Journal of Chemical Technology and Metallurgy, 61, 1, 2026, 17-31

MICROBIAL ELECTROLYSIS CELLS: ELECTROCATALYSTS AND CHARACTERIZATION METHODS - A REVIEW

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Received 19 August 2025
Accepted 31 October 2025
DOI: 10.59957/jctm.v61.i1.2026.2

ABSTRACT

The growing global energy demand and depletion of fossil fuels require the development of sustainable alternatives. Hydrogen is widely recognized as a clean energy carrier due to its high energy density and environmentally benign combustion, producing only water. However, the high cost of hydrogen production remains a major barrier to its large-scale application, which stimulates research into novel production methods.

One of the newest methods in this direction is biocatalyzed electrolysis, in which, along with hydrogen production, simultaneous purification of biodegradable waste products is carried out. Unlike traditional electrolyzers, the oxidation of the substrate is facilitated with the help of specific microorganisms capable of transferring extracellular electrons, generated by their catabolite processes to the anode of bioelectrochemical systems. One of the most important advantages of microbial electrolysis cell (MEC) is that they use substrates from renewable sources and are characterized by high efficiency. The reaction in which hydrogen is released at the cathode is inherent in several industrial electrolysis processes with aqueous electrolytes. The choice of cathode material has a strong influence on the rate of hydrogen release. A crucial factor for the practical implementation of MEC is to find effective cathode materials for operation at neutral pH, since electrogenic microorganisms are used.

This paper reviews the basic principles of microbial electrolysis cell, as well as various methods for physicochemical and electrochemical characterization of potential cathode materials for bioelectrochemical hydrogen production.

Keywords: *microbial electrolysis cell, electrocatalysts, cathode material, electrochemical characterization methods.*

INTRODUCTION

One of the great challenges of our time is to solve the energy crisis while protecting the environment. The search for alternative and environmentally friendly energy sources is directing scientists to hydrogen as an environmentally friendly fuel [1, 2]. However, obtaining pure hydrogen is still expensive, which prevents its widespread production. That is why in the last few years, a lot of work has been done in the field of obtaining hydrogen. One of the newest methods in this direction is biocatalyzed electrolysis, in which, along with the production of hydrogen, the purification of biodegradable waste products is also carried out simultaneously [3, 4]. Therefore, the search for new, renewable, environmentally friendly sources of energy is becoming one of the most relevant and urgent tasks of our time.

Increasingly, scientists are focusing their efforts on renewable energy technologies, such as solar, wind, and biomass, to address these global challenges [1, 2]. Biomass and organic wastes can be converted into value-added energy carriers such as biohydrogen, biofuels, and biochemicals through advanced processes including pyrolysis, anaerobic digestion, and bioelectrochemical systems [3 - 5]. Microbial electrolysis cells (MECs) represent a promising approach that couples renewable waste conversion with hydrogen generation.

Bioelectrochemical Systems (BESs) are innovative technologies that merge microbiology and electrochemistry to convert chemical energy from organic compounds into electrical energy or valuable products (e.g., hydrogen, methane, or chemicals). They are primarily used for wastewater treatment**,** energy production**,** and biosensing**.** The main components and the different types of BES are presented respectively in Table 1 and Table 2.

Most experts believe that hydrogen will be the primary source of energy in the future, replacing current natural gas, oil, coal, and electrical infrastructure. Still, obtaining pure hydrogen is expensive, which hinders its widespread production. That is why in the last few years, the efforts of many research groups around the world have been focused on developing new methods and technologies for obtaining hydrogen. One of the newest approaches in this direction is biocatalyzed electrolysis, in which, along with the production of hydrogen, the simultaneous purification of biodegradable waste products is carried out [19 - 22]. The development of cheap and efficient cathode materials for MEC is of great importance for the practical application of this innovative technology.

This review outlines the basic functioning of microbial electrolysis cells and examines the methods used to assess the physical and electrochemical properties of cathode materials for hydrogen production in bioelectrochemical system.

ELECTROCATALYSTS

Microbial electrolysis cell (MEC) can be a potential solution to the above-discussed problems regarding energy needs and environmental protection. Solving the problem of finding alternative cathode materials in MEC

Table 1. Basic components in BES.

Component	Function
Anode	Site where microorganisms oxidize the substrate and release electrons.
Cathode	Site where reduction reactions occur (e.g., oxygen reduction).
Microbial biofilm	A layer of electrogenic microbes growing on the anode surface.
Proton Exchange Membrane (PEM)	Allows protons to pass from anode to cathode chamber (in some systems).
External Circuit	Provides the path for electron flow between electrodes.

Table 2. Type of BES.

Type	Application/Function
Microbial Fuel Cell (MFC)	Generates electricity from organic waste [6, 7]
Microbial Electrolysis Cell (MEC)	Produces hydrogen or methane using external voltage [8, 9]
Microbial Desalination Cell (MDC)	Desalinates water while generating electricity [10, 11].
Microbial Electrosynthesis Cell (MESC)	Produces chemicals (e.g., acetate, ethanol) from CO_2 [12, 13].
Microbial electrochemical snorkel (MES)	Water purification from organic pollutants at a high speed, soil decontamination, etc. [14] Metal recovery from aqueous solutions [15 - 18].

is one of the main challenges for the practical application of biocatalyzed electrolysis. A specific requirement of bioelectrochemical systems (BES), as well as MEC, is the use of electrolytes with neutral pH and temperatures close to room temperature. This necessitates a thorough investigation of any potential catalytic material under these conditions [23, 24].

