

Magnesite-based ceramic membrane for microbial fuel cells treating domestic wastewater: fabrication, statistical optimization, and electrochemical performance

Vajihe Yousefi ^{*}, Fatemeh Najafi-Rad, Hosein Shokuhi-Far

Chemical Engineering Department, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran

ARTICLE INFO

Keywords:

Microbial fuel cell (MFC)
Ceramic membrane
Magnesite
Sintering temperature
Response surface methodology (RSM)
Proton conductivity

ABSTRACT

Magnesite-based ceramic membranes were developed using locally abundant magnesite, K-feldspar, and clay as sustainable and cost-effective separators for microbial fuel cells (MFCs). The combined effects of magnesite content (20–80%) and sintering temperature (1000–1300 °C) were optimized using Response Surface Methodology (RSM). MANCOVA confirmed that both factors significantly influenced maximum power density (MPD) and coulombic efficiency (CE), while porosity was not a meaningful covariate. ANOVA further revealed strong nonlinear interactions between the processing parameters. The optimized membrane (80% magnesite, sintered at 1150 °C) exhibited balanced porosity (51.7%), high proton conductivity (0.31 S/cm), and favorable electrochemical performance, yielding an MPD of 50.69 mW/m² and a CE of 64.7%. All membranes maintained high wastewater treatment efficiency, with COD and BOD removal exceeding 90%. These findings highlight magnesite-rich ceramics as accessible and economically attractive membranes for bioelectricity generation and wastewater treatment.

1. Introduction

The global transition toward sustainable and low-carbon energy systems has intensified research on technologies that support clean electricity generation and hydrogen production. Within this context, bioelectrochemical systems (BESs), including microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), offer a complementary pathway by converting biodegradable waste streams into renewable energy carriers such as bioelectricity, biohydrogen, and biomethane [1–3]. MFCs are particularly attractive because they couple wastewater treatment with clean energy recovery within a single platform [4,5]. Nevertheless, their practical deployment remains constrained largely by the performance and cost of the proton exchange membrane (PEM), which governs proton transport and strongly influences overall cell output [6].

Commercial PEMs such as Nafion® offer high proton conductivity but present challenges including high cost, limited durability in neutral environments, oxygen crossover, and susceptibility to biofouling. These drawbacks restrict operational stability and hinder cost-effective scaling of MFC technology. Consequently, developing alternative membranes that are inexpensive, chemically stable, mechanically robust, and

environmentally benign has become a key research priority [7–9].

Ceramic membranes have attracted attention due to their mechanical strength, thermal stability, and tunable ionic transport [10–13]. However, conventional ceramic membranes typically rely on industrially processed oxides such as alumina, zirconia, or silica, whose production involves high-purity precursors and sintering temperatures exceeding 1400 °C [14–16]. These requirements lead to high manufacturing costs, undermining the economic feasibility of ceramic PEMs for practical MFC applications. Therefore, identifying mineral resources that can serve as low-cost precursors and enable lower-temperature sintering is crucial for promoting ceramic membranes as viable PEM alternatives.

Magnesite and feldspar are abundantly available in Iran, offering an accessible raw-material base for developing cost-effective ceramic components [17]. Upon thermal decomposition, magnesite releases CO₂ and generates an interconnected pore network that can be advantageous for membrane applications. However, previous magnesite-based research has predominantly focused on structural ceramics or solid oxide fuel cell components [18], typically employing high sintering temperatures in the range of 1300–1600 °C. Studies such as Wang et al. [19], Aşkın et al. [20], and Manni et al. [21] demonstrate the potential

^{*} Corresponding author. Chemical Engineering Department, Faculty of Engineering, University of Sistan and Baluchestan, PO Box 98164-161, Zahedan, Iran.
E-mail address: v.yousefi@eng.usb.ac.ir (V. Yousefi).

of magnesite-derived porous ceramics; nevertheless, many reported processing routes still depend on very high sintering temperatures, which generally produce dense microstructures with predominantly closed porosity and thus limit their applicability as MFC membranes [22–25]. These gaps highlight the need for optimized, lower-temperature fabrication strategies tailored to the open-porosity requirements of microbial fuel cell systems.

As a result, the appropriate magnesite-based ceramic composition, processing conditions, and microstructural characteristics required to achieve suitable conductivity, porosity, and bioelectrochemical compatibility have not yet been systematically established in the context of MFC applications. Building upon prior advancements in ceramic membrane configurations, this study addresses these aspects by developing and optimizing ceramic composite membranes derived from natural magnesite, feldspar, and pottery clay. Using response surface methodology (RSM), the critical formulation and processing variables governing membrane conductivity, porosity, and mechanical integrity are identified. The optimized membranes are subsequently evaluated in double-chamber MFCs to assess electrochemical performance, internal resistance, and power output. This integrated materials-engineering and statistical-optimization framework provides a cost-effective pathway rooted in indigenous mineral resources and clarifies how ceramic composition and microstructure influence MFC performance.

Specifically, this work contributes to the field through (i) the systematic formulation of magnesite–feldspar ceramic composites tailored for MFC membranes, (ii) the quantitative optimization of their structural properties using RSM, and (iii) establishing explicit correlations between ceramic microstructure and electrochemical output. These contributions advance the design of durable, affordable membrane technologies for next-generation bioelectrochemical and sustainable energy systems.

2. Materials and methods

2.1. Materials and reagents

The magnesite and K-feldspar samples used in this study were obtained from the Kalateh Araban Magnesite Mine (Sarbisheh, Iran) and the Niloufar Tile Factory (Birjand, Iran), respectively. Pottery clay was purchased from a local market in Zahedan, Iran. All materials and reagents used for characterization and testing were procured from reputable suppliers and were of laboratory-grade quality.

2.2. MFC components and microbial cultures

A box-shaped MFC system was used in this study. It consisted of two identical Plexiglas chambers (4 cm × 4 cm × 2.5 cm), serving as the anode and cathode compartments, which were separated by a ceramic

membrane (4 cm in diameter). The anode electrode was composed of carbon cloth (CC; three layers, each 10 cm × 4 cm, Zoltek Panex 35), while the cathode electrode consisted of granular graphite (GG; 700 m²/m³, approximately 4 mm in diameter and 10–20 mm in length). Two perforated stainless-steel sheets (SS 316L) were employed as the anodic and cathodic current collectors in each chamber. In the anode chamber, the three layers of carbon cloth were suspended from the SS current collector using copper wires, providing a suitable surface for the growth and proliferation of anaerobic bacteria on the carbon fabrics.

During the anodic bio-oxidation of substrates in the wastewater, CO₂, H⁺, and electrons were generated. The produced electrons were transferred to the external circuit via the anodic current collector. Subsequently, the cathodic oxygen reduction reaction (ORR) occurred through the combination of electrons, protons, and oxygen to produce water. All components of the MFC—including the anode and cathode chambers and the ceramic membrane—were assembled and sealed using large screws and rubber gaskets.

Fig. 1 shows a photograph of the assembled MFCs inside the temperature-controlled chamber, along with a schematic diagram of their components. The anodic chamber was continuously fed with domestic wastewater collected from the septic tank of the wastewater treatment plant at the University of Sistan and Baluchestan. The liquid permeating through the ceramic membrane entered the cathode chamber, where it served as the catholyte and was aerated using an aquarium air pump to maintain an adequate oxygen supply for the oxygen reduction reaction (ORR). In each experiment, at least two identical microbial fuel cells were placed inside the constant-temperature chamber to achieve accurate and reproducible results and to minimize potential sources of error.

2.3. Preparation of magnesite-based ceramic membrane

The magnesite ore was crushed in multiple stages using a jaw crusher (Retsch BB200), a disc mill (Retsch DM200), and a sliding mill (HERZOG) until the particle size was reduced to below 45 µm. During grinding, 1–2 g of boric acid or approximately 8–10 drops of isopropanol were added to prevent agglomeration of fine particles. A 45-µm (325-mesh) sieve was then used to determine particle size and verify uniformity. An Alpine sieve (SCL), equipped with a dust trap and vacuum suction, was used to pass the powder through the mesh. Approximately 6% of the magnesite particles remained on the 45-µm sieve, while 94% were smaller than 45 µm and passed through. K-feldspar was similarly sieved to obtain particles finer than 45 µm, whereas pottery clay was used as received without sieving. K-feldspar and clay were incorporated to reduce the melting temperature of magnesite and to improve the ceramic's strength and proton conductivity, respectively.

