a JEOL JSM-6610LV electron microscope.

Physical treatment of the zeolite

The zeolite was ground in a mortar and then sifted through a sieve or physical test sieve of the MONT-INOX brand, with mesh numbers 60 (opening 0.0098 inches) and 80 (opening 0.0070 inches).

Activation and purification of Nafion 115 membrane

This process is necessary for the removal of organic and inorganic contaminants as well as the hydration of the membrane for its proper functioning. The Nafion 115 membrane was purified as follows, subjected to a 3% H₂O₂ solution at 85°C for 30 minutes. Once this purification is done, the membrane is washed with deionized water at 100°C for 30 minutes, this step is repeated twice; subsequently, it is activated with a protonation for 1 hour in 0.5 M sulfuric acid at 85°C. To finish, the membrane is left to rest for 48 hours in H₂SO₄ 1M to ensure adequate protonation and good performance. Subsequently, the membranes are stored in deionized water until they are used in the fuel cell.

Catalyst Preparation

Intense research efforts have been made to get a low-cost catalyst layer on the market for fuel cell applications, in the last 10 years including metal alloys, shell-core nanostructured catalysts, and carbon catalysts with non-precious metals-(Deng *et al.*, 2020). The catalyst was prepared by a mechanical mixture in a 1:1:3 ratio of zeolite, lignite carbon, and hydrogel under ultrasound for 10 min at 25°C to favor the homogenization of the mixture, this catalyst was used for the anode and cathode in the fuel cell that was designed.

Cell Design

The microcell design consists of two protective plates, one for the cathode and the other one for the anode. For the cathode, a square of 30 mm x 30 mm, with an open part for oxygen exposure of 20 mm x 20 mm and an extraction on the left side of 15 mm x 5 mm was used. This extraction is done with the intention that the plate protrudes to have connection points when electrical load is obtained in the fuel cell. The space of the plate has a depth cut of 1mm; for the anode, the protective plate is 4.00 mm and the internal thickness for the location of the electricity collector plates is 1 mm. In addition to two brass electrodes through which the current would flow, the fuel cell designed in SolidWorks software is shown in Figure 1.

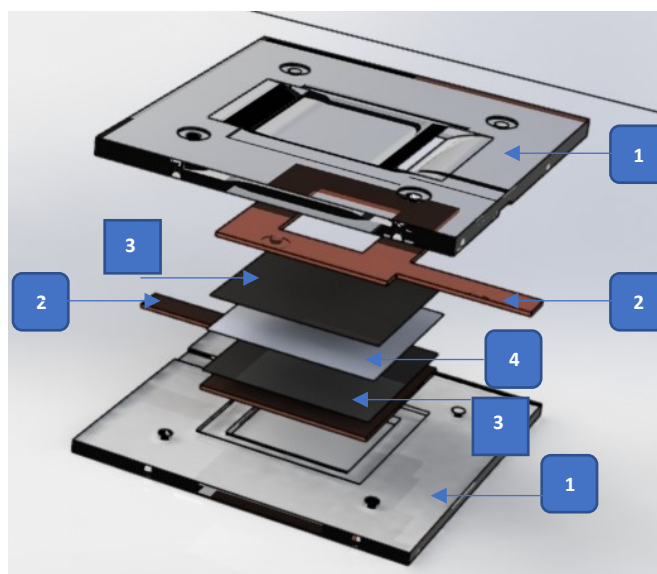


Figure 1. Visualization of the built fuel cell (1. Protective plates; 2. Brass electrode 3. Collector plates, 4. Nafion membrane).

Cell Preparation

For our electrochemical tests, the Keithley model 2450 equipment was used, one of its main characteristics is the measurement of the I-V characteristics of any device.

For the preparation of the cell, a uniform amount of hydrogel was placed on the brass plates with a mixture of the solid catalyst, then the previously activated Nafion 115 membrane was placed, which in this case would be used for the separation of the hydrogel layer. Since the amount of hydrogel in the anode and cathode should not be mixed because the mixture would damage the reaction, once the Nafion membrane was placed, another mass of hydrogel was placed with the catalyst mixture, to seal the cell were used four screws and bioethanol was injected into the anode part; in the cathode part atmospheric air was used to complete the reaction, with which it would begin to give voltage and current. Figure 2 shows the prototype microcell prepared to be tested.