The performance of microbial electrolysis cells (MECs) strongly depends on the choice of cathode electrocatalyst for the hydrogen evolution reaction (HER) [25].

In the early stages of MEC studies, the Pt cathode was popularly used due to its excellent catalytic activities toward HER. However, the use of Pt in MECs is not practical due to its very high price. Other noble metals such as Pd, Au, Rh, and Ru have also been investigated, showing excellent catalytic activity but similar economic barriers [26].

Although Pd, Rh, and Ru have been successfully tested as cathode catalysts in MECs, providing low overpotentials and high exchange current densities for HER, their large-scale application is limited by economic and stability issues. In real MEC environments, which often involve complex wastewaters, biofilm formation and surface poisoning significantly reduce the long-term activity of these noble metal catalysts. Recent research has therefore focused on integrating noble metals into hybrid or composite systems, where they are used in small amounts as dopants or nanoparticle coatings on cheaper supports (e.g., carbon cloth, nickel foam, MoS_2). Such approaches enable the preservation of their high intrinsic catalytic activity while reducing cost and improving durability under biologically relevant conditions [27, 28].

Noori et al. highlights how biocathodes can reduce the need for costly platinum catalysts, improve performance through low internal resistance and pH balance and that optimizing microbial and electrode interactions is crucial for future commercialization of MEC technology [19].

Thus, alternative cathode catalysts have been developed in two directions: (1) synthesizing metal catalyst composites and (2) providing larger active surface areas for catalysts [29] Partial replacement or reduction of the platinum load are among the main strategies applied [29].

The choice of a proper support material strongly affects the hydrogen production rate too [30, 31].

Kye et al. showed that Pt-Au electrocatalysts have a larger active surface area than Pt nanoparticles alone [32].

Recent advances in cathode electrocatalysts for MECs have focused on non-noble materials combining efficiency, cost-effectiveness, and durability. For example, beta-nickel molybdate ($NiMoO_4$) coatings on nickel foam have demonstrated significantly enhanced HER performance in MECs treating real wastewater streams [$NiMoO_4$-Coated NF, 2020]. Furthermore, nickel-molybdenum (NiMo) alloys synthesized by hydrothermal methods achieved rates exceeding 80 L H_2 L^{-1} d^{-1} and Coulombic efficiencies above 97 % at low overpotentials [33]. These findings easily outperform earlier Ni-based catalysts and approach Pt-level performance without the high cost.

Non-precious metal catalysts like nickel, molybdenum, and stainless steel were popularly studied in MECs. Nickel (Ni), cobalt (Co), molybdenum (Mo), and their alloys or compounds are among the most studied alternatives to Pt. Ni-based materials exhibit good HER performance in neutral pH, which is relevant for MECs, while molybdenum sulfide (MoS_2) and cobalt phosphide (CoP) have shown promising catalytic activity at a significantly lower cost [34, 35]._

Carbon materials such as carbon cloth, carbon felt, graphite, and carbon nanotubes are widely used due to their conductivity, chemical stability, and biocompatibility with electrogenic microorganisms. Their catalytic activity is generally lower, but surface modification (e.g., doping with N, S, or metal nanoparticles) can significantly improve HER performance [24, 29]. Different classes of materials have been explored, each with advantages and limitations in terms of activity, stability, and cost [34].

Metal oxides (e.g., TiO_2, MnO_2, Fe_2O_3) have been explored as stable and corrosion-resistant supports. When combined with conductive phases (carbon, graphene) or active metals, they can enhance both catalytic activity and durability. Composite catalysts often show synergistic effects that outperform single-component systems [34].

Recent studies highlight transition metal sulfides (MoS_2, WS_2), phosphides (Ni_2P, CoP), carbides, and nitrides (Mo_2N) as cost-effective and efficient alternatives for HER. These materials exhibit high electrochemical activity and are tunable through morphology and surface engineering [28, 36].

When selecting electrocatalysts for MEC applications, not only catalytic activity but also stability under neutral pH, resistance to biofouling, cost-effectiveness, and compatibility with microbial biofilms must be considered. Thus, developing scalable and durable non-noble metal catalysts remains a key research priority [34].

PRINCIPLE OF OPERATION OF MEC

Microbial electrolysis cell is a technology for hydrogen production closely related to microbial fuel cells (MFCs). Whilst MFC's produce an electric current from the microbial decomposition of organic compounds, MECs partially reverse the process to generate hydrogen or methane from organic material by applying electric current [22]. The process that occurs at the anode in MEC is the same as that in microbial fuel cells (MFCs), and the process of the cathodic half-reaction mirrors that in traditional water electrolysis [37 - 39].

Microbial electrolysis cells (MECs) couple microbial oxidation of organic substrates at the anode with proton reduction at the cathode to generate hydrogen.

