



Article New Application of Polyoxometalate Salts as Cathode Materials in Single Chamber MFC Using Wastewater for Bioenergy Production

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Abstract: Microbial fuel cells (MFCs) are a promising technology that can be applied in a bifunctional process in which wastewater treatment is used for renewable electric power generation. In this study, novel transition metal-modified Keggin-type lacunar polyoxometalate salts (L-POMs) $Cs_5PMo_{11}M(H_2O)O_{39}$ (M = Fe, Co), were synthesized and characterized by X-ray diffraction, SEM, EDX, IR, TGA/DSC, and UV-Vis/DSR spectroscopies to be tested, for the first time, as a cathode component in wastewater-fed air chamber MFCs. Both materials were tested in the presence and absence of light to evaluate their photocatalytic behavior. The best performance in terms of electricity production was obtained for the MFC containing the Co-modified POM-based cathode, which showed a maximum power of 418.15 mW/m² equivalent to 331 mW per cubic meter of treated wastewater, and a maximum COD removal percentage of 97% after 96 h of MFC operation. Co- and Fe-modified POMs had outstanding optical behavior with lower energy gap values, 1.71 and 2.68 eV, respectively. The newly developed materials can be considered as promising alternative cathode catalysts in a new generation of MFC devices integrating full carbon removal from wastewater and a fast reduction of oxygen.

Keywords: Keggin polyoxometalate salt; cobalt; microbial fuel cell; electrocatalyst; photocathode; energy production; wastewater treatment

1. Introduction

In the context of exponential world population growth, the depletion of energy resources and the search for sustainable development, today's society is faced with two major challenges: (i) water availability and (ii) energy production. To meet these challenges, there is an urgent need for all types of water, including wastewater, as well as the search for new and renewable sources of energy. Much of the scientific effort is directed at these two major challenges, and in recent years microbial fuel cell technology has gained great importance with the intention of addressing these challenges at the same time.

Microbial fuel cell (MFC) technology uses microorganisms to transform chemical energy of organic compounds into electricity [1,2]. Carbon sources contained in domestic or industrial waste can be used as chemical energy carriers to convert into biopower. The chemical energy is provided by the oxidation of carbon contained in the organic matter; the electrons released in this process are transferred to a terminal electron acceptor to produce an electric current. A typical MFC contains anode and cathode compartments separated



Citation: Lachquer, F.; Touach, N.-e.; Benzaouak, A.; Oulmekki, A.; Lotfi, E.M.; El Mahi, M.; Hernández-Fernández, F.J.; Toyir, J. New Application of Polyoxometalate Salts as Cathode Materials in Single Chamber MFC Using Wastewater for Bioenergy Production. *Processes* **2023**, *11*, 836. https://doi.org/10.3390/ pr11030836

Academic Editor: Maria Jose Martin de Vidales

Received: 26 January 2023 Revised: 7 March 2023 Accepted: 8 March 2023 Published: 10 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). by a cationic membrane (selective to protons). In the anode, organic matter serves as an electron donor after the oxidation bioprocess and, in the cathode, there is an electron acceptor species which is submitted to a reduction process which takes place on the surface of the cathodic material. Oxygen is widely used for this purpose due to its practical use and high oxidative potential. Other electron acceptors (e.g., nitrates, persulfates, etc.) can be used in case the reduction in their concentration is of interest, for example when they act as pollutants [3]. The composition of each cell component: anode, cathode, and membrane, are one of the key parameters to ensure a proper performance of the MFC device. In this study, we focused on the development of a cathode component that works with oxygen from the air as an electron acceptor in an MFC process using domestic wastewater from the region of Rabat (Morocco). To accelerate the reduction in oxygen on the surface of the cathode, platinum is often used as a cathodic component due to its high catalytic properties [4–6]. However, the use of such expensive and not easily accessible metal is difficult for a sustainable implementation of a fuel cell-based technology such as MFC. Hence, the focus of researchers is directed towards replacing platinum for a low-cost alternative catalyst.