The mixing ratios of magnesite, feldspar, and clay powders were selected based on the RSM experimental design. Ceramic separators

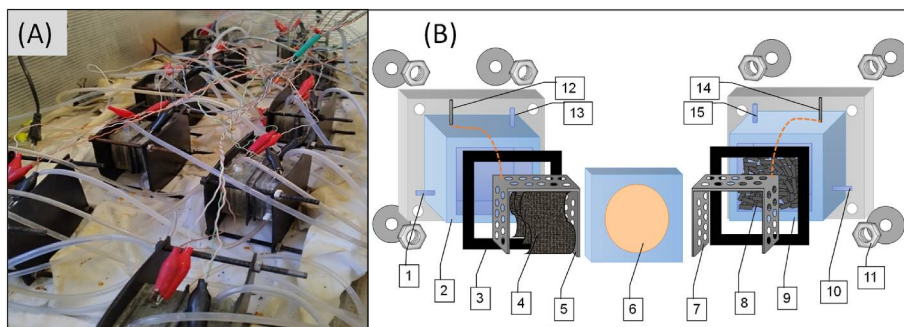


Fig. 1. (A) A picture of the assembled MFCs positioned inside the temperature-controlled chamber. (B) Schematic diagram of the MFC components: (1) anode inlet, (2) anode chamber, (3) rubber gasket, (4) anode carbon cloth, (5) internal anodic current collector (perforated stainless steel plate), (6) ceramic membrane, (7) internal cathodic current collector (perforated stainless steel plate), (8) cathode electrode (granular graphite), (9) cathode chamber, (10) cathode inlet, (11) nuts and bolts, (12) external anode current collector (stainless steel rod), (13) Anode outlet, (14) external cathode current collector (stainless steel rod), (15) cathode outlet.

were fabricated using the conventional dry-pressing method, following standard procedures reported in previous ceramic-forming studies [26]. Approximately 7 mL of water per 100 g of dry powder was added to improve granulation, and the moistened mixture was kept in a sealed nylon bag for 24 h to ensure uniform moisture distribution. The granulated powders were then pressed in a 4 cm-diameter mold at 5–10 MPa for 30 s. The resulting green bodies (1–1.5 mm thick) were dried at 100 °C for 24 h prior to sintering.

The heating profile was carefully controlled due to the thermal decomposition of magnesite ($\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$) during firing. The temperature was raised from room temperature to 600 °C at 3 °C/min and held for 2 h to prevent defect formation. It was then increased to the final sintering temperatures (1000, 1100, 1150, 1200, and 1300 °C) at the same rate and held for 2 h to ensure full densification and stable bonding.

2.4. Experimental design using RSM

2.4.1. Selection of process variables and their ranges

RSM was employed to optimize the proportions of magnesite, clay, and potassic feldspar in the ceramic formulation, as well as the sintering temperature. Magnesite content was defined as the first independent variable and was examined at five levels: 20%, 40%, 50%, 60%, and 80%. The selected levels of magnesite used in the experimental design are summarized in Table S1.

Since feldspar acts as the melting aid in the ceramic mixture, its content was defined as a linear function of the magnesite percentage, varying between 0% and 20%. The addition of feldspar as a fluxing agent was essential to promote vitrification and ensure the mechanical integrity of the ceramic matrix at the moderate sintering temperatures (1000–1300 °C); therefore, a feldspar-free formulation was not suitable for membrane fabrication. Higher magnesite levels require higher feldspar content, and accordingly, feldspar could not be treated as an independent variable in the optimization. The linear relationship was established such that at the maximum magnesite level (80%), the feldspar content reached its upper limit of 20%, while at the minimum magnesite level (20%), it was reduced to zero. Accordingly, the feldspar content was calculated using Equation (1):

$$F(\%) = 0.333 \text{ Mg}(\%) - 0.6667 \quad (1)$$

where $F(\%)$ and $\text{Mg}(\%)$ denote the potassic feldspar and magnesite fractions in the ceramic formulation, respectively. The remaining portion of the composition was completed with clay to achieve a total of 100%.

Because the optimal sintering temperature is strongly dependent on the raw material chemistry, the final sintering temperature was included as the second independent variable in the design. Five temperatures—1000, 1100, 1150, 1200, and 1300 °C—were selected (Table S1). The resulting ceramic samples were designated as $C\text{-}x\text{Mg}\text{-}T$, where x represents the magnesite content (%), and T denotes the final sintering temperature (°C).

2.4.2. Design of experiments (Central Composite Design)

The experimental design was developed using RSM and a Central Composite Design (CCD) with five levels for two independent factors: magnesite content and final sintering temperature, as specified in Design-Expert 12. As presented in Table S2, the design included ± 1 factorial levels, a center (0) level, and axial points at $\pm \alpha$. The axial value α was set to 3 to extend the design space and capture broader variable effects. Magnesite content and sintering temperature were selected as independent factors due to their decisive influence on membrane porosity, density, strength, and proton conductivity.

A total of twenty experiments were designed (Table S2). Each run was performed at least in duplicate, while two formulations (C 0.8 Mg 1150 and C 0.5 Mg 1150) were replicated four times to enhance

reproducibility and minimize experimental error. Mean values along with standard deviations are reported for all measured parameters; for statistical analysis, individual replicate data points were used rather than averaged. These replication schemes were carefully tailored to balance the requirements of the Design of Experiments (DoE) framework with the long-term operational constraints inherent to MFC systems, which require extended stabilization periods. While this replication strategy ($n = 2/4$) is sufficient for identifying key performance trends and establishing a reliable baseline for membrane comparison, the authors acknowledge that the limited number of biological replicates represents an inherent limitation of this study. In contrast, for material characterization—where operational time-scales are not a constraint—at least ten membranes were fabricated per composition, and measurements such as porosity were conducted with five repeats to ensure robust data reliability.

Statistical analyses were carried out using SPSS 26.0 and Design-Expert 12.0. Given the multivariate nature of MFC behavior, a multivariate analysis of covariance (MANCOVA) was first applied, with maximum power density (MPD) and coulombic efficiency (CE) as dependent variables. Magnesite content (%) and sintering temperature (°C) were used as independent variables, and porosity was included as the covariate. In the subsequent phase, separate ANOVA tests were performed for MPD and CE.

2.5. Membrane characterization techniques

The dimensions of the ceramic samples were measured using a caliper and an ASIMETO thickness meter (Japan). Surface morphology at the micrometer scale was examined using FESEM (KYKY EM-8000F) on both the surface and cross-sections of the membranes. EDS spectra and elemental mapping were collected simultaneously. The chemical composition of the ceramics was analyzed using XRF (ED 2000, OXFORD) in accordance with ISO/IEC 17025:2005, and FTIR spectra were obtained using a Bruker Tensor II instrument.

The apparent porosity and water absorption capacities of the ceramics were measured following the ASTM C373-88 standard procedure [27]. Briefly, samples were dried, weighed, boiled in distilled water, and then kept immersed for 24 h to ensure full saturation. The dry, saturated, and suspended weights were subsequently recorded, and porosity and water absorption were calculated accordingly.

The linear shrinkage of the ceramics was determined based on the change in diameter before and after sintering, using the ratio of the dimensional change to the initial diameter [28].

2.6. MFC performance evaluation

The open-circuit voltage (OCV) and current output of the MFCs were monitored at regular intervals using a digital multimeter (VC 9805, Zhangzhou Weihua Electronic Co., Ltd., Fujian, China). Current generation was evaluated at two external resistances ($R_{\text{ex}} = 100 \Omega$ and $1 \text{ k}\Omega$) using Ohm's law ($I = V/R_{\text{ex}}$).

A concentration-polarization test was conducted by varying the external resistance from 46,000 Ω to 15 Ω , and the corresponding stabilized voltages were recorded. Power ($P = VI$) and current ($I = V/R_{\text{ex}}$) were then calculated, and the power density (PD, mW/m^2) and current density (CD, mA/m^2) were normalized to the effective membrane surface area (12.56 cm^2) for constructing the polarization curves.

The chemical oxygen demand (COD) of the wastewater was measured using a CSB/COD-AL38 reactor in combination with an AQUALYTIC AL250 photometer. Biological oxygen demand (BOD) was determined with OxiTop® IS BOD measurement bottles. The wastewater treatment efficiency was calculated according to Equation (2):

$$\text{COD removal}(\%) = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{out}}}{\text{COD}_{\text{in}}} \times 100 \quad (2)$$

where COD_{in} and COD_{out} represent the inlet and outlet COD concentrations, respectively. The BOD removal efficiency was calculated analogously.

The Coulombic efficiency (CE, %) of the MFCs was defined as the ratio of the total electrons experimentally recovered to the theoretical electrons obtainable from complete substrate oxidation (Equation (3)) [29,30]:

$$CE(\%) = \frac{M \int_0^t Idt}{F n V_{anode} \Delta COD} \quad (3)$$

where $M = 32 \text{ g mol}^{-1}$ is the molecular mass of oxygen, F is the Faraday constant, $n = 4$ is the number of electrons transferred per mole of oxygen, V_{anode} is the anode chamber volume, and ΔCOD is the difference between inlet and outlet COD values.