This is realized using specific microorganisms capable of transferring extracellular electrons generated by their catabolic processes to the anode of the BES. The use of a bioanode significantly reduces the theoretical decomposition voltage and makes it possible to release hydrogen at the cathode when an external voltage of less than one volt is applied. In microbial electrolysis cells (MECs), electrogenic microorganisms oxidize organic substrates at the anode, releasing electrons and protons, while at the cathode protons are reduced to hydrogen gas under the influence of a small external voltage. These electrons flow through an external circuit to the cathode, while the generated protons migrate through the electrolyte. At the cathode, the electrons and protons combine to form molecular hydrogen via the hydrogen evolution reaction (HER) [5, 40]. Compared to conventional electrolysis, MECs operate at neutral pH and ambient temperature, require significantly lower energy input (< 1 V), and utilize renewable or waste-derived substrates [8, 41, 42]. These features make MECs highly attractive for sustainable hydrogen production and wastewater treatment. This process takes place in a system known as a microbiological electrolyzer or microbial electrolysis cell (MEC). A schematic representation of the MEC process is shown in Fig. 1.

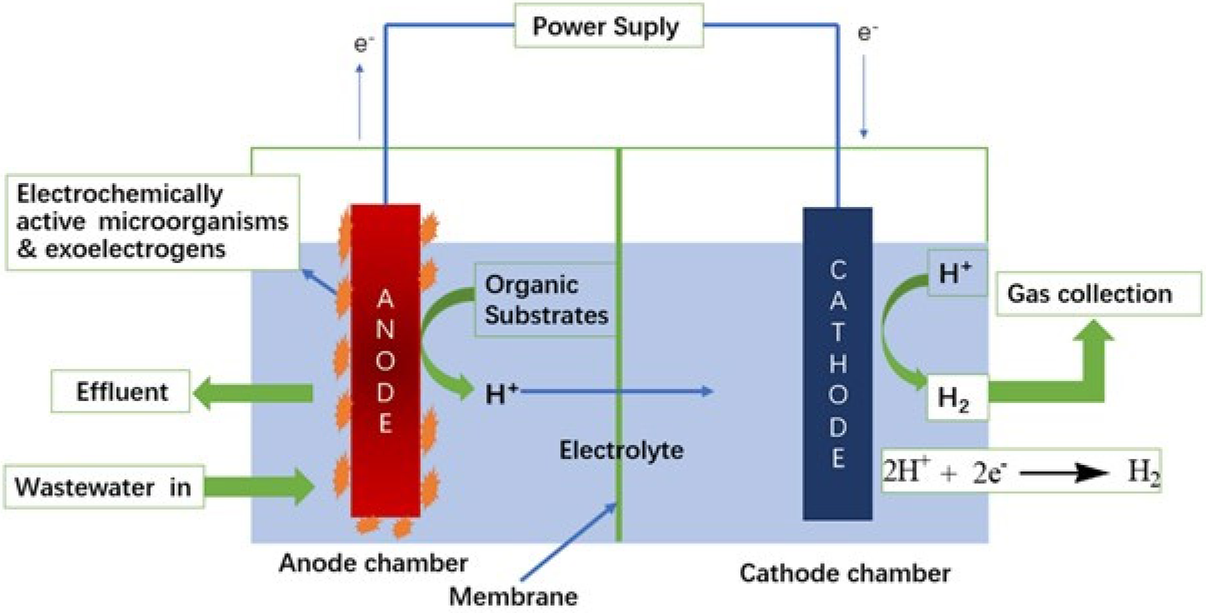

Fig. 1. Reaction schematic diagram of double-chamber MEC [43].

Functionally, MFC are electrochemical energy converters that generate electric current during a spontaneous ($G < 0$) redox reaction. Unlike conventional electrochemical current sources (batteries, accumulators, fuel cells) that use chemical electrocatalysts, in MGEs the anodic half-reaction is catalyzed by electrochemically active (exoelectrogenic) microorganisms. During the catabolite processes, these microorganisms oxidize the substrates present in the medium, the decomposition of which produces electrons and protons. The generated electrons are transferred extracellularly to the anode, and the protons migrate to the cathode. When a substance with a more positive redox potential than that of the bioanode is present in the cathodic space, an electromotive force arises in the system, due to which, with a closed external circuit, electrons spontaneously pass from the anode to the cathode, generating electric current. When using an air gas diffusion electrode as a cathode, electrons reaching the cathode through the external circuit reduce oxygen, combining it with protons to form water. In MEC, in the absence of oxygen in the cathode space, electrons released during the decomposition of an organic substrate and reaching the cathode via the external circuit reduce protons to hydrogen. The reduction of hydrogen ions H^+ to hydrogen gas H_2 at the cathode, however, is characterized by a lower redox potential than at the anode and electrons do not spontaneously pass through the circuit, i.e., the electrolysis process is not thermodynamically possible. Therefore, for the reaction to proceed, it is necessary to apply an external voltage. Due to the participation of electrochemically active microorganisms, the voltage required for electrolysis in MEC is much lower than the theoretically calculated one for water electrolysis (1.23 V, Table 3) [9, 44, 45].

The anode potential in most MFC, respectively. MEC reaches E_{AN}=-0.30 V vs. normal hydrogen electrode (NHE). At pH = 7 the potential of the hydrogen half-reaction is E_{CAT} = - 0.41 V (vs. NHE). Therefore, the theoretical voltage required for the electrochemical process to occur is - 0.11 V [46]: The mathematical expression is represented in Eq. (1):

$$E = E_{CAT} - E_{AN} = (-0.41) - (-0.30) = -11V \qquad (1)$$

Despite the differences, for both MECs and MFCs the exoelectrogenic microorganisms used and the mechanism of extracellular electron transport are of great importance, which largely determine the kinetics of the ongoing bioelectrochemical processes.