The efficiency of MFC devices is directly affected by several parameters, including the performance of the cathode and thus, the materials used to make it [7,8]. Several researchers have tested many materials as cathode catalysts for the oxygen reduction reaction, among the works that have already been reported is that of L. Birry et al. [9] who studied ironbased catalysts; and the team of Touach et al., who tested ZrP_2O_7 [10], LiNbO₃ [11], and MnO_2 [12]. Benzaouak et al. succeeded in reducing COD loading by 79% using a solid solution of mixed oxides of LiTaO₃ with WO₃ [13]. Liu et al. developed high performance fuel cells catalyzed solely by a polyoxometalate (POM) solution, with not solid metal or metal oxide [14]. In another study, Zhao and Zhu [15] developed a biomass fuel cell using polyoxometalates (POMs) to directly convert lignin into electricity. The use of H₃PMo₁₂O₄₀, as a cathode catalyst, was found to increase the power density, making the cells promising as a stable electrochemical energy source. In addition, X. Zhao et al. [16] developed a new process to generate electricity from cellulose using an polyoxometalate and ferric ions as electron mediators and proton carriers.

It is worth nothing that the polyoxometalate compounds (POMs) are widely studied due to their specific properties such as superacidity, redox behavior, and thermal stability. Hence, there is growing interest in these flexible structures to develop protocols to tune the properties of these polyoxometalate supramolecular clusters towards various applications in several fields such as biotechnology, nanotechnology, solar cells, medicine, electrochemistry, and catalysis [17–23]. POMs are defined as a family of metal-oxygen molecular clusters [24]. Compared with other inorganic clusters, POMs offer great structural and compositional diversity. The most popular POMs are those with a Keggin structure, with general formula $[XM_{12}O_{40}]^{n-}$, where X is a heteroelement (X = Si, P, S, Ge, As, etc.) which is the assembling atom and located in a tetrahedral of oxygen atoms in the center of the metallic oxocluster formed by octahedra (MO₆/M = V, Nb, Ta, Mo, and W) [25].

Several studies have already been developed to investigate the structure and properties of these materials. For example, in recent studies, El Arrouji et al. revealed an interesting electrochemical property for modified POMs salts [25]. In fact, it is mentioned that, in the polyoxometalates family, heteropolysalts compared with heteropolyacids, have properties that can be more easily oriented to the desired applications by selecting appropriate counter cations [26]. For example, the addition of Co²⁺, Ag⁺, Ni²⁺, and Sn²⁺ has been reported to enhance redox interchange in HPA systems, which greatly improves their redox properties [27]. Moreover, proton exchange with metal cations combined with the insertion of a suitable transition metal into the polyanionic cavity has been effective in enhancing the optical behavior by reducing the semi-conducting energy bandgap HPAs from ultraviolet to the visible range [28]. As for the structural effect, it is important to note that the addition of the counter cation improves the stability of the three-dimensional structure of HPAs resulting in a more compact configuration [29].

In the present work, two cation-modified POMs salts (Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉) were prepared by inorganic condensation and characterized by different analytical spectroscopic techniques to evaluate their optical behavior and to test them, for the first time, as cathode catalysts in a wastewater-fueled MFC using wastewater as fuel. Carbon fabric cathodes coated with POM salts were evaluated in a single-chamber MFC device operated with wastewater to study the catalytic activity of these materials in relation to energy performance. Chemical oxygen demand (COD) was also measured to evaluate wastewater treatment in the studied MFC systems.