2.7. Electrochemical characterization methods

Cyclic voltammetry (CV) was employed to investigate the kinetics of electrochemical reactions and the electron-transfer behavior in the MFCs. CV measurements were performed over a potential range from -1.0 to $+1.0 \text{ V}$ at a scan rate of 0.1 V s^{-1} , using the cathode as the working electrode and the anode as the counter electrode. Electrochemical impedance spectroscopy (EIS) was conducted to determine the internal resistance of the MFCs and to evaluate the proton conductivity of the membrane in the frequency range of 5 mHz – 1 MHz with an AC perturbation amplitude of 10 mV . Electrochemical analyses were carried out using a potentiostat/galvanostat (Autolab PGSTAT302 N, Metrohm, The Netherlands).

The internal resistance components were extracted by fitting the impedance spectra with an equivalent electrical circuit (EEC) model using ZView software (Version 3.4e). The proton conductivity (σ , S cm^{-1}) of the ceramic membranes was calculated according to Equation (4):

$$\sigma = \frac{L}{R_s A} \quad (4)$$

where L (cm), A (cm^2), and R_s (Ω) denote the membrane thickness, cross-sectional area, and ohmic resistance, respectively.

3. Results

3.1. Characterization of ceramic membranes

3.1.1. Physical properties of ceramics

The physical properties of the ceramic membrane samples were significantly influenced by both composition and sintering temperature. The key parameters—including shrinkage ratio, porosity, water absorption, and particle/pore sizes—are summarized in Table 1. FESEM surface and cross-sectional images are presented in Fig. 2, and particle/pore size distributions in Fig. S1.

The C-0.5 Mg-1300 sample (1300°C) exhibits a densified

microstructure with markedly reduced porosity, consistent with enhanced particle coalescence at high temperatures. It also shows the highest shrinkage (16.25%), largest particle size ($1.105 \mu\text{m}$), and smallest pore size ($0.062 \mu\text{m}$), indicating intensive grain growth and pore closure. Its low porosity (35.94%) and water absorption (23.29%) further confirm advanced densification.

In contrast, C-0.5 Mg-1000 and C-0.4 Mg-1100 show the lowest shrinkage (1.25%) and maintain high porosity and water absorption (52.68%/47.90%; 38.39%/32.04%). Their smaller particle sizes and moderate pore sizes reflect limited diffusion and inhibited grain growth at lower temperatures. C-0.5 Mg-1000 exhibited insufficient mechanical strength and was therefore excluded from FESEM imaging.

Samples sintered at intermediate temperatures (1150 – 1200°C)—C-0.2 Mg-1150, C-0.5 Mg-1150, C-0.8 Mg-1150, C-0.6 Mg-1200, and C-0.4 Mg-1200—show moderate shrinkage (3.5–5.125%) with composition-dependent porosity and water absorption. Among them, C-0.8 Mg-1150 demonstrates high porosity ($51.722 \pm 2.184\%$), controlled shrinkage ($4.437 \pm 0.972\%$), and high water absorption ($39.181 \pm 3.703\%$), indicating balanced densification that preserves functional porosity essential for MFC membranes. FESEM images show uniform grain–pore distribution, with mild grain agglomeration insufficient to cause pore closure. The C-0.2 Mg-1150 sample, containing the highest clay fraction, shows the largest pore size ($0.622 \pm 1.034 \mu\text{m}$) and a broad particle-size distribution (0.3 – $4 \mu\text{m}$) due to unsieved clay particles. Its high porosity ($47.719 \pm 5.457\%$), water absorption ($28.611 \pm 3.096\%$), and FESEM evidence of large open pores confirm a highly permeable structure (pore volume $\sim 31.73\%$).

Samples sintered at 1200°C —C-0.6 Mg-1200 and C-0.4 Mg-1200—display moderate shrinkage, high water absorption, and small particle/pore sizes, indicating limited but effective densification without excessive grain growth. FESEM images show uniform, sufficiently porous microstructures.

Overall, increased sintering temperature ($>1200^\circ\text{C}$) leads to enhanced shrinkage, grain growth, and pore elimination, while lower temperatures preserve porosity and inhibit grain coalescence. FESEM results correlate closely with particle-size distributions, confirming that the interplay of thermal treatment and raw-material composition governs densification pathways and final membrane microstructure—critical for optimizing ceramic separators for MFC applications.

Overall, increased sintering temperature ($>1200^\circ\text{C}$) leads to enhanced shrinkage, grain growth, and progressive pore elimination, whereas lower temperatures preserve porosity and inhibit grain coalescence. FESEM observations correlate closely with particle size distributions, confirming that the interplay of thermal treatment and raw material composition governs densification pathways and final membrane microstructure. Importantly, membrane porosity represents an inherent transport trade-off: although higher pore volume and connectivity facilitate ionic mobility and reduce ohmic resistance, excessive openness may promote oxygen and substrate crossover, compromising anodic anaerobicity, Coulombic efficiency, and operational stability [11,29,30]. Thus, optimal performance in ceramic MFC separators does not arise from maximizing porosity, but from achieving a balanced microstructure that preserves proton-conductive pathways while

Table 1
Physical specifications of the ceramic samples.

Ceramic membrane	Thickness (mm)	D-ceramic (mm)	Shrinkage ratio (%)	Apparent Porosity (%)	Water Absorption (%)	Particle size (μm)	Pore size (μm)
C-0.2 Mg-1150	2.029 ± 0.024	38.10 ± 0.011	3.54 ± 0.125	47.719 ± 5.457	28.611 ± 3.096	0.460 ± 0.390	0.622 ± 1.034
C-0.5 Mg-1300	1.859 ± 0.092	33.50 ± 0.015	16.25 ± 0.235	35.943 ± 3.676	23.288 ± 1.395	1.105 ± 0.797	0.062 ± 0.172
C-0.5 Mg-1150	1.826 ± 0.029	38.25 ± 0.016	4.38 ± 0.312	49.021 ± 4.673	30.791 ± 1.590	0.354 ± 0.282	0.075 ± 0.255
C-0.8 Mg-1150	1.869 ± 0.048	37.95 ± 0.014	4.44 ± 0.972	51.722 ± 2.184	39.181 ± 3.703	0.139 ± 0.513	0.053 ± 0.248
C-0.5 Mg-1000	1.869 ± 0.119	39.5 ± 0.009	1.25 ± 0.533	52.681 ± 7.977	38.386 ± 15.333	0.348 ± 0.255	0.079 ± 0.288
C-0.6 Mg-1200	1.847 ± 0.027	38.35 ± 0.024	4.13 ± 0.471	47.984 ± 15.145	39.764 ± 1.918	0.203 ± 0.162	0.066 ± 0.162
C-0.4 Mg-1100	1.8135 ± 0.033	39.5 ± 0.012	1.25 ± 0.327	47.902 ± 11.166	32.035 ± 4.133	0.203 ± 0.140	0.058 ± 0.198
C-0.4 Mg-1200	1.947 ± 0.091	38.6 ± 0.007	3.50 ± 0.625	50.914 ± 0.213	35.075 ± 0.427	0.205 ± 0.117	0.061 ± 0.181