MEC has some significant advantages over the technologies used so far for obtaining hydrogen from organic matter. One of the most important advantages is that MEC uses substrates from renewable sources (e. g. wastewater) and is characterized by high efficiency. Even some substrates that were previously considered unsuitable for hydrogen production due to the endothermic nature of the conversion reactions can be converted with this technology. In addition to hydrogen generation, microbial electrolysis cells have been applied for the treatment of various wastewaters [47]. A recent study demonstrated a dual-chamber MEC

Table. 3. Electrode reactions and potentials of MEC, MFC and water electrolysis at pH = 7. Acetate was used as an electron donor in MEC and MFC.

Process	Anodic reaction E, V	Cathodic reaction E, V	Theoretical voltage, V	Spontaneity of reaction
MEC	$CH_3COO^- + 4H_2O \rightarrow$ $2HCO_3^-+9H^++8e^-$ E = -0.279	$2H^++2e^- \rightarrow H_2$ E = -0.414	-0.135	No
MFC	$CH_3COO^- + 4H_2O \rightarrow$ $2HCO_3^-+9H^++8e^-$ E = -0.279	$O_2+4H^++4e^- \rightarrow H_2O$ E = 0.806	1.085	Yes
Electrolysis of water	$2H_2O \rightarrow O_2+4H^++4e^-$ E = 0.815	$2H^++2e^- \rightarrow H_2$ E = -0.414	-1.229	No

operated with winery wastewater, achieving stable hydrogen production (0.7 ± 0.3) L H_2 L^{-1} d^{-1}, COD removal above 55 %, and cathodic hydrogen recovery of nearly 87 % [48].

The first pilot plant demonstrating the capabilities of the MEC technology for obtaining hydrogen from wastewater was built at the Napa Wine Company, Oakville, USA in 2010. This pilot-scale system was fed winery wastewater and operated under continuous-flow conditions. The study compared the net energy recovery between microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) when treating real winery and domestic wastewaters. Organic removal efficiencies and values of the different energy products were compared for MFCs and MECs fed winery or domestic wastewater. The results highlighted that MECs could produce recoverable hydrogen energy, whereas MFCs produced electricity but with a much lower overall energy output. The authors also reported the economic implications, noting that although MECs required an external power supply, the net energy recovered in the form of hydrogen from winery wastewater was significantly higher than that from electricity generated in MFCs [49].

CHARACTERIZATION OF POTENTIAL CATHODE MATERIALS IN MEC

Surface characterization

The catalytic performance of cathode materials in MECs is strongly linked to their surface morphology, composition, and chemical states. Therefore, a set of classical characterization techniques is commonly employed, including SEM/EDS for morphology and elemental composition, XRD for crystalline phases, FTIR and XPS for functional groups and surface states, and BET analysis for surface area. To gain deeper insights into catalyst behavior under realistic MEC operating conditions, recent studies increasingly combine these with in situ or operando methods. For instance, in situ Raman spectroscopy has been applied to track active phase formation during HER [50]. Comprehensive overviews of such advanced methods are now available [45].

Yahya et al. used the response surface method to determine the optimal operating conditions for MECs, and the results showed that when the MEC voltage was 0.5 V, the hydrogen production rate was the highest (85.13 mL H_2/gVS_{in}) [51].

Scanning Electron Microscopy (SEM)

SEM provides high-resolution imaging that reveals surface morphology, topography, and microstructural features of electrode materials, which are critical for understanding and optimizing their electrochemical performance. In MECs, SEM has been widely used to visualize porosity and roughness, bacterial adhesion, biofilm growth, and catalyst deposition on cathode surfaces. As a result of the performed electrolysis, Ni-foam samples were covered with electrodeposits with different size and shapes. In both cases the loading of the particles is not uniform. Modified carbon-based electrodes often display enhanced roughness that improves microbial colonization and increases the density of active HER sites.

X-ray Diffraction (XRD)

X-ray Diffraction (XRD) identifies crystalline phases and crystal structure; helps determine the degree of crystallinity in metal or metal oxide catalysts. XRD is used to identify the crystalline phases and crystal structure of metal or metal oxide catalysts. It helps determine the degree of crystallinity and assess structural changes of the catalysts before and after operation in microbial electrolysis cells [42]. In our previous research the phase composition of the modified cathode materials (magneli-phase titanium sub-oxide, the monometallic catalysts) was studied by XRD and in addition SEM was performed. The results are presented in Fig. 2.

The reflections show that both Ni and Co are in the crystal state, and the crystallographic orientation of Ni particles is mainly in (111) and (200), while for Co particles are in (100) and (002) crystallographic planes. The SEM images show fine dispersion of the catalytic particles over the whole surface of the support.