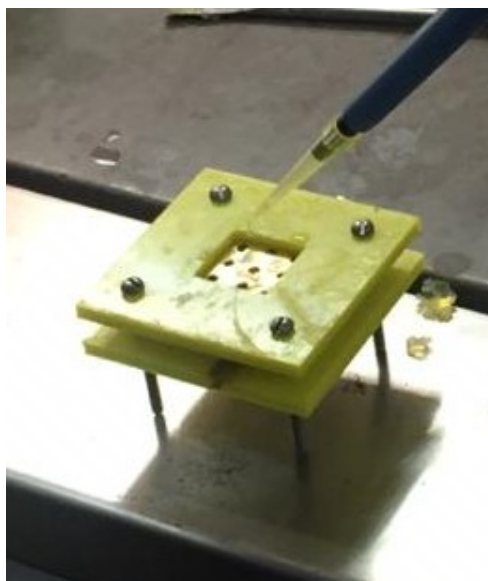


Figure 2. Prototype of microcell

Results and Discussion

X-ray diffraction (XRD)

The XRD tests were carried out in an X-ray diffractometer: BRUKER D8 DISCOVER, the Figure 3 shows the X-ray diffraction patterns that were obtained from the clinoptilolite zeolite samples- (Treacy & Higgins, 2007).