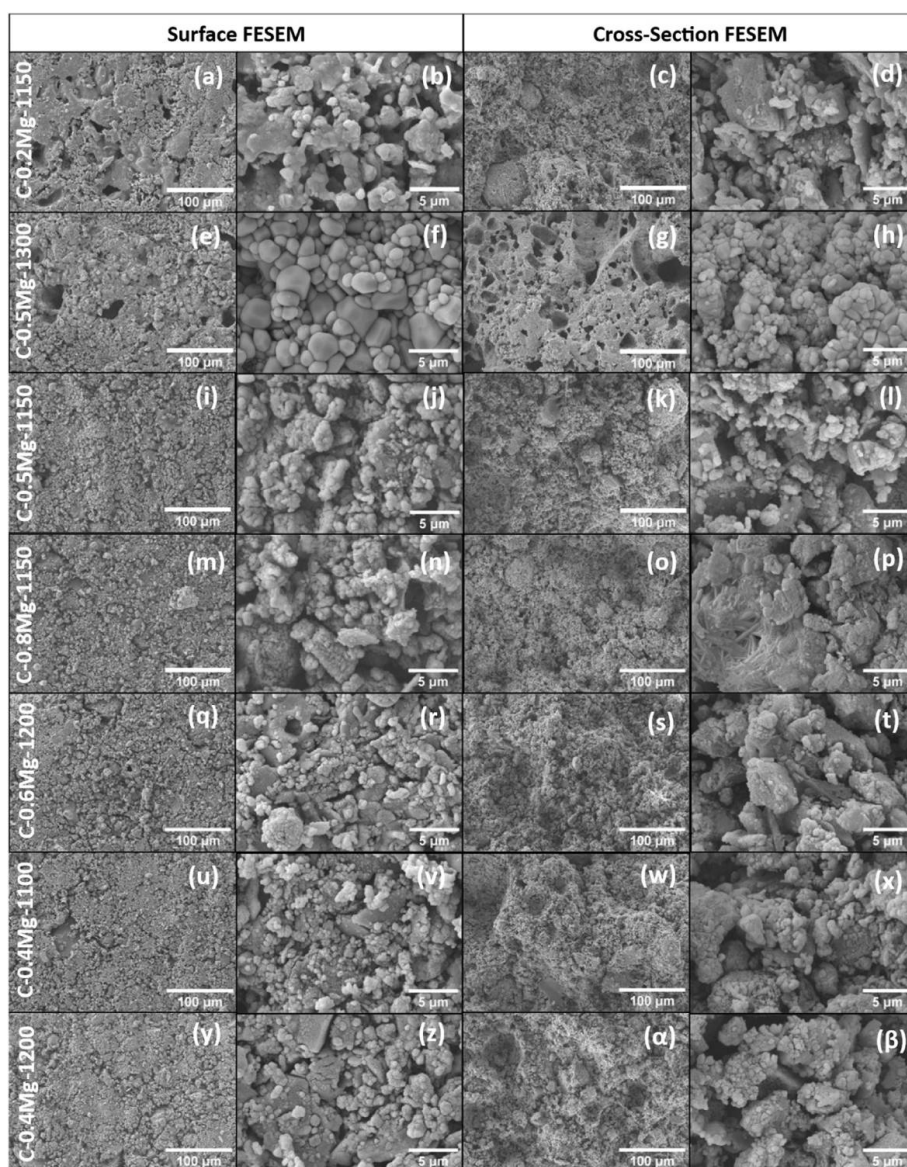


Fig. 2. FESEM micrographs of the ceramic separator samples. The first and second columns display the surface morphology, while the third and fourth columns present the corresponding cross-sectional images at varying magnifications. Each row corresponds to a distinct ceramic membrane composition: C-0.2 Mg-1150, C-0.5 Mg-1300, C-0.5 Mg-1150, C-0.8 Mg-1150, C-0.6 Mg-1200, C-0.4 Mg-1100, and C-0.4 Mg-1200.

maintaining selectivity and mechanical integrity.

3.1.2. Chemical composition and structure

3.1.2.1. XRF results. The chemical composition of the raw materials (magnesite and K-feldspar) is summarized in Table S3. Magnesite shows a high MgO content (45.35%), confirming its suitability as the primary magnesium source. The loss on ignition (LOI) value is notably high at 49.51%, which is attributed to the decomposition of MgCO_3 during heating. Minor constituents, including small amounts of SiO_2 , CaO , and Fe_2O_3 , together with trace oxides (Al_2O_3 , K_2O , Na_2O , MnO , P_2O_5 , SO_3), indicate the potential formation of secondary silicate/aluminate phases that may influence sintering behavior and densification.

K-feldspar contains high SiO_2 (81.30%) and Al_2O_3 (10.95%) and serves as the primary fluxing agent. The presence of K_2O (5.06%) promotes vitrification and facilitates the formation of a liquid phase during sintering. Minor oxides such as CaO , Fe_2O_3 , BaO , TiO_2 , and MgO appear in small amounts, while other oxides remain below detection limits.

Overall, the XRF data confirm the chemical compatibility of

magnesite and feldspar for ceramic membrane fabrication. Magnesite provides MgO-rich structural stability, while K-feldspar enhances liquid-phase formation and densification during sintering.

3.1.2.2. FTIR spectroscopic analysis. FTIR analysis of the C-0.8 Mg-1150 sample (80% magnesite and 20% feldspar, sintered at 1150 °C) is presented in Fig. S2. The FTIR spectroscopy results provide crucial insights into the phase changes and the compounds formed during the high-temperature treatment.

The absence of characteristic carbonate bands at $\sim 1420\text{--}1450\text{ cm}^{-1}$ and $\sim 2500\text{ cm}^{-1}$ confirms the complete decomposition of MgCO_3 and the formation of periclase (MgO). The broad absorption band between 1006.29 and 958.32 cm^{-1} corresponds to asymmetric stretching of Si–O–Si and Si–O–Al groups, indicating the development of aluminosilicate glass and/or crystalline silicate phases derived from feldspar melting.

Additional bands in the $775\text{--}610\text{ cm}^{-1}$ region correspond to O–Si (Al)–O bending modes, while features around $504\text{--}475\text{ cm}^{-1}$ are associated with O–Si–O deformation and Mg–O vibrations. The band near

876.87 cm^{-1} can be attributed to Mg–O stretching or mixed Mg–Si–O vibrations, suggesting interaction between MgO released from magnesite decomposition and silicate phases from feldspar. This interaction supports the potential formation of magnesium silicates, such as forsterite or enstatite.

These spectral features collectively indicate effective phase evolution at $1150\text{ }^{\circ}\text{C}$, leading to a mixed magnesium–aluminosilicate structure with a continuous glassy phase.

3.1.2.3. EDS and elemental mapping. EDS results for the C-0.8 Mg-1150 sample (Table S4) reflect the final elemental distribution after sintering. The composition is dominated by Mg-bearing phases (Mg: 28.04 wt%, corresponding to $\sim 46.5\text{ wt}\%$ MgO). Significant amounts of SiO_2 (27.75 wt%) and Al_2O_3 (6.91 wt%) originate from feldspar, while CaO, FeO, Na_2O , and K_2O appear as minor constituents related to natural impurities. The sample exhibits refined microstructural characteristics, with an average pore size of $0.053\text{ }\mu\text{m}$ and average particle size of $0.139\text{ }\mu\text{m}$, confirming effective sintering and particle coalescence at $1150\text{ }^{\circ}\text{C}$. The high MgO content contributes to enhanced liquid-phase formation and improved ionic transport pathways, promoting densification while limiting excessive grain growth.

Elemental mapping (Fig. S3) shows a homogeneous spatial distribution of Mg, Si, and Al, confirming efficient interaction and formation of a uniform magnesium–silicate network. The relatively even distribution of K further supports the presence of a dispersed glassy phase. The absence of elemental agglomeration indicates proper diffusion and chemical homogenization during sintering.

3.2. MFC performance with magnesite-based ceramic membranes

3.2.1. Electricity generation performance

Table 2 presents the average electrochemical performance of the MFCs from 20 runs, including OCV, current generation under $100\text{ }\Omega$ and $1000\text{ }\Omega$ loads, CE, MPD, MCD, and treatment efficiencies. After ~ 10 days of operation, OCV values ranged between $375 \pm 89\text{ mV}$ (C-0.6 Mg-1200) and $493.5 \pm 33\text{ mV}$ (C-0.4 Mg-1100), showing modest variation in intrinsic cell potential.

Under a $100\text{ }\Omega$ load, C-0.2 Mg-1150 exhibited the highest current ($1.49 \pm 0.41\text{ mA}$), followed by C-0.8 Mg-1150 ($1.04 \pm 0.16\text{ mA}$). Conversely, C-0.5 Mg-1000 and C-0.5 Mg-1300 recorded the lowest outputs, reflecting differences in internal resistance and charge-transfer dynamics. The poor performance of C-0.5 Mg-1000 is attributed to inadequate sintering and low proton conductivity, whereas excessive densification at $1300\text{ }^{\circ}\text{C}$ reduced porosity and water uptake, hindering proton transport. Thus, both under- and over-sintering restrict membrane efficiency.

Currents under $1000\text{ }\Omega$ were lower ($0.139\text{--}0.324\text{ mA}$), as expected.

CE varied widely—from $23.05 \pm 3.63\%$ (C-0.5 Mg-1000) to $74.69 \pm 1.39\%$ (C-0.2 Mg-1150)—indicating significant differences in electron recovery. Overall, membranes sintered at intermediate temperatures with balanced MgO/feldspar ratios (notably C-0.2 Mg-1150 and C-0.8 Mg-1150) exhibited superior electrochemical and treatment performance, highlighting the strong linkage between microstructure, proton transport, and MFC efficiency.

As shown in Fig. 3A, the power density–current density curves display nonlinear and multi-peaked profiles, reflecting the coupled electrochemical and biological processes governing MFC operation. At low current densities, power output increases as electron transfer proceeds efficiently; however, beyond a threshold, kinetic limitations at both electrodes reduce reaction rates, causing a decline in power density. These limitations arise from restricted substrate transport to the anode, oxygen diffusion to the cathode, and biologically mediated electron-transfer kinetics that weaken under higher loads.

Internal ohmic resistances—including ionic transport resistance, membrane resistance, and biofilm impedance—further distort the expected bell-shaped curve, producing skewed or multiple peaks. Biological instability during polarization testing, particularly the sensitivity of microbial activity to rapid changes in external resistance, also contributes to the oscillatory pattern observed in several curves.

A notable feature of the polarization curves is the broadness of the main peaks. Such wide plateau-like regions indicate that, over intermediate current densities, the system achieves a temporary balance between electron generation, mass transfer, and electrode kinetics, allowing relatively stable power output across a wider operational range than typically reported for MFCs.

At higher current densities, the sharp fluctuations and rapid voltage decay observed in both Fig. 3A and B are characteristic of concentration polarization. Here, the consumption rate of electroactive species exceeds their diffusion rate to the electrode surface, leading to local depletion, reduced reaction rates, voltage loss, and ultimately a steep drop in power density. These effects collectively underscore the intertwined influence of microstructure, mass transfer, and bioelectrochemical kinetics on the performance of the ceramic-based MFCs.