Energy Dispersive X-ray Spectroscopy (EDS or EDX)

This is an important technique commonly coupled with Scanning Electron Microscopy (SEM) for the elemental characterization of cathode materials in Microbial Electrolysis Cells (MECs). It provides qualitative and semi-quantitative analysis of the elemental composition, helping researchers understand the chemical state and surface interactions that occur during MEC operation. EDS helps detect catalyst

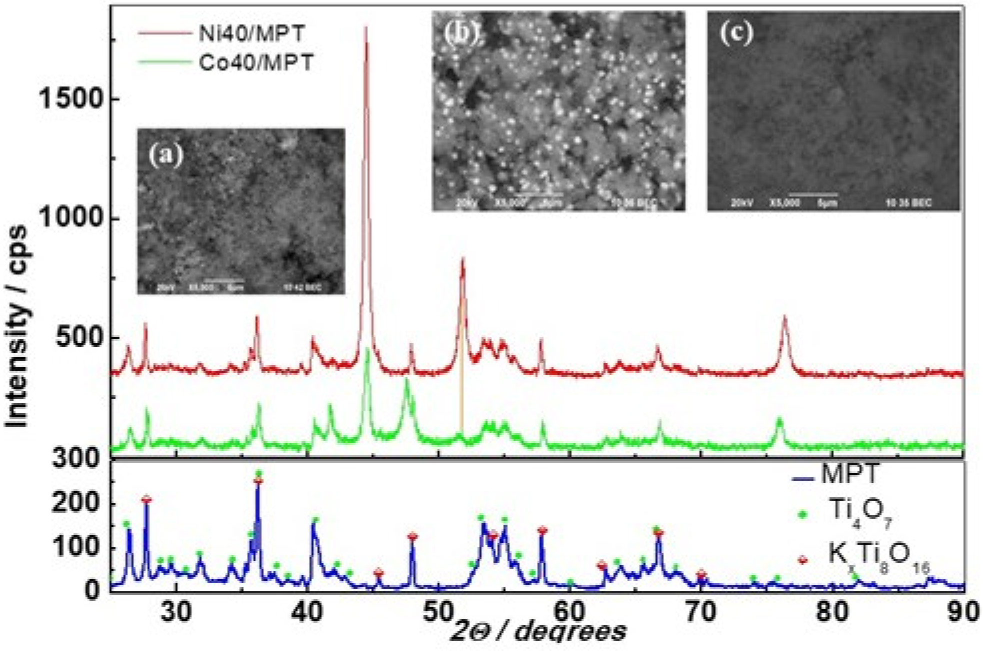

Fig. 2. XRD patterns of the Magneli-phase titanium sub-oxide (MPT) support and the Ni40/MPT.

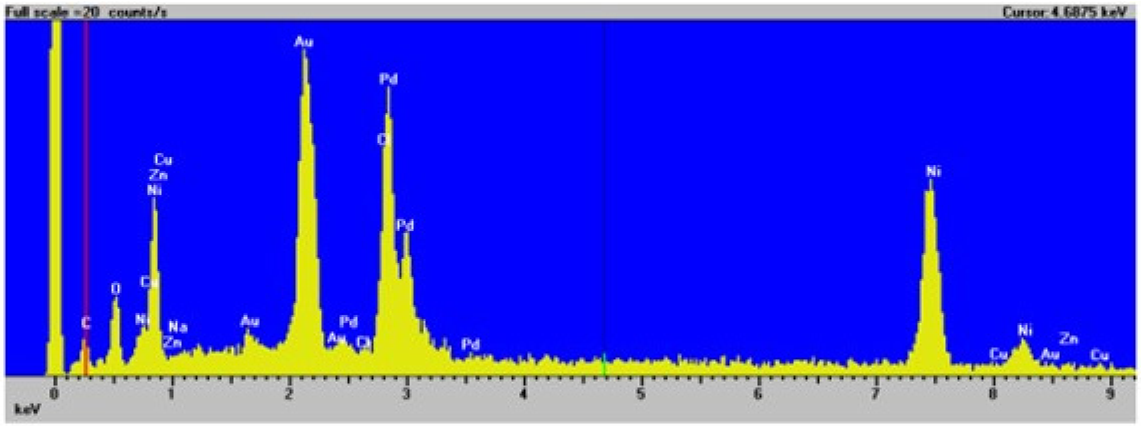

Fig. 3. EDS-spectrum of $Pd_{50}Au_{50}$/Ni-foam [53].

distribution (e.g., Pt, Ni, Mo, Co), surface fouling or corrosion (e.g., Fe, S, P, Ca deposition), biofilm-related elements (e.g., N, P from microbial residues), impurities or degradation products. The recorded EDS spectra, of the electrochemical co-deposition of Pd and Au on Ni-foam (RCM-Ni-4753.016), confirm the co-presence of Pd and Au in the deposits Fig. 3 [52, 53].

Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier-Transform Infrared Spectroscopy analyzes functional groups and chemical bonding on material surfaces; useful for studying interactions with biofilms or modifiers. The use of FTIR is very important because the surface chemistry of cathode materials can strongly influence: microbial attachment; catalytic activity; electron transfer efficiency; HER performance. FTIR is especially useful for detecting organic functional groups (e.g., -OH, -COOH, C=O), biofilm-related compounds (proteins, polysaccharides, lipids), oxide layers on metal cathodes, surface treatments or coatings (e.g., polymer or composite coatings) [8, 41].

X-ray Photoelectron Spectroscopy (XPS)

XPS provides information on surface elemental composition and oxidation states, essential for analyzing redox-active materials and surface-modified electrodes. Ideal for detecting biofouling, corrosion, and catalyst degradation. XPS is a powerful tool for understanding the surface chemistry of cathode materials in microbial electrolysis cells. It provides essential information on catalyst oxidation states, biofilm composition, fouling, and degradation processes that impact MEC performance. When combined with SEM, EDS, and FT-IR, XPS enables a comprehensive evaluation of cathode surface behavior before and after MEC operation [54].

Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET surface area analysis is a widely used method to measure the specific surface area and porosity of solid materials. In the context of Microbial Electrolysis Cells (MECs), BET analysis plays a critical role in the characterization of cathode materials, particularly in understanding how surface area and pore structure influence electrochemical performance and microbial interaction. This is of great importance, considering that the cathode surface area and porosity directly affect the rate of HER, the accessibility of electroactive sites, microbial attachment and colonization, gas and ion transport efficiency. BET analysis helps determine total surface area (m^2 g^{-1}), pore volume and pore diameter, micro-, meso-, and macroporosity profiles [55 - 57].

Electrochemical methods

The performance and durability of cathode materials in microbial electrolysis cells (MECs) are strongly influenced by their surface morphology, chemical composition, electrochemical properties, and structural stability. Electrochemical methods are essential tools for investigating and evaluating potential cathode materials for MECs. They enable both qualitative and quantitative assessment of electrochemical properties, including cathodic activity, electrical conductivity, corrosion resistance, and electrode reaction kinetics.

Cyclic Voltammetry (CV) and Linear Voltammetry (LV)

Cyclic voltammetry (CV) is widely applied in MEC studies to evaluate the redox behavior and electroactivity of electrode materials. The choice of potential range and scan rate is critical, since processes that appear reversible at low scan rates may become irreversible at higher ones. For instance, López Zavala et al. demonstrated how changing the scan rate from 25 to 50 mV s^{-1} significantly influenced the voltammetric response of bioelectrochemical electrodes [58]. A representative voltammogram from MEC studies is presented in Fig. 3. Linear sweep voltammetry (LSV), on the other hand, is commonly employed to determine the onset potential for hydrogen evolution, the overpotential (V_e), and the Tafel slope (V_h), which provide direct information about the kinetics of HER at the cathode [44, 58, 59, 60]. These methods make it possible to quantitatively compare the performance of different cathode materials under MEC conditions.

Linear voltammetry (LV) follows the same principles as CV, with the difference that the potential is applied only in one direction. When the equilibrium potential of the working electrode is known, LV can be used to determine the exchange current density of a given electrode material with respect to the hydrogen evolution reaction (HER). In MEC studies, LV is widely employed to evaluate key kinetic parameters such as the onset potential for hydrogen evolution (V_e) and the Tafel slope (V_h), which reflects the rate-determining step of HER on a given electrode surface [44, 59]. From the polarization curves obtained by LV, the overpotential of the cathodic reaction and the exchange current density can be derived, providing quantitative information for comparing the efficiency of different cathode materials. Tafel slopes are usually extracted directly from the linear portion of the LV data, making it unnecessary to include idealized polarization curves.

LV obtained with the newly produced Ni and Co modified graphitized paper (GP) with different loading of catalysts and non-modified graphitized paper are compared in Fig. 4 [35].

Linear voltammetry [61, 62] is also used to study corrosion processes. In this case, the potential is unfolded in the anodic direction, starting before and ending after the corrosion potential, E_{corr}. The recorded polarization dependence is most often presented in Tafel coordinates. The corrosion behavior, in neutral phosphate buffer, of the supported material (Ni-foam RCM-Ni-4753.016) and modified Ni-foam with NiW and NiMo respectively, is presented in Fig. 5 [35].

By extrapolating the linear sections of the cathodic

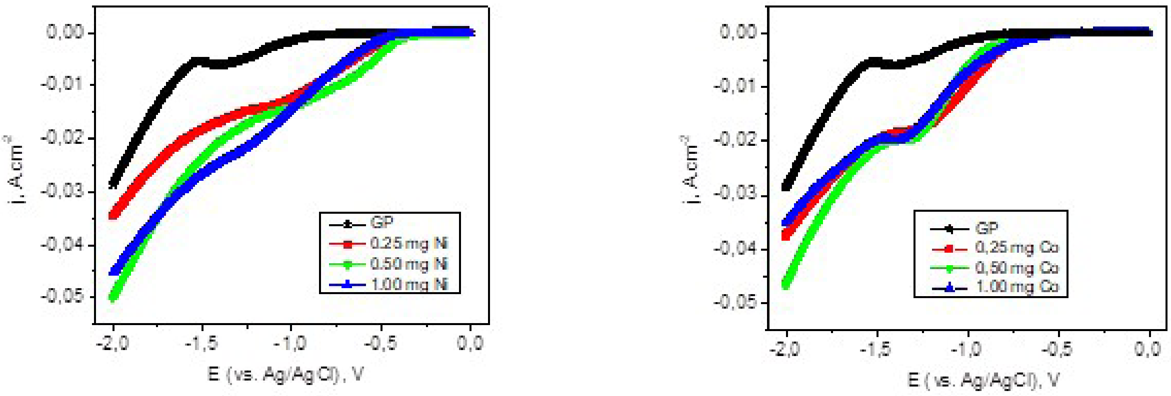

Fig. 4. Linear voltammetry obtained with non-modified GP and modified GP with: (a) Nickel catalysts/GP; (b) Cobalt catalyst/GP [35].