2. Materials and Methods

2.1. Preparation of POMs

All commercial products used in the present work are obtained from Sigma Aldrich and are used without any further purification. The materials prepared are lacunar salts of polyoxometalates of Keggin-type $Cs_5PMo_{11}(H_2O)MO_{39}$ (M = Fe(II), Co(II)). The technique used for the synthesis is inorganic condensation. Heteropolyacid $H_3PMo_{12}O_{40}$. xH_2O was used as the starting material dissolved in distilled water. The pH value of the solution was maintained at 4.8 using sodium hydroxide (NaOH). Then, 1 eq of metal cation obtained from MCl₂. nH_2O (M = Fe²⁺, Co²⁺) was added to the starting solution. The mixture was heated to 80 °C under strong magnetic stirring for 1 h. Then, CsCl. 5H₂O was added to the mixture, the final pH being 4.8. The excess water was removed by filtration. The salts obtained were rinsed several times with distilled water to eliminate the sodium [30–33]. The prepared materials were defined as $Cs_5PMo_{11}(H_2O)MO_{39}$ (M = Fe(II), Co(II)).

2.2. MFCs Operation

The prepared salts were tested in single chamber MFCs. The reactors used were glass bottles with a volume of 250 mL, covered with an external jacket to stabilize the temperature (25 °C). The anode compartment was carried out in batch mode and was fed with a volume of 125 mL of raw domestic wastewater from the region of Skhirat-Rabat as fuel (Table 1), and 100 g of graphite particles with a diameter of 2 mm and a graphite rod with a diameter of 3.2 mm constituting the anode. The cathode was composed of POMs salt mixed with 60 wt% polytetrafluoroethylene (PTFE) as a binder, mixed in water and isopropanol, mechanically pressed on a 1 cm² surface of a piece of carbon cloth, and then the prepared cathodes were dried in ambient air before use. Nafion[®] polymer (4 cm diameter) was used as a membrane to separate the cathode and anode chamber, which was treated in advance for 3 h at a temperature of 80 °C with different solutions, starting with hydrogen peroxide (H_2O_2) , then sulfuric acid (H_2SO_4) , and finally deionized water, and stored in deionized water until use. The MFCs were tested in the absence and presence of a light source. A xenon lamp (7W) placed 15 cm from the cathode was used as the light source. Polarization curves and power profiles were obtained by changing the external resistance from 11 M Ω to 1 Ω [34,35]. Current (I) and power (P) densities were calculated using the following equations: I = V/R and $P = V^2/R$, where V is the cell voltage and R is an external resistance, and then normalized to the geometrical area of the cathode. The voltage was also plotted against the current to obtain the polarization curve. The internal resistance was calculated from the power curve at the maximum power point. Wastewater treatment efficiency was evaluated in terms of chemical oxygen demand (COD) reduction, which is determined using the APHA protocol, using a Spectroquant Nova 30 spectrophotometer (Merck, Frankfurt, Germany) and calculated with the following Equation (1) [36]:

$$COD_{removal} = \frac{[C]_{initial} - [C]_{final}}{[C]_{initial}} \times 100\%$$
(1)

where $[C]_{initial}$ and $[C]_{final}$ represent the COD of the effluent (mg/L) in the anode chamber at the beginning and end of the experiment, respectively.

	COD (mg L ⁻¹)	Dissolved Oxygen (mg L ⁻¹)	pН	Temperature (C°)
Wastewater tested	1545	0.7	7.02	26.1

Table 1. Initial physico-chemical parameters of wastewater.

2.3. Characterization Methods

The materials used were characterized by different techniques. The crystal structure of the prepared compounds was observed by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Germany) with Cu-K α radiation in the 10–60° 2 θ range, using a stepwise of 0.02 and a scan speed of 0.05 s^{-1} . The Keggin structure was verified by infrared spectroscopy (FT-IR) using the Nicolet 6700 spectrometer, equipped with a laser source and a DG detector. The spectra were collected with recorded IR vibrations between 4000 and 400 cm⁻¹ with a resolution of 2 cm⁻¹, the number of scans was 64 in absorbance mode. The samples were prepared using the KBr pellet technique. Morphology, chemical composition, and elemental mapping distribution analyses were identified by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis on a QUATTRO S-FEG-Thermo Fisher equipment. The differential scanning calorimetry coupled to thermogravimetry (TGA/DSC) were performed using a Mettler Toledo TGA 2 apparatus operating in the temperature range of 0–1000 °C (heating rate of 10 °C min⁻¹ in dry air). UV-Vis diffuse reflectance spectra (UV-Vis/DRS) were recorded with a Perkin Elmer Lambda 900 spectrometer, measured at wavelengths between 190 and 850 cm⁻¹ using BaSO₄ as reference.