Fig. 3B illustrates the characteristic polarization behavior of the MFCs, revealing the three operational regions typically observed in bioelectrochemical systems. In the activation-controlled region ($0\text{--}\sim 100\text{ mA/m}^2$), a steep voltage drop occurs due to the energy required to initiate anodic oxidation and cathodic reduction reactions, indicating pronounced kinetic limitations at both electrodes. As the current increases to the medium range ($\sim 100\text{--}400\text{ mA/m}^2$), the voltage decline becomes more gradual, reflecting dominant ohmic losses associated with ionic transport through the electrolyte, membrane resistance, and electrical connections. At higher current densities ($>500\text{ mA/m}^2$), the voltage rapidly approaches zero as concentration polarization

Table 2

The electricity production and wastewater treatment efficiencies of the MFCs.

Membrane	OCV (mV)	I vs. $100\text{ }\Omega$ (mA)	I vs. $1000\text{ }\Omega$ (mA)	CE (%)	MPD (mW/m^2)	MCD (mA/m^2)	COD removal (%)	BOD removal (%)
C-0.2 Mg-1150	399.26 ± 38.67	1.49 ± 0.41	0.287 ± 0.07	74.69 ± 1.39	32.78 ± 0.72	1035.03 ± 56.29	93.241 ± 0.17	93.518 ± 1.75
C-0.5 Mg-1300	412.23 ± 16.18	0.78 ± 0.05	0.324 ± 0.04	45.56 ± 5.19	30.95 ± 6.51	716.56 ± 2.46	93.426 ± 0.43	90.741 ± 2.31
C-0.5 Mg-1150	389.71 ± 32.18	0.96 ± 0.13	0.222 ± 0.06	47.76 ± 5.45	20.57 ± 2.44	547.37 ± 56.30	96.29 ± 0.26	91.67 ± 3.93
C-0.8 Mg-1150	397.98 ± 9.87	1.04 ± 0.16	0.200 ± 0.05	64.74 ± 11.78	50.69 ± 9.05	1404.94 ± 165.05	93.56 ± 0.72	89.81 ± 3.93
C-0.5 Mg-1000	442.5 ± 10.61	0.57 ± 0.21	0.228 ± 0.06	23.05 ± 3.63	44.09 ± 0.14	322.45 ± 5.63	93.241 ± 0.65	92.593 ± 1.75
C-0.6 Mg-1200	375 ± 89.09	1.02 ± 0.27	0.243 ± 0.04	62.63 ± 1.02	43.79 ± 2.76	268.71 ± 14.07	92.685 ± 0.21	90.741 ± 2.45
C-0.4 Mg-1100	493.5 ± 33.23	0.53 ± 0.27	0.139 ± 0.06	35.42 ± 1.41	6.15 ± 2.29	105.49 ± 19.70	93.056 ± 0.14	89.815 ± 2.31
C-0.4 Mg-1200	481.5 ± 12.02	0.74 ± 0.46	0.252 ± 0.04	23.73 ± 2.43	47.03 ± 7.05	445.86 ± 16.21	91.667 ± 0.24	90.741 ± 1.75

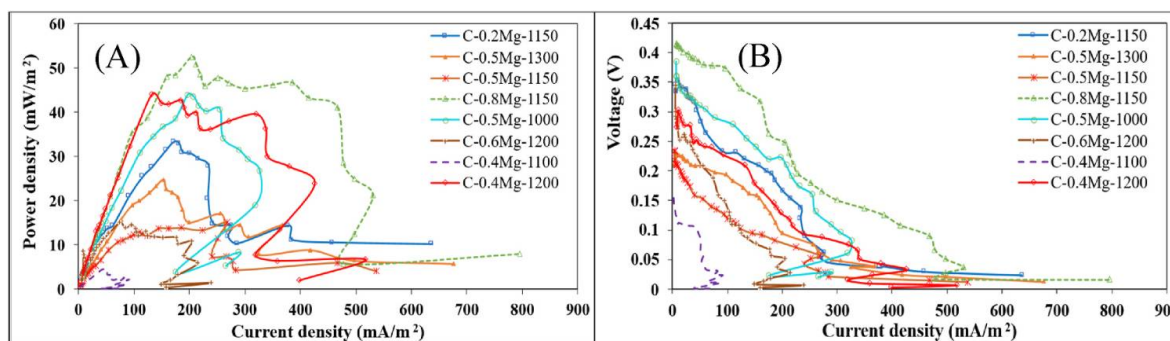


Fig. 3. The polarization results: (A) the power density versus the current density plots, (B) the closed-circuit voltage versus the current density plots.

becomes significant; here, reactant consumption exceeds mass-transfer rates, leading to reactant depletion near electrode surfaces and severe voltage decay.

Consistent with these behaviors, Table 2 shows that the highest MPD and MCD were achieved by C-0.8 Mg-1150 ($50.69 \pm 9.05 \text{ mW/m}^2$ and $1404.94 \pm 165.05 \text{ mA/m}^2$, respectively). Although C-0.4 Mg-1200 produced a comparable MPD ($47.03 \pm 7.05 \text{ mW/m}^2$), its maximum current density was substantially lower ($445.86 \pm 16.21 \text{ mA/m}^2$), indicating higher internal resistance or stronger mass-transfer limitations despite reasonable power output.

Overall, the polarization responses confirm the inherent trade-off between voltage, current generation, power density, and electron-utilization efficiency (CE). These trends reinforce that both ceramic composition and sintering treatment exert significant influence on electrochemical behavior, governing the balance between kinetic, ohmic, and mass-transfer processes within the MFCs.

3.2.2. Wastewater treatment performance

Table 2 summarizes the wastewater treatment performance of the ceramic-based MFCs. The septic-tank domestic wastewater utilized in this study had an average initial COD of $1080 \pm 57.87 \text{ mg/L}$, BOD_5 of $540 \pm 34.18 \text{ mg/L}$, pH of 7.2 ± 0.2 , and electrical conductivity of $1.8 \pm 0.2 \text{ mS/cm}$. The chemical composition of wastewater [29] is exhibited in Table S5 in the supplementary information file.

All membranes achieved high removal efficiencies, with COD reduction ranging from 91.67% to 96.29% and BOD_5 removal between 89.81% and 93.52%. The C-0.5 Mg-1150 membrane showed the highest performance, reaching 96.29% COD and 93.52% BOD_5 removal. Although the high organic removal (>90%) can partially involve non-electrogenic pathways, such as aerobic degradation facilitated by oxygen crossover through the porous ceramic structure (~35–52% open porosity), the high Coulombic efficiency (64.7%) suggests that electrogenesis remained the dominant pathway in the optimized system. Nonetheless, future studies focusing on pH gradients across the membrane and microbial community dynamics are required to fully delineate these transport phenomena.

Statistical analysis using one-way ANOVA followed by Tukey's post-hoc test indicated that most differences among the samples were not significant at the 95% confidence level. Only the COD removal between C-0.5 Mg-1150 and C-0.4 Mg-1200 was statistically different ($p < 0.05$). Overall, the ceramic membranes exhibited broadly comparable treatment efficiencies, particularly regarding BOD_5 reduction.

3.2.3. Electrochemical performance

3.2.3.1. The EIS results. EIS measurements were conducted to quantify the internal impedance of the MFCs using an equivalent electrical circuit (EEC). The Nyquist plots are shown in Fig. 4, and the fitted parameters are listed in Table 3. The EEC includes the ohmic resistance (R_s), charge-transfer resistances at the anode and cathode (R_{ct-a} , R_{ct-c}), Gerischer

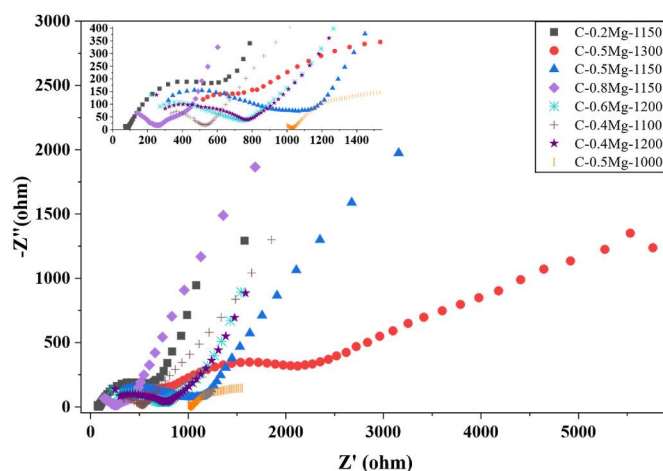


Fig. 4. The results of the Electrochemical Impedance Spectroscopy (EIS) analysis, the inset shows the high-frequency parts of each Nyquist plot with a higher resolution.

elements (GE), and constant-phase elements (CPE), consistent with previous models [29–31]. A comparative summary of R_s , R_{ct-a} , R_{ct-c} , diffusion-related resistances (R_{d-a} , R_{d-c}), total internal resistance, proton conductivity, and effective double-layer capacitance is provided in Fig. 5 to illustrate differences among the ceramic configurations.