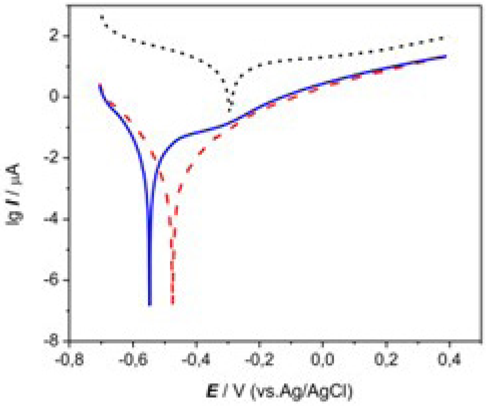

Fig. 5. Tafel plots of Ni-foam (short dash line), NiMo/Ni-foam (solid line) and NiW/Nifoam (dash line) in neutral phosphate buffer; scan rate 2 mVs^{-1} [35].

and anodic parts of the curve, the value of the corrosion current, Icorr, is determined. The density of the corrosion current icorr is a measure of the corrosion rate. The smaller icorr, the greater the corrosion resistance of the tested material in the respective environment. On the other hand, the corrosion potential Ecorr. evaluates the tendency for a corrosion process to occur - the more positive Ecorr. is, the less the tendency of the given material to corrosion. The main advantage of voltammetric methods over classical ones is their greater productivity and precision.

The kinetics of the hydrogen evolution reaction (HER) are often analyzed using the semi-empirical Tafel equation, which relates the overpotential (η) to the current density (i) as shown in Eq. (2):

$$\eta = a + b\ .\ \lg i \qquad (2)$$

where: η - verpotential, V, a - tafel constant (depending on the electrode material and reaction), b - Tafel slope (influenced by the reaction mechanism, temperature, and number of electrons transferred), *i* - current density, A/m².

For HER, *a* typically varies from ~0.3 V for platinum to ~1.3 V for lead, while *b* usually ranges between 0.06 and 0.12 V. These variations imply that even at the same overpotential, the reaction rate can differ by more than ten orders of magnitude between different electrode materials, which explains the strong research focus on developing efficient and low-cost HER electrocatalysts [63].

The Tafel slope can also be expressed theoretically as as shown in Eq. (3):

$$b = \frac{2{,}303\ .R.T}{a\ .n\ .F} \qquad (3)$$

where: R - universal gas constant (8.314 J mol^{-1} K^{-1}); T - temperature in kelvins (K); α - charge transfer coefficient; n - number of electrons transferred; F Faraday constant (96 485 C mol^{-1}).

Differential pulse voltammetry (DPV)

Differential Pulse Voltammetry (DPV) is an electrochemical technique used to characterize the redox behavior, catalytic activity, and surface electrochemical properties of cathode materials in Microbial Electrolysis Cells (MECs). It is a sensitive method capable of detecting small changes in current related to specific electrochemical reactions, making it especially useful for analyzing modified electrodes and assessing their hydrogen evolution reaction (HER) activity. In MECs, the cathode plays a crucial role in driving hydrogen production through HER. DPV provides valuable insights into electrocatalytic activity of cathode materials, presence and stability of surface-bound redox-active species, electron transfer kinetics at the electrode-electrolyte interface, effects of catalyst coatings, modifications, or biofilms. For example, it has been applied to monitor electron transfer features in biofilms of Geobacter sulfurreducens on anodes, revealing changes in surface-bound redox centers with maturation of the biofilm [64]. Incorporating DPV or other pulse-based techniques remains a promising avenue for detecting surface-active species and fine-grained electrochemical changes under MEC-relevant conditions.

Electrochemical Impedance Spectroscopy (EIS) and LPR - Linear Polarization Resistance

Electrochemical Impedance Spectroscopy (EIS) is a powerful electrochemical technique used to investigate the electrical properties and interfacial processes occurring at the surface of cathode materials, is valuable for dissecting charge transfer resistance components and biofilm effects within MECs. It is particularly useful for analyzing charge transfer resistance, double-layer capacitance, and mass transport phenomena, which are critical for understanding and optimizing the hydrogen evolution reaction (HER) and overall MEC performance. Electrochemical impedance spectroscopy (EIS) is another important technique frequently used to understand microbial degradation processes and can be ilustrated as Nyquist or Bode plots. EIS has been shown to be a safe technique for studying microbial corrosion as it does not cause damage to the biofilm and microbial population [65].

A deeper insight into the electrochemical kinetics of the electrodes can be achieved through EIS. Nyquist plots of the graphitized paper and modified materials carried out at -1.2V (vs. Ag/AgCl) are presented in Fig. 6 [35].

Detailed and reliable information on corrosion phenomena can be obtained when different techniques are combined [66].

Linear Polarization Resistance (LPR) analysis is another widely used electrochemical technique for evaluating the corrosion behavior and charge transfer resistance of electrode materials. In this method, the current response is measured within a narrow potential range (typically ± 10 - 20 mV) around the open circuit potential (OCP). The slope of the resulting linear region of the polarization curve provides the polarization resistance (Rp), which is inversely proportional to the corrosion rate. In microbial electrolysis cells (MECs),