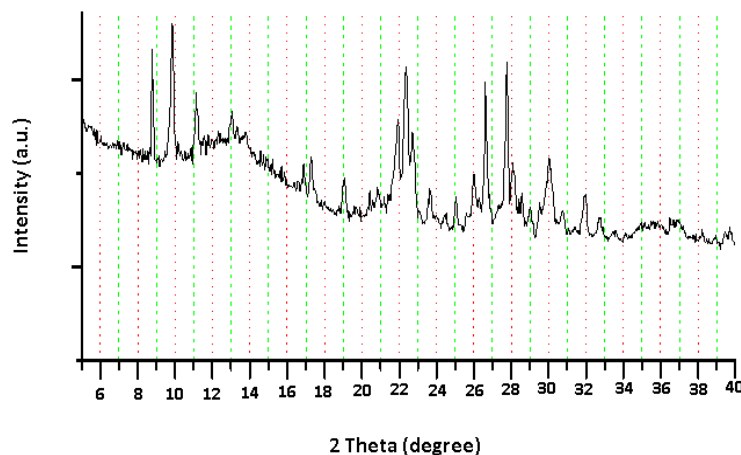


Figure 3. X-ray * diffraction patterns of the samples Clinoptilolite Zeolite

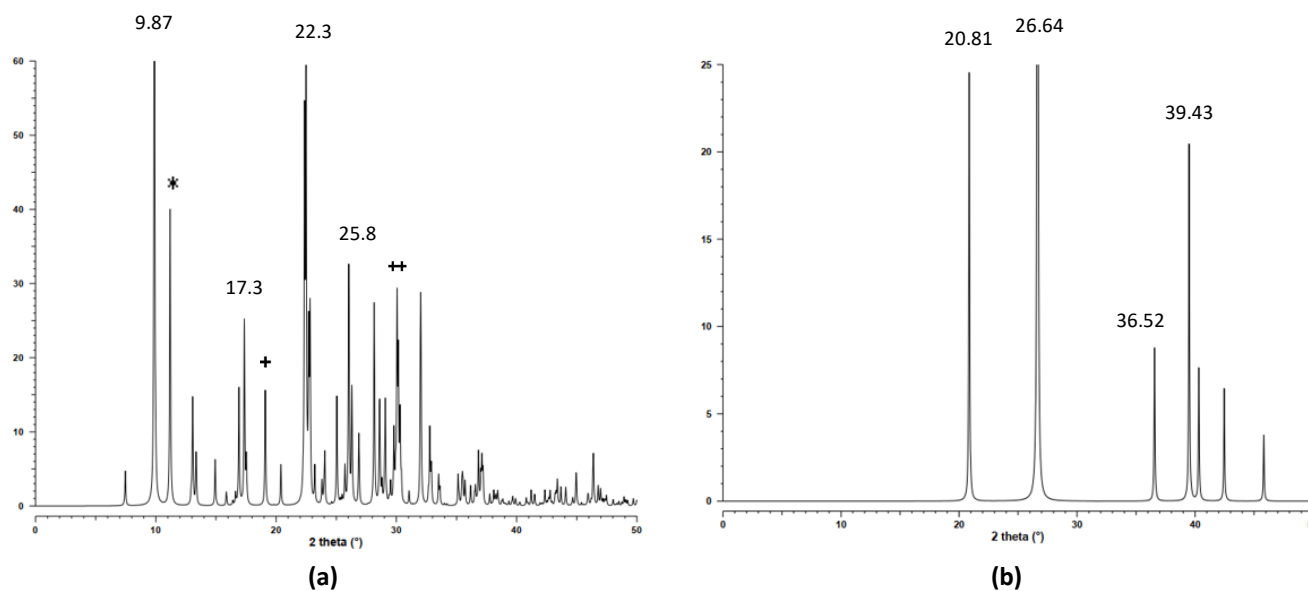


Figure 4. Diffraction pattern a) clinoptilolite, b) quartz (Treacy & Higgins, 2007).

In the X-ray diffraction patterns of the sample (Figure 3), the crystalline phases were observed. This analysis allowed to determine that this zeolite corresponds mainly to the clinoptilolite type of card JCPDS 04-013-6126 and quartz from card JCPDS 3-0427 (Figure 4). The signs shown by the material in 2θ are 7.44° , 9.875° , $^* 11.149^\circ$, 13.047° , 14.902° , 16.907° , 17.306° , $^+ 19.071^\circ$, 20.399° , 22.342° , 22.754° , 23.986° , 25.035° , $25.035^\circ 2^\circ$, 26.865° , 28.127° , 28.587° , 29.024° , $^{++} 30.054^\circ$, 31.995° , 32.778° , 33.575° , 35.496° , 36.116° , 36.527° , 36.853° , and 37.089° , all corresponding to the clinoptilolite zeolite, quartz signal in 2θ was at 26.644° . Both correspond to what was reported by Treacy and Higgins (2007). The diffractograms show an acute shape in the signals, indicating crystallinity in the zeolite.

Scanning Electron Microscopy (SEM)

SEM technique was performed in a JEOL JSM-6610LV electron microscope. The morphology and composition of the zeolite clinoptilolite particles can be seen in Figure 5, the presence of crystals of different shapes and sizes is observed. Images from clinoptilolite samples were obtained in different magnifications

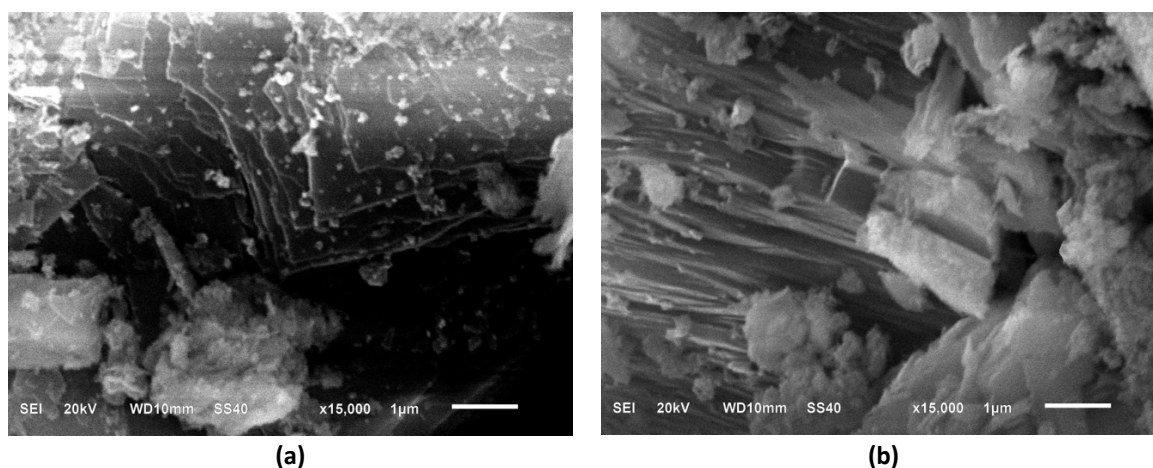


Figure 5. Scanning electron microscopy (SEM) of the AT-NAT sample with a magnification of: a) 15000x and b) 15000x.