Proton conductivity (σ) showed a broad distribution across the ceramic membranes, spanning from $600.24 \mu\text{S/cm}$ in C-0.5 Mg-1000 to over $3 \times 10^5 \mu\text{S/cm}$ in C-0.8 Mg-1150. The latter also exhibited the lowest ohmic resistance ($R_s = 0.531 \Omega$), confirming that both magnesite content and an adequate sintering temperature (1150°C) jointly promote membrane hydration and proton mobility. In contrast, insufficient sintering (C-0.5 Mg-1000) and oversintering (C-0.5 Mg-1300) produced the highest ohmic impedances (254.2Ω and 200.7Ω , respectively), attributable to inadequate pore development in the former and excessive grain growth and densification in the latter.

Cathodic charge-transfer resistance (R_{ct-c}) ranged from 20.43Ω (C-0.2 Mg-1150) to 995.3Ω (C-0.5 Mg-1150), while anodic charge-transfer resistance (R_{ct-a}) varied between 22.01Ω (C-0.6 Mg-1200) and 538.2Ω (C-0.2 Mg-1150). The extremely low R_{ct-c} but high R_{ct-a} in C-0.2 Mg-1150 correlate with its large pore sizes, causing oxygen and electrolyte crossover that suppressed anodic biofilm maturation while enhancing cathodic ORR kinetics. The generally elevated R_{ct} values across all systems reflect the early-stage operation of the MFCs, during which microbial communities are not yet electrochemically optimized.

Diffusion-related resistances (R_{d-a} , R_{d-c}), derived from the Gerischer elements, further highlighted the influence of sintering conditions. C-0.5 Mg-1000 exhibited the highest diffusion impedances at both electrodes ($\approx 950 \Omega$), confirming the detrimental effect of insufficient

Table 3
The internal resistance components obtained from the EIS results.

EEC Elements	C-0.2 Mg-1150	C-0.5 Mg-1300	C-0.5 Mg-1150	C-0.8 Mg-1150	C-0.5 Mg-1000	C-0.6 Mg-1200	C-0.4 Mg-1100	C-0.4 Mg-1200
R_s (Ω)	64.6 ± 3.57	200.7 ± 15.61	34.27 ± 2.88	0.531 ± 0.016	254.2 ± 20.13	3.901 ± 0.56	208.7 ± 35.41	21.39 ± 2.56
σ ($\mu S/cm$)	2756.87 ± 221.02	1051.47 ± 104.67	4654.86 ± 391.87	312598.08 ± 7919.11	600.24 ± 52.14	41014.51 ± 242.18	709.46 ± 102.18	7781.55 ± 67.14
R_{ct-c} (Ω)	20.43 ± 9.12	349.5 ± 11.23	995.3 ± 54.73	353.7 ± 117.80	778.67 ± 124.55	759.7 ± 34.15	320.2 ± 21.35	805.4 ± 30.01
$GE-c \times 10^3$	4.924 ± 1.23	32.757 ± 3.17	2.461 ± 0.81	20.577 ± 1.31	1.056 ± 0.561	3.854 ± 0.891	2.891 ± 0.923	10.886 ± 4.561
$GE-c-P$	6.654 ± 2.451	0.017109 ± 0.0012	0.01013 ± 0.0007	18.72 ± 2.02	0.01675 ± 0.0002	1.75 ± 0.005	0.95901 ± 0.006	1.33 ± 0.02
R_{d-c} (Ω)	203.091 ± 42.18	30.528 ± 3.14	429.55 ± 141.62	48.695 ± 3.094	946.342 ± 5.47	259.484 ± 10.31	345.937 ± 33.16	91.861 ± 25.76
$CPE-c \times 10^6$	7.83 ± 0.43	14.1 ± 1.23	494.99 ± 68.9	3.003 ± 0.957	0.547 ± 0.011	12.8 ± 2.01	0.659 ± 0.001	20.3 ± 8.71
$CPE-c-P$	0.605 ± 0.01	0.310 ± 0.003	0.220 ± 0.02	0.420 ± 0.024	0.306 ± 0.0045	0.339 ± 0.0061	0.574 ± 0.012	0.307 ± 0.034
$Ceff-c \times 10^{12}(F/cm^2)^{1/2}$	64.572 ± 12.45	0.032 ± 0.001	$5.428 \times 10^{-3} \pm 7.67 \times 10^{-4}$	$2.435 \times 10^{-4} \pm 3.26 \times 10^{-5}$	$1.484 \times 10^{-6} \pm 7.36 \times 10^{-7}$	$1.538 \times 10^{-4} \pm 6.29 \times 10^{-5}$	1.821 ± 0.002	$1.480 \times 10^{-3} \pm 0.005$
R_{ct-a} (Ω)	538.2 ± 98.14	59.99 ± 14.09	296.1 ± 148.77	150.49 ± 98.30	444.3 ± 21.45	22.01 ± 2.87	50.07 ± 9.19	161.1 ± 15.23
$GE-a \times 10^3$	5.078 ± 0.001	$2.98 \times 10^{-3} \pm 0.0004$	1.598 ± 1.12	4.233 ± 1.51	1.045 ± 0.123	1.699 ± 0.045	1.66 ± 0.003	3.274 ± 0.245
$GE-a-P$	$1.35 \times 10^{-3} \pm 0.0003$	44.02 ± 10.045	$1.15 \times 10^{-2} \pm 0.013$	0.2134 ± 0.114	0.9011 ± 0.0056	0.6627 ± 0.0061	1.669 ± 0.001	$5.55 \times 10^{-3} \pm 0.0004$
R_{d-a} (Ω)	196.912 ± 17.47	335547.950 ± 126.78	833.437 ± 58.82	252.286 ± 90.014	956.388 ± 9.98	588.270 ± 11.23	602.119 ± 35.89	305.399 ± 61.42
$CPE-a \times 10^3$	0.354 ± 0.009	0.299 ± 0.012	5.161 ± 0.361	2.751 ± 0.190	4.91 ± 0.230	8.756 ± 0.022	6.316 ± 0.170	3.058 ± 0.034
$CPE-a-P$	0.670 ± 0.003	0.135 ± 0.004	0.500 ± 0.086	0.745 ± 0.129	0.407 ± 0.120	0.842 ± 0.141	0.790 ± 0.111	0.613 ± 0.023
$Ceff-a \times 10^6(F/cm^2)^{1/2}$	0.433 ± 0.002	$2.704 \times 10^{-12} \pm 9.004 \times 10^{-13}$	7.517 ± 0.614	2.106 ± 1.119	29.220 ± 7.891	37.501 ± 11.345	36.593 ± 8.770	4.221 ± 0.126
R_{total} (Ω)	1023.23 ± 89.450	336188.67 ± 1540.123	2588.66 ± 826.79	805.702 ± 73.589	3379.90 ± 145.09	1633.37 ± 79.456	6946.10 ± 231.671	1385.15 ± 102.468
Equivalent Electrical Circuit (EEC)								

^a The effective capacitance of the anodic and cathodic double layer was normalized by the surface area of the anode (120 cm²) and the cathode (336 cm²) electrodes, respectively.

sintering on mass transport. Conversely, C-0.5 Mg-1300 showed the lowest cathodic diffusion resistance (30.53 Ω) but an extraordinarily high anodic diffusion resistance ($>3 \times 10^5 \Omega$), indicating that excessive densification severely restricts substrate and proton transport at the anode, compromising microbial activity despite the high GE-a-P value (44.02).

Analysis of the CPE elements [32] and the calculated double-layer capacitances (Ceff) [30,33] revealed that anodic capacitance was consistently orders of magnitude higher than cathodic capacitance, consistent with thicker anodic biofilm formation. The almost negligible anodic capacitance in C-0.5 Mg-1300 ($2.70 \times 10^{-12} \mu F/cm^2$) indicates minimal biofilm adhesion, further explaining its high anodic diffusion and charge-transfer resistances.

It should be noted that the present study was designed to compare the effects of membrane composition and sintering-derived microstructure under short-term MFC operation, rather than to assess long-term durability or fouling resistance. While charge-transfer and diffusion-related resistances may evolve during biofilm maturation, ohmic resistance and proton conductivity are more directly governed by intrinsic membrane properties such as thickness, porosity, pore connectivity, and ionic transport pathways. Consequently, long-term stability, fouling progression, and regeneration performance should be addressed in future works.

Overall internal resistance (R_{total}) varied substantially among the ceramics, from 805.70 Ω (C-0.8 Mg-1150) to 336 k Ω (C-0.5 Mg-1300). These results demonstrate that proton conductivity is the predominant determinant of internal resistance and interfacial charge-transfer behavior. The comparative analyses confirm that optimized ceramic composition combined with an appropriate sintering temperature is essential for tailoring porosity, water retention, and electrochemical interface properties, ultimately enhancing MFC performance.