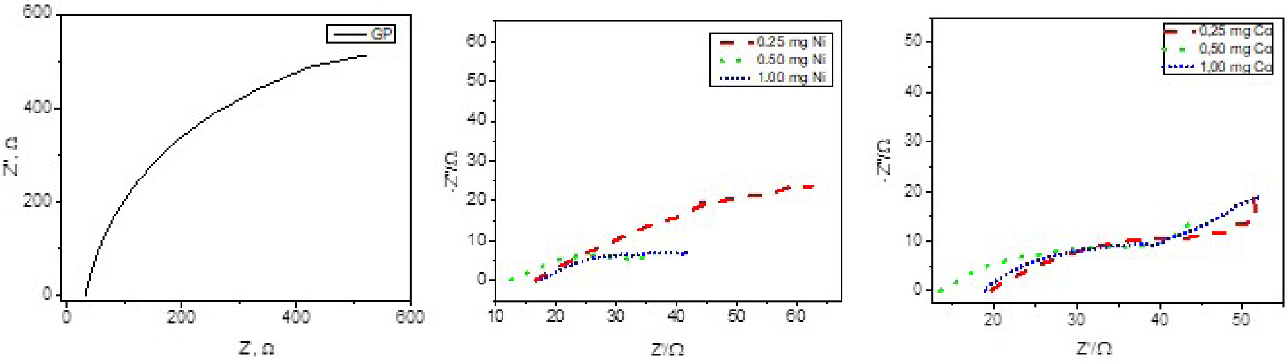

Fig. 6. Nyquist plots of the EIS of the: (a) Graphitized paper; (b) Nickel catalysts/GP; (c) Cobalt catalyst/GP [35].

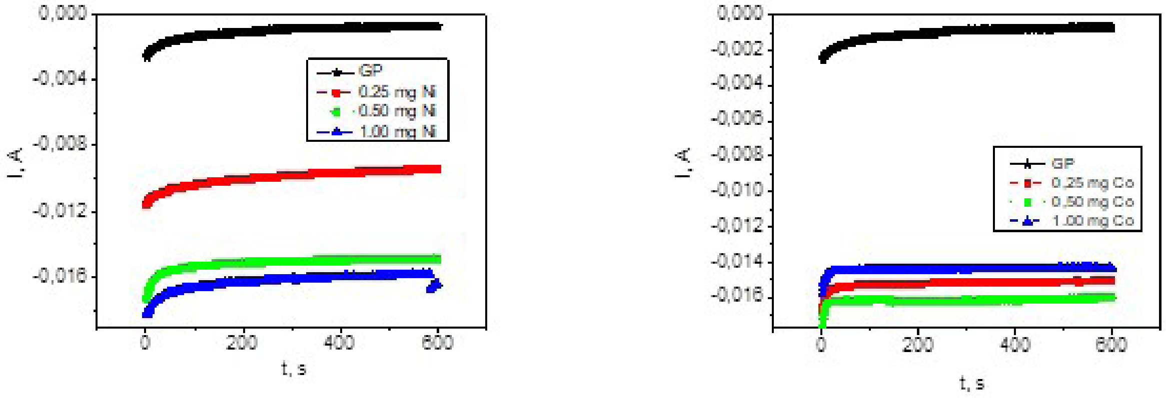

Fig. 7. Chronoamperometric curves obtained at potential -1.2V with investigated materials: (a) Ni/GP; b) Co/GP [35].

LPR is particularly useful for assessing the stability and durability of cathode materials under biological and electrochemical operating conditions.

Chen et al. [67] compensated the solution resistance by IR, to reduce the interference of the solution resistance on the polarization internal resistance during the measurement [68].

Chronoamperometry and Chronopotentiometry

Chronoamperometry (CA) can be used to study the catalytic activity of a cathode material with respect to the hydrogen evolution reaction. CA enables evaluation of catalytic efficiency, detection of electrode fouling, and assessment of microbial activity when biocatalysts are involved [54].

Chronopotentiometric (CP) methods are based on measuring the dependence of the potential on time at set current values or when the current changes in a certain way. When a controlled, usually constant current flows through the working electrode, i.e. in a galvanostatic regime, the electrode potential changes because of depletion of the electrochemically active substance near the electrode surface. The change in potential with time can be used both for quantitative analytical determinations and for studying the kinetics of processes occurring on the surface of the working electrode.

Chronoamperometry and chronopotentiometry further provide data on long-term operational stability of electrocatalysts.

Chronoamperograms obtained with non-modified GP and investigated materials (Ni/GP; Co/GP) at -1.2V (vs. Ag/AgCl) in PBS are presented in Fig. 7 a, b [35].

CONCLUSIONS

Characterization of electrocatalysts for cathodes in microbial electrolysis cells is essential for enhancing the overall performance, efficiency, and stability of hydrogen production systems. Through a combination of electrochemical techniques, such as cyclic and linear voltammetry, electrochemical impedance spectroscopy, linear polarization etc., critical parameters including electrocatalytic activity, corrosion resistance, electron transfer resistance, and long-term stability can be effectively assessed. A comprehensive understanding of electrocatalyst behavior not only supports the development of more efficient MEC systems but also contributes to the broader field of sustainable hydrogen production. Future research should focus on cost-effective, scalable, and environmentally benign materials, as well as on integrating biological and electrochemical insights to optimize MEC design and operation.

Acknowledgements

This study was supported by the project RP-A2/25.

Authors' contributions

E.Ch.: Writing - original draft, Supervision, Methodology, Project administration, Funding acquisition, Conceptualization, Writing - review & editing; N.I.: Writing - original draft, Investigations, Summarizing; I.B.: Investigations, Summarizing; K.A.: Investigations, Summarizing; Y.A.: Investigations, Summarizing.

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