3. Results

3.1. Physico-Chemical Catalyst Characterization

3.1.1. X-ray Diffraction

XRD was employed to verify the crystallinity and conservation of the Keggin structure after the insertion of the metal cations. The XRD results of $Cs_5PMo_{11}FeO_{39}$ and $Cs_5PMo_{11}CoO_{39}$ (Figure 1) show similar patterns with diffraction peaks at $2\theta = 13.14^{\circ}$, 13.86° , 20.36° , 21.08° , 24.96° , and 25.8° that correspond to the structural type of Keggin phosphomolybdic acid (JCPDS: 01-075-1588) [33,37]. However, the peak positions are not precisely the same as those of $H_3PMo_{12}O_{40}$, because the counter cation was changed, and the transition metal was incorporated into the lacunar position of phosphomolybdate.



Figure 1. X-ray diffractograms of Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉.

The vibrational analysis of Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉ solids was carried out by FT-IR spectroscopy. Figure 2 shows the corresponding spectra of samples and Table 2 summarizes the characteristic vibrational bands of the prepared salts. The characteristic bands of [PMo₁₂O₄₀]³⁻ polyanions in Keggin-type phospho-molybdic heteropolyacids are typically observed at 1065, 962, 870, and 789 cm⁻¹, which correspond to the symmetric and antisymmetric vibrational modes ν_{as} (P–O_a), ν_{s} (Mo = O_t), ν_{as} (Mo-O_b-Mo), and ν_{as} (Mo-O_c-Mo), respectively [31–33]. The prepared molybdic heteropolysalts show bands in the same wavenumber regions of the characteristic bands of H₃PMo₁₂O₄₀ heteropolyacid, indicating that the Keggin structure was conserved. However, the substitution of an octahedron MoO₆ by a metal cation leads to a decrease in the symmetry of the P–O_a bond which is illustrated by the formation of a shoulder at 1078 cm⁻¹ on the P–O_a vibration. The PO₄ tetrahedron then evolves from a tetrahedral symmetry to a C₃ symmetry due to the elongation of one of the P–O_a bonds. Moreover, the creation of the new metal-oxygen bands is visible in the range between 400 and 800 cm⁻¹ [38].



Figure 2. IR spectra of Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉.

Table 2. IR frequencies (cm^{-1}) of Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉.

Title 1	ν_{as} (P–O _a)	$\nu_{\rm s}$ (Mo = O _t)	ν_{as} (Mo-O _b -Mo)	ν_{as} (Mo-O _c -Mo)	ν (M-O)
Cs ₅ PMo ₁₁ FeO ₃₉	1038	923	852	720	532
Cs5PMo11CoO39	1027	930	869	786	475

3.1.3. Morphology and Composition

The morphology, microstructure, and composition of the POMs salts were investigated by SEM and EDX analysis. As shown in Figure 3, both $Cs_5PMo_{11}FeO_{39}$ and $Cs_5PMo_{11}CoO_{39}$ materials present a surface morphology showing irregular-sized agglomerated nanoparticles ranging between 385 and 500 nm for the Fe-based material and between 313 and 477 nm for the Co-based material.

The EDX analysis mapping illustrates a homogeneous dispersion of Cs, and the incorporated metals Fe and Co. Figure 4 presents the chemical composition of the synthesized heteropolysalts. The presence of all the elements of the starting precursor (P, Mo, and O) is confirmed by the appearance of new peaks corresponding to the insertion of metals (Cs, Fe, and Co) with stoichiometric ratios quite such as those determined theoretically.