Energy Dispersive Spectrometry (EDS)

The EDS analysis was performed in a JEOL JSM-6610LV electron microscope. With this technique, it was possible to determine the chemical composition of the zeolite. The chemical composition of the zeolite was obtained (Table 1). The Si/Al ratio of the samples presented a value above the literature, which is 5.5 for clinoptilolite-type zeolite (Tsitsishvili *et al.*, 1992). We can see the amount of percentage of cations such as magnesium (Mg), potassium (K), and calcium (Ca) with a minimum decrease present in the structure of the zeolite, and in turn, an increase in the percentage of silicon (Si) and (Fe). Tsitsishvili *et al.*, (1992). Figure 6 shows an imagen of the EDS analysis.

Table 1. Chemical composition for the zeolite sample (weight %).

Sample	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	Si/Al
Clinoptilolite	4.41	18.2	63.7	5.83	2.24	2.71	6.16

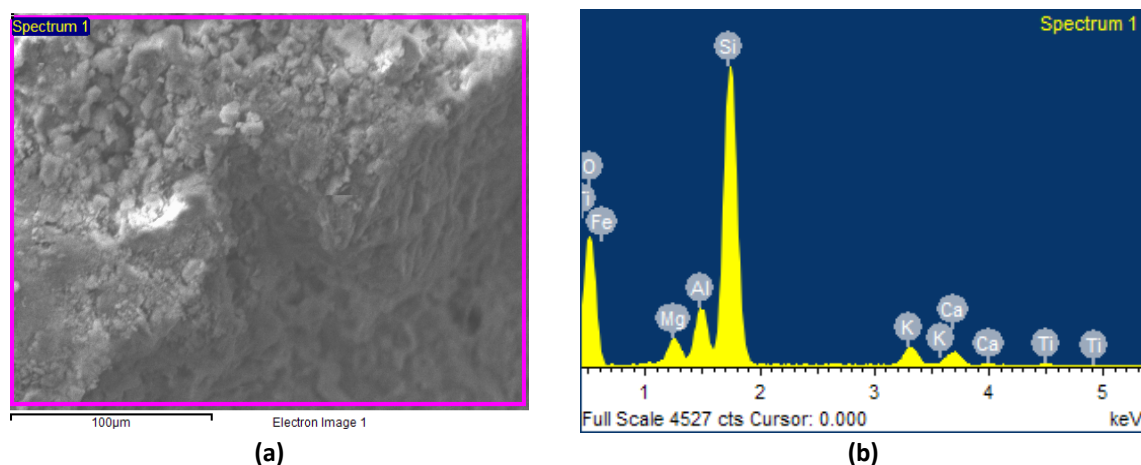
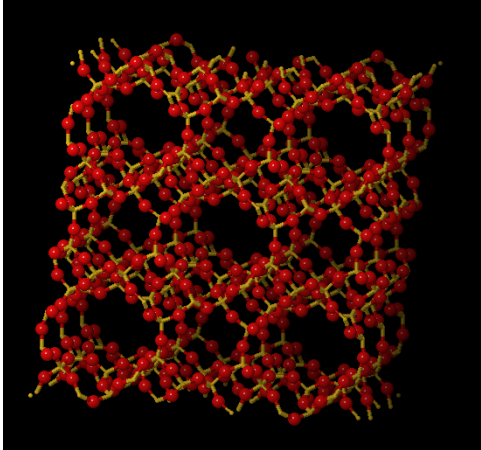


Figure 6. Example analysis: a) Electron image of clinoptilolite, b) EDS spectrum of clinoptilolite

Its structure consists of an outer framework of silica and alumina tetrahedrons, within which water molecules and exchangeable cations (for example, calcium, potassium, sodium) freely migrate, as shown in Table 2, where the 3d chemical structure and its molecular formula.