3.2.3.2. The cyclic voltammetry (CV) results. Fig. 6 shows the CV profiles of the MFCs constructed with the synthesized ceramic membranes. As summarized in Table S6, the anodic/cathodic peak currents ($I_{p-anode}$, $I_{p-cathode}$), peak separation (ΔI_p), and enclosed CV area vary substantially among samples. Capacitance values, calculated using Eq. (S1) from the integrated oxidative and reductive branches, confirm that larger CV areas correspond to higher charge-storage capacity and more efficient double-layer formation.

The C-0.8 Mg-1150 membrane exhibited the strongest electrochemical performance, with the largest CV area (0.7546 mA V), highest capacitance (1.8866 mF), and one of the widest peak separations ($\Delta I_p = 4.0799$ mA). The pronounced and well-resolved anodic and cathodic peaks reflect efficient oxidation and oxygen-reduction kinetics, supported by an optimized 80/20 magnesite–feldspar composition and controlled sintering at 1150 °C, which enhances porosity, improves proton transport, and reinforces surface electrocatalytic activity.

Other samples displayed weaker redox activity, as reflected by lower peak currents, reduced ΔI_p , and smaller CV areas. The C-0.2 Mg-1150 membrane showed a pronounced cathodic peak (−3.9399 mA) but limited anodic response (1.1468 mA), indicating restricted oxidation despite favorable conditions for oxygen reduction, consistent with EIS indications of pore-mediated oxygen/electrolyte crossover.

The C-0.5 Mg-1300 membrane exhibited the poorest anodic activity (0.2302 mA), a small CV area (0.1417 mA V), and low capacitance (0.3542 mF), attributable to a dense microstructure with hindered proton mobility. The C-0.5 Mg-1000 sample delivered the weakest overall profile—minimal peak currents, the smallest ΔI_p (0.8415 mA), CV area (0.0294 mA V), and capacitance (0.0735 mF)—highlighting the inadequacy of insufficient sintering.

Altogether, the CV data reinforce the critical role of ceramic composition and thermal processing in governing charge-storage behavior, redox responsiveness, and electrochemical efficiency in MFCs.

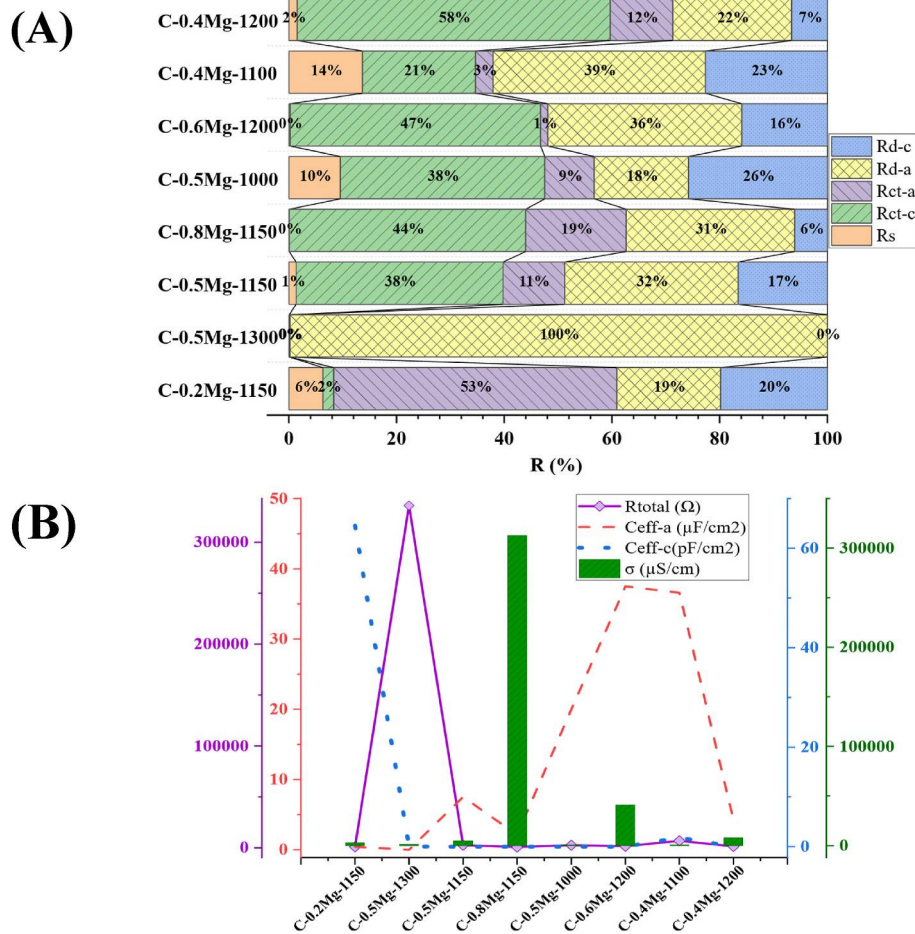


Fig. 5. (A) the comparison of the internal resistance components (%) for the ceramic membranes, (B) the comparison of the values of internal resistance (R_{total} , Ω), proton conduction (σ , $\mu\text{S}/\text{cm}$), and the effective capacitance of DL in the anode (C_{eff-a} , $\mu\text{F}/\text{cm}^2$) and the cathode (C_{eff-c} , pF/cm^2).

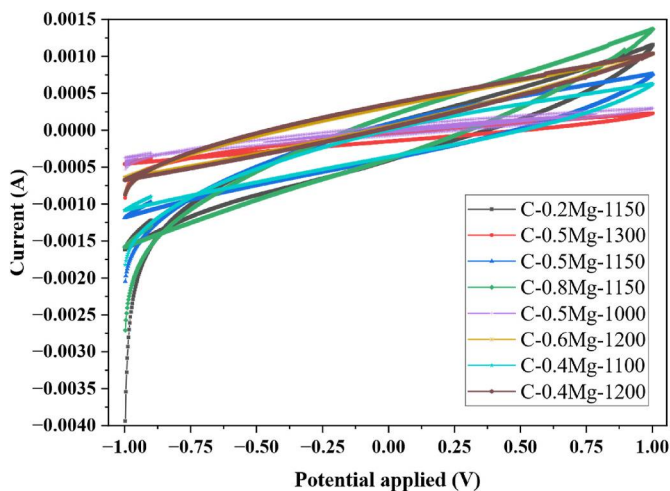


Fig. 6. The cyclic voltammetry (CV) results of the MFCs.

3.3. Statistical analysis of experimental data

Statistical analysis of the experimental data was performed to evaluate the effects of magnesite percentage and sintering temperature on microbial fuel cell outputs. Because biological systems such as MFCs can yield multiple correlated responses, a multivariate analysis of covariance (MANCOVA) was first applied, with MPD and CE as dependent

variables and ceramic porosity included as a covariate.

The MANCOVA assessed how magnesite content, sintering temperature, and porosity collectively influenced the two responses and revealed significant main effects. However, it did not provide sufficient resolution to interpret the interaction between the two independent variables. Therefore, separate ANOVA tests were subsequently performed for each response variable to more precisely evaluate both individual and interactive effects of the factors.

Together, the MANCOVA and ANOVA results offer a comprehensive statistical interpretation of system behavior. The experimental dataset used for these analyses is presented in Table S7.

3.3.1. The MANCOVA results

Before applying and interpreting the MANCOVA results, the assumptions and prerequisites of the test were examined. After confirming the normality of the data distribution across groups, the second fundamental assumption—homogeneity of the covariance matrices of the dependent variables across groups—was assessed. This assumption is critical; if violated, the interpretation of MANCOVA outputs becomes unreliable. The null hypothesis of equal covariance matrices was evaluated using the M-box test. Based on the Fisher statistic and its significance value ($F(3, 6480) = 0.705$, $p = 0.549 > 0.05$) at the 5% significance level, there is no evidence to reject the hypothesis of homogeneous covariance matrices among the groups.

Additionally, Levene's test was used to evaluate the equality of error variances across groups. The non-significant p-values for MPD (0.203) and CE (0.184), both greater than 0.05, indicate that the error variances of the dependent variables do not differ significantly across the groups.

The Wilks' Lambda results further show that magnesite content and sintering temperature exert statistically significant multivariate effects on the response variables ($p < 0.05$), whereas porosity does not ($p = 0.160$).

To ensure the homogeneity of regression slopes—another requirement for valid MANCOVA—a model incorporating interactions between the independent variables and the covariate was constructed, and an interactive MANCOVA was performed. Standard MANCOVA assumes that the covariate is linearly related to the dependent variables in the same way across all groups; if this linear relationship varies among groups, the assumption is violated, and the analysis becomes invalid. In the interactive model, the interactions between the independent variables (magnesite percentage and sintering temperature) and the covariate (porosity) were included. The null hypothesis stated that no interaction exists between each independent variable and the covariate (i.e., slopes are homogeneous), while the alternative hypothesis assumed significant interactions.

The analysis of covariance on the interactive model showed that the interaction terms magnesite $\times$ porosity ($p = 0.596$ for MPD; $p = 0.183$ for CE) and sintering temperature $\times$ porosity ($p = 0.571$ for MPD; $p = 0.187$ for CE) were not statistically significant ($p > 0.05$). Thus, the assumption of homogeneous regression slopes is upheld, supporting the use of the standard MANCOVA results (without interaction terms) with confidence.

Table 4 summarizes the results of the standard MANCOVA, evaluating the combined effects of magnesite content, sintering temperature, and porosity (as a covariate) on MPD and CE. The analysis revealed that magnesite content ($p < 0.001$) and sintering temperature ($p = 0.002$) exert statistically significant multivariate effects, confirming their substantial impact on MFC performance. In contrast, the effect of porosity was not statistically significant ($p = 0.160$), indicating its limited role under the tested experimental conditions.

Following the MANCOVA, which assessed the overarching effects of magnesite content and sintering temperature on the combined response variables, we conducted univariate ANOVA tests for each dependent variable. This step was essential not only to evaluate how each independent factor influences MPD and CE individually but also to investigate potential interaction effects between parameters that MANCOVA might not have explicitly identified.

3.3.2. ANOVA analysis for MPD

Table 5 presents the complete ANOVA results for MPD. The regression model is highly significant ($p < 0.0001$), confirming that at least one main factor or interaction exerts a meaningful influence on the response. The coefficient of determination ($R^2 = 0.9442$) indicates that

Table 4
The results of the standard MANCOVA analysis.

Source	Dependent Variable	Type III Sum of Squares	df	F-value	p-value	Partial η^2
Corrected Model	MPD (mW/m ²)	4665.739	8	6.579	0.003	0.827
	CE (%)	6334.484	8	11.130	0.000	0.890
Magnesite	MPD (mW/m ²)	2245.766	3	8.445	0.003	0.697
	CE (%)	2966.673	3	13.900	0.000	0.791
SinTemp	MPD (mW/m ²)	2653.629	3	9.978	0.002	0.731
	CE (%)	1149.445	3	5.386	0.016	0.595
Porosity	MPD (mW/m ²)	162.821	1	1.837	0.203	0.143
	CE (%)	186.373	1	2.620	0.134	0.192
Error	MPD (mW/m ²)	975.106	11			
	CE (%)	782.567	11			

Note: Model fit statistics were $R^2 = 0.827$ and adjusted $R^2 = 0.701$ for MPD, and $R^2 = 0.890$ and adjusted $R^2 = 0.810$ for CE.

Table 5

The results of ANOVA for MPD.

Source	Sum of Squares	df	F-value	p-value
Model	38.34	6	36.66	< 0.0001
A-Magnesite	2.61	1	14.96	0.0019
B-Temperature	1.19	1	6.84	0.0213
AB	0.4858	1	2.79	0.1190
A ²	9.06	1	51.97	< 0.0001
B ²	5.47	1	31.39	< 0.0001
A ² B	15.62	1	89.59	< 0.0001
Residual	2.27	13		
Lack of Fit	0.0064	1	0.0338	0.8572

Note: $R^2 = 0.9442$, Adjusted $R^2 = 0.9184$, Predicted $R^2 = 0.8747$.

94.42% of the total variation in MPD is explained by the model, demonstrating excellent predictive capability. The adjusted R^2 value (0.9184), closely aligned with R^2 , further confirms the absence of overfitting and validates the model's generalizability.

Both magnesite content ($p = 0.0019$) and sintering temperature ($p = 0.0213$) have statistically significant main effects on MPD. While the linear interaction term AB is not significant ($p = 0.1190$), several nonlinear contributions—including the quadratic terms (A^2 and B^2) and the third-order interaction A^2B —are highly significant ($p < 0.0001$). These nonlinearities highlight the strong curvature and complex dependence of MPD on both factors, with the A^2B term displaying the highest F-value and thus the most dominant influence.

The lack-of-fit test returns a p-value of 0.8572 (> 0.05), confirming that the model adequately represents the experimental data without systematic bias. Additional quality metrics also verify model precision: the Adequate Precision ratio (18.2244) greatly exceeds the recommended minimum of 4, while the standard deviation (0.4175) and coefficient of variation (7.29%) indicate low dispersion around the predicted values. Overall, the statistical evidence demonstrates that the regression model is robust, accurate, and well-suited for predicting MPD under varying operational conditions.

Equations (5) and (6) represent the final empirical models for predicting the square root of maximum power density (MPD^{0.5}) based on magnesite content (A: Mg, wt.%) and sintering temperature (B: $T_{\text{sintering}}$, °C) in coded and actual terms, respectively:

$$\text{MPD}^{0.5} = +4.55 + 0.226 A - 0.182 B - 0.327 AB + 0.207 A^2 + 0.172 B^2 + 1.97 A^2B \quad (5)$$

$$\text{MPD}^{0.5} = -1065.32 + 4581.85 (\text{Mg}) + 0.85 (T) - 4.00 (\text{Mg} \times T) - 4504.39 (\text{Mg}^2) + 6.9 \times 10^{-5} (T^2) + 3.93 (\text{Mg}^2 \times T) \quad (6)$$

The coded model (Eq. (5)) reveals the relative impact of the factors: magnesite content (A) exerts a direct positive effect (+ 0.226), whereas temperature (B) shows an inverse relationship (− 0.182). The quadratic terms (A^2 and B^2) confirm non-linear responses. Notably, the high positive coefficient of the cubic interaction term A^2B (1.97) indicates a strong synergistic effect between magnesite content and sintering temperature on the power output. While Eq. (5) is preferred for analyzing factor interactions due to its dimensionless scale, the actual-factor model (Eq. (6)) serves as a predictive tool for optimization under real laboratory conditions.

3.3.3. ANOVA analysis for CE

Table 6 summarizes the ANOVA results for the reduced third-order regression model developed for CE. The overall model is highly significant ($p < 0.0001$), demonstrating that at least one factor or interaction meaningfully affects CE. The model explains 87.94% of the observed variability ($R^2 = 0.8794$), while the close agreement with the adjusted R^2 (0.8238) verifies strong predictive reliability without overfitting.

Among the linear terms, sintering temperature exerts a significant influence on CE ($p = 0.0233$), whereas magnesite content ($p = 0.1669$) and the AB interaction ($p = 0.1028$) do not show significance at the

Table 6

The results of univariate regression analysis (ANOVA) for CE.

Source	Sum of Squares	df	F-value	p-value
Model	5507.17	6	15.80	< 0.0001
A-Magnesite	124.52	1	2.14	0.1669
B-Temperature	383.74	1	6.61	0.0233
AB	178.85	1	3.08	0.1028
A²	1788.76	1	30.80	< 0.0001
B²	224.85	1	3.87	0.0708
AB²	879.80	1	15.15	0.0019
Residual	755.09	13		
Lack of Fit	198.17	1	4.27	0.0611

Note: $R^2 = 0.8794$, Adjusted $R^2 = 0.8238$, Predicted $R^2 = 0.7644$.

linear level. In contrast, nonlinear contributions play a dominant role: the quadratic term A^2 is highly significant ($p < 0.0001$), and the cubic interaction AB^2 is also strongly influential ($p = 0.0019$). These findings indicate a notably nonlinear and coupled relationship between the factors, underscoring the importance of curvature and higher-order effects in defining CE.

Model adequacy is supported by the lack-of-fit test ($p = 0.0611 > 0.05$), indicating no evidence of systematic deviation from the experimental trends. Furthermore, the Adequate Precision

value of 11.0604 greatly exceeds the minimum acceptable threshold, confirming a strong signal-to-noise ratio and stable predictive performance across the design space.

Collectively, these results demonstrate that CE is governed by a combination of main effects, curvature, and higher-order interactions, with nonlinear terms playing the most substantial role. The regression models in Eqs. (7) and (8) quantify the combined effects of magnesite content (A , Mg, %) and sintering temperature (B , Sin-Temp., °C) on coulombic efficiency (CE) in coded and actual forms, respectively:

$$CE = +43.61 - 1.61 A + 3.16 B + 6.33 AB + 2.85 A^2 - 1.10 B^2 + 14.73 AB^2 \quad (7)$$

$$CE (\%) = -38755.23 + 76145.78 (\text{Mg}) + 68.18 (T) - 134.22 (\text{Mg} \times T) + 285.12 (\text{Mg}^2) - 0.03 \times (T^2) + 0.06 (\text{Mg} \times T^2) \quad (8)$$

In the coded model (Eq. (7)), the negative linear coefficient of magnesite (-1.61) and the positive linear coefficient of temperature ($+3.16$) indicate opposite first-order trends of these factors on CE. The response is strongly non-linear, dominated by the interaction term AB^2 ($+14.73$), highlighting that the influence of magnesite on CE is highly temperature-dependent, particularly at elevated sintering temperatures. Equation (8) is provided for direct prediction using actual process