Figure 3. SEM images of Cs₅PMo₁₁FeO₃₉ (**A**,**B**), Cs₅PMo₁₁CoO₃₉ (**C**,**D**), and elemental mappings (E–J).



Figure 4. EDX spectra of $Cs_5PMo_{11}FeO_{39}$ (A) and $Cs_5PMo_{11}CoO_{39}$ (B).

3.2. Thermal Stability

Figure 5 shows the (TGA/DSC) profiles which were determined to reveal the thermal stability of the POM salts obtained from the heteropolyacid $H_3PMo_{12}O_{40}$ after substitution with Fe and Co metal. Mass losses were observed, which are manifested by endothermic peaks at temperatures between 168 °C and 458 °C, due to their dehydration. After the dehydration step, the salts decompose above 500 °C. For both prepared salts, two exothermic peaks are observed and their positions depend on the incorporated metal. The first one appeared at 554 and 575 °C and the second one at 707 and 750 °C for Cs₅PMo₁₁Fe(H₂O)O₃₉ and Cs₅PMo₁₁Co(H₂O)O₃₉, respectively.



Figure 5. TGA/DSC curves of Cs₅PMo₁₁FeO₃₉ (a) and Cs₅PMo₁₁CoO₃₉ (b).

The first step can be due to the crystallographic reorganization between the transition metals (Fe and Co) and the counter cation Cs [39,40]. This reorganization can be considered as an important step to improve the thermal stability of the salts. The second step is probably the result of the decomposition of the salts forming a mixture of oxides (CsO₂, P_2O_5 , MoO₃, and MO). The proposed decomposition sequence for the salts is presented in Figure 6.

$$Cs_{5}PMo_{11}M(H_{2}O)O_{39}.xH_{2}O \xrightarrow{-x H_{2}O} Cs_{5}PMo_{11}M(H_{2}O)O_{39} \xrightarrow{-x H_{2}O} Cs_{5}PMo_{11}MO_{39} \xrightarrow{-x H_{2}O} Cs_{5}PMo_{11}NO_{39} \xrightarrow{-x H_{2}O} Cs_{5}PMo_{11}NO_{5} \xrightarrow{-x H_{2}O} Cs_{5}PMO_{5} \xrightarrow{-x H_{2}O}$$

Figure 6. Proposed scheme of thermal decomposition process for POMs salts.

3.3. Optical Behavior

UV-Vis spectroscopy was performed to obtain more details on the chemical elements that make up the POMs and their characteristics. Figure 5 shows the UV-Vis spectra recorded between 200 and 850 nm. According to the literature, H₃PMo₁₂O₄₀ has two high intensity bands centered at 280 and 429 nm, these bands are attributed to the $d\pi$ $p\pi$ electronic transition of the Mo = O_t bonds and $d\pi$ - $p\pi$ - $d\pi$ of the Mo-O-Mo bridge, respectively [41]. UV-Vis analysis of the prepared salts shows a shift in the absorption of the Mo-O-Mo band which can be attributed to the elimination of the MoO₆ octahedron from the Keggin structure. The insertion of the metal cations Fe(II) and Co(II) produced new bands appearing at 464 and 503 nm, respectively, which probably attribute to the d-d Mo(VI)-M (Fe, Co)(II) transition [33]. For cesium, which is in the counter cation position, no absorbance was observed. It is worth noting that the shift in molybdenum absorbance in the UV interval suggested an increase in the sample's oxidation potential [42]. According to this result, Cs₅PMo₁₁Co(H₂O)O₃₉ would be more oxidizing than Cs₅PMo₁₁Fe(H₂O)O₃₉. UV-Vis/DRS also provides useful information on the optical properties of the prepared POM salts in order to check their performance as cathode components of MFC process operating under visible light or without irradiation. The UV-Vis/DRS results were exploited by the Tauc plot using the Kubelka–Munk function in the direct transition. Band gaps (*Eg*) were calculated from the absorbance spectrum using the Beer and Willardson equation:

$$(\alpha hv) = A(hv - Eg)^n \tag{2}$$

where *Eg* is the bandgap energy of the material, v is the frequency of the incident radiation, *h* is Planck's constant, *A* is a constant related to the material, the coefficient *n* refers to the nature of the transition (n = $\frac{1}{2}$ for direct gap), and α is the absorption coefficient in cm⁻¹, determined by the following equation:

Ι

$$=I_0 e^{-\alpha t} \tag{3}$$

where I_0 and I are the incident and transmitted intensities, respectively.

As seen in Figure 7, the band gaps vary significantly with the nature of the metal inserted into the heteropolysalt framework. The salts showed energy gaps at 2.68 and 1.71 eV for Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉, respectively. According to these results, the two synthesized POMs salts have a higher optical response in the visible light range, hence the interest of using them as components for photocatalytic converters. The optical behavior observed for the prepared Cs-based salts is not surprising since other studies previously reported on a series of lacunary heteropolysalts of Ni_{2.5}PMo₁₁M (Fe, Co, Cu, and Zn)O₃₉ showed that the bandgap energy is correlated with the nature of the incorporated cation [32]. Furthermore, the study of the arrangement between $H_3PW_{12}O_{40}$ and the silver cation in a lattice structure showed a modification in the formation of the band gap in this POM compound [43]. This combination that is created between the POMs and the cations increases the HOMO and LUMO energy gaps through the formation of the conduction and valence bands [44]. Moreover, it has been reported that the electronegativity of cations is a key factor in the formation of the band gap. In the family of POM compounds, the bandgap energy is correlated with the electronegativity of the inserted cations such that the bandgaps decrease in the opposite direction to the electronegativity of the cations, which is consistent with the values found for our materials [44].



Figure 7. UV-Vis spectra in solid of Cs₅PMo₁₁FeO₃₉ and Cs₅PMo₁₁CoO₃₉ (a), and Tauc plot (b).

The performance of fuel cell devices, including a microbial cell, is classically evaluated by plotting a polarization curve obtained by flowing the cell through resistances of different values. Figure 8A–D illustrates the polarization curve and power output of an MFC equipped with a heteropolysalt-coated air-cathode, MFC electrochemical performance was measured during 96 h in the presence and absence of a UV-vis light source.



Figure 8. Polarization and power density curves of air-cathode MFCs: Cs₅PMo₁₁FeO₃₉ (**A**,**B**) and Cs₅PMo₁₁CoO₃₉ (**C**,**D**).

The polarization curves in Figure 8a,c show the existence of a linear characteristic curves. In general, these characteristic curves showed the coexistence of two inflection points with three sections. The first corresponds to a fast voltage drop when current flows through the circuit (at high external resistance); the second corresponds to an almost linear voltage drop; and the last corresponds to a second fast voltage drop at high current density [1]. The slope of the second section can be tied to the internal resistance of the system. A steeper slope of this section is a result of higher internal resistance in MFCs, affecting the global performance of the cell in terms of power production as described above [45].

When the $Cs_5PMo_{11}FeO_{39}$ and $Cs_5PMo_{11}CoO_{39}$ catalysts were irradiated, the open circuit potential of the MFC system increased from 504 to 554 and from 470 mV to 516 mV, respectively. Comparing the two catalysts under light and no-light conditions, it is clear that the internal resistance of the system was higher in the second case, as indicated by the values shown in Table 2.