Table 2. Formula and chemical structure of clinoptilolite zeolite

Molecular	Chemical Structure
$(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72}H_2O$	

(Back et al., 2013)

Test in Cell

The maximum power provided by the cell is 0.005892 mW in 900 mm² as can be seen in Figure 7. This is considered a positive result. The clinoptilolite catalyst was used because it showed greater power, this is attributed to a greater amount of Fe in its structure, this curve will be able to predict how the cell will behave over a period of time because in the cell test, the resistance was varied in order to accelerate the fuel cell discharge process, that is, if a constant load was maintained for a period of time, we would have similar results.

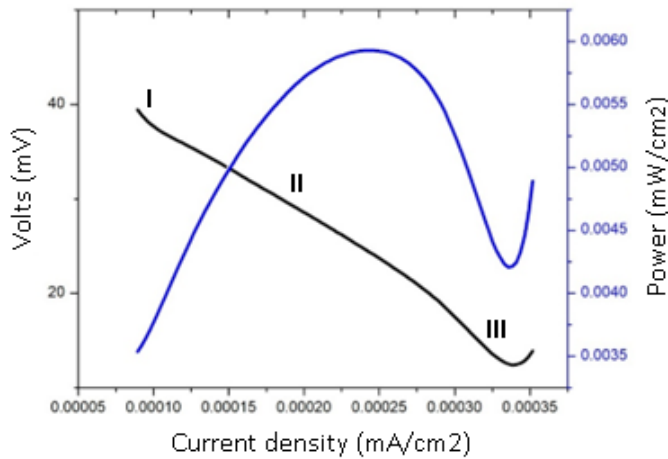
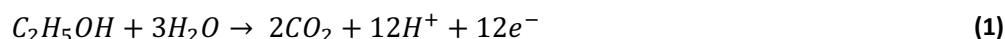


Figure 7. Graph Voltage, Current and Power

With this graph, we can affirm that our fuel cell is functional because it has a typical behavior of a fuel cell; shown a drop in potential is observed mainly due to three sources: I) polarization by activation, II) ohmic polarization, and III) polarization by concentration. Zone I is found at high potentials and low current density and is determined by cathode activation; zone II is characterized by the resistance of the materials and is what determines the shape of the graph; Zone III is observed at high densities and is determined by the concentration and transport of reagents.

In addition to the fact that the clinoptilolite-type zeolite catalyst used is efficient and allows obtaining electrical energy through the cell without using platinum-based catalysts which are expensive and quickly deactivate. The activity of the catalyst for the production of electrical energy through the micro-cell, using bioethanol as fuel, is attributed to the diversity of ions present in the zeolite such as: Ca, Mg, Al, Si, K, Fe; which some of them acting as co-supports and others as an active phase, allowing the oxidation of bioethanol in the anode and the reduction of oxygen in the cathode, according to the reactions proposed by Pethaiah *et al* (2016):

Anode



Cathode



Reaction 1 is carried out at the anode where the bioethanol dissolved in water reacts with the catalyst to generate CO₂, protons and electrons, the protons cross the Nafion membrane to reach the cathode and the electrons travel through the circuit to reach the cathode. The reduction of oxygen from air takes place in the cathode (Reaction 2). The reaction also involves protons and electrons that migrated from the anode to form water. Various microcells can be connected in series or parallel to achieve the desired voltage and current for real application. (Guerrero-Lemus & Martínez-Duart, 2013).

Conclusions

In this work, a prototype of a functional fuel cell was obtained with a significant reduction in size using materials that are easy to assemble and economically viable, in addition, the clinoptilolite zeolite proved to be functional for the electrooxidation and electroreduction reactions in the same cell, allowing the production of electrical energy using bioethanol as fuel. It is suggested to continue working with the zeolite to increase the efficiency of the reactions.

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Author contributions: J.D.B.-R.: cell design and development; M.A.T.-R.: characterization of clinoptilolite; N. E.-T.: test in cell; N.T.-M., L.A.P.-S. and J. C.-P-: redaction, editing, provide materials and interpretation of data.
E. F: Analysis of data.

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