These results are in agreement with other works in the literature that found that light irradiation significantly influences the polarization resistance (R_p) of the catalyst [46]. Maximum power density is reached by the MFC using the photocathode Cs₅PMo₁₁CoO₃₉, 418.15 mW m⁻², followed by the Cs₅PMo₁₁FeO₃₉ that achieved 206.72 mW m⁻². As can be observed in Figure 8 b and d, in the absence of light source, maximum power densities are reduced to 119.62 mW m⁻² (Cs₅PMo₁₁CoO₃₉) and 163.87 mW m⁻² (Cs₅PMo₁₁FeO₃₉), which is a significant drop in power density. This increase in power density observed in the presence of the light source is attributed to the photocatalytic activity of POM salts, which increased the rate at which electrochemical reactions occurred on the catalyst surface [47,48]. It is worth noting that when comparing the maximum power density (P_{max}) values obtained in the presence of light, it clearly appeared that the insertion of cobalt significantly improves the photocatalytic performance of Keggin POMs. This result agrees with the UV-Vis/DRS results, which showed that the cobalt-modified material exhibits lower band gap than the iron-modified one, which means that the incorporation of Co into the Keggin structure of the molybdic POM with Cs in the position of counter cation had a promoting effect on the photocatalytic performance of these materials. This modification may effectively enhance the transport of the photo-induced electron-hole charge carriers to the catalyst interfaces. Therefore, the oxygen reduction reaction (ORR) processes can be favored at the active side of the candidate material according to the following mechanism (Equations (1)–(3)).

$$POMs + h\nu \to e_{cb}^- + h_{vb}^+ \tag{4}$$

$$4H^{+} + O_{2} + 4e/e_{cb}^{-} \to 2H_{2}O$$
(5)

$$h_{vb}^+ + e^- \rightarrow recombination$$
 (6)

Pt-based cathodes as reference catalysts in MFCs are reported in several works for their outstanding energy output. Zhang et al. [49] developed a carbon fabric cathode with Pt for an air chamber MFC, where they generated a maximum power density of 1060 mW m⁻². However, the cost performance of this material is relatively high, because platinum is an expensive metal (368 EUR/g) (Sigma-Aldrich catalogue, CAS number: 7440–06-4, Pt powder, 99.995% trace metals basis), which limits its practical application compared with the precursor H₃PMo₁₂O₄₀ used for the preparation of POMs salts (2.05 EUR/g) (Sigma Aldrich catalogue, CAS number: 51429-74-4, > 99.99%). The performance is clearly higher compared with other alternative cathodes reported in previous work, e.g., PbO₂, MnO₂, and CoTMPP (cobalt tetramethoxyphenylporphyrin) that provided maximum power values of 78, 161 and 369 mW m⁻², respectively [12,50,51].

The performance of the MFCs can also be assessed by their ability to treat wastewater with high organic load due to the anaerobic conditions in the anode chamber.

To verify the water treatment capacity of the studied system, chemical oxygen demand (COD) was measured in the presence and absence of the light source before and after the experiment (Table 3). The reduction in COD measured after 96 h shows that the initial value (1545 mg L⁻¹) was reduced by 83.92% (248.4 mg L⁻¹) and 89.5% (162.22 mg L⁻¹), respectively, in the absence and presence of the light for the Fe-based material. While for the Co-based material the corresponding abatement rate reached 75.90% (372.3 mg L⁻¹) and 97% (46.4 mg L⁻¹), respectively, in the absence and presence of light. This demonstrates a remarkable efficacy in wastewater treatment, which correlates well with the maximum power density results.

Cathodes	Light Source	OCV (mV)	Pmax (mW m ⁻²)	I at Pmax (mA m ⁻²)	Rint (Ω)	CODr after 96 h (%)
Cs ₅ PMo ₁₁ FeO ₃₉	Without	504	163.87	641	3983.62	83.92
	With	554	206.72	828	3018.84	89.5
Cs ₅ PMo ₁₁ CoO ₃₉	Without	470	119.62	489	4994.33	75.90
	With	516	418.15	2040	1004.29	97

Table 3. Performance of MFCs equipped with polyoxometalate salts cathode in the presence and absence of light.

Table 4 compiles several representative photocathodes according to their performance in terms of power output per cubic meter of wastewater feedstock and COD reduction rate. CsFe and CsCo heteropolysalts catalysts are among the most useful systems for photocatalytic oxygen reduction in MFC operating under the same conditions with air as oxygen for the cathode and wastewater as feedstock in the anodic compartment. CsFe and CsCo systems stand out from the others by their better optical behavior with lower energy gap values, 2.68 and 1.71 eV, respectively. The best performance in terms of electricity production per cubic meter of wastewater input was obtained for the MFC containing CsCo heteropolysalt-based cathodes, which showed a maximum power output of 331 mW m⁻³, and a maximum COD removal percentage of 97% after 96 h of MFC operation.

Table 4. Comparison of recent results in terms of bandgap, power output, and COD reduction rate of various MFC representative cathodes.

Cathodes	Band Gap ^a (eV)	P _{max} (mW m ⁻³)	COD _r (%)	Ref.
CsFe	2.68	135 ^b 151 ^c	84 ^b 89 ^c	This work
CsCo	1.71	104 ^b 331 ^c	76 ^b 97 ^c	This work
$({\rm Li}_{0.95}{\rm Cu}_{0.15}){\rm Ta}_{0.76}{\rm Nb}_{0.19}{\rm O}_3$	3.46	20 c	- 93 c	[52]
LiNbO ₃	4.08	40 ^b 131 ^c	54 ^b 76 ^c	[11]
LiTaO3	4.81	17 ^a 55 ^c	55 ^b 66 ^c	[53]
$Li_{1-x}Ta_{1-x}W_xO_3$	3.85	60 ^a 107 ^c	59 ^b 79 ^c	[13]

^a Determined from UV-Vis DRS Tauc Plot. ^b Values measured with MFC operating with no-light source. ^c Values measured with MFC operating with light source.

4. Conclusions

In this work, novel transition metal-modified Keggin-type lacunar polyoxometalate salts (L-POMs) $Cs_5PMo_{11}M(H_2O)O_{39}$ (M = Fe, Co) synthesized by inorganic condensation and characterized by X-ray diffraction, SEM, EDX, TGA/DSC, and IR, UV-Vis/DSR spectroscopies were successfully tested, for the first time, as a cathode component in wastewater-fed air chamber MFC. Both cathode components showed remarkable electroand photo-catalytic performance in the bifunctional MFC process producing high wastewater purification and efficient electric production under visible light. The best performance in terms of electricity production was obtained with the MFC containing a co-modified POM-based cathode, which showed a maximum power of 418.15 mW m⁻², and a maximum COD removal percentage of 97% was achieved after 96 h of MFC operation.

The remarkable power output of the systems developed is explained by the structural flexibility, acidity, and specific redox properties of the polyoxometallate salts. Therefore, Coand Fe-based POMs can be considered as promising alternative cathode catalysts in a new generation of MFC devices incorporating full wastewater carbon removal and fast oxygen electron reduction. In conclusion, POMs catalysts have the potential to be a promising material for use in microbial fuel cells, offering improved performance and cost-effectiveness compared with other materials. Further research is needed to overcome the challenges and fully realize its potential, contributing to the growth of the sustainable energy.

Author Contributions: Performing experimental works, data interpretation and writing—original draft preparation, F.L.; assistance in the realization of the electrochemical experiments, visualization and exploitation of results, N.-e.T.; visualization, catalytic data and electrochemical measurements interpretation, A.B.; helping in synthesis and characterization of POMs materials, A.O.; funding resources, E.M.L.; investigation and validation, M.E.M.; supervision, writing—review FJ.H.-F.; supervision, writing—review and editing, J.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets supporting reported results during the current study are available from the corresponding author on reasonable request.

Acknowledgments: We would like to thank the Moroccan Ministry of Higher Education, Scientific Research, and Innovation.

Conflicts of Interest: The authors declare no conflict of interest.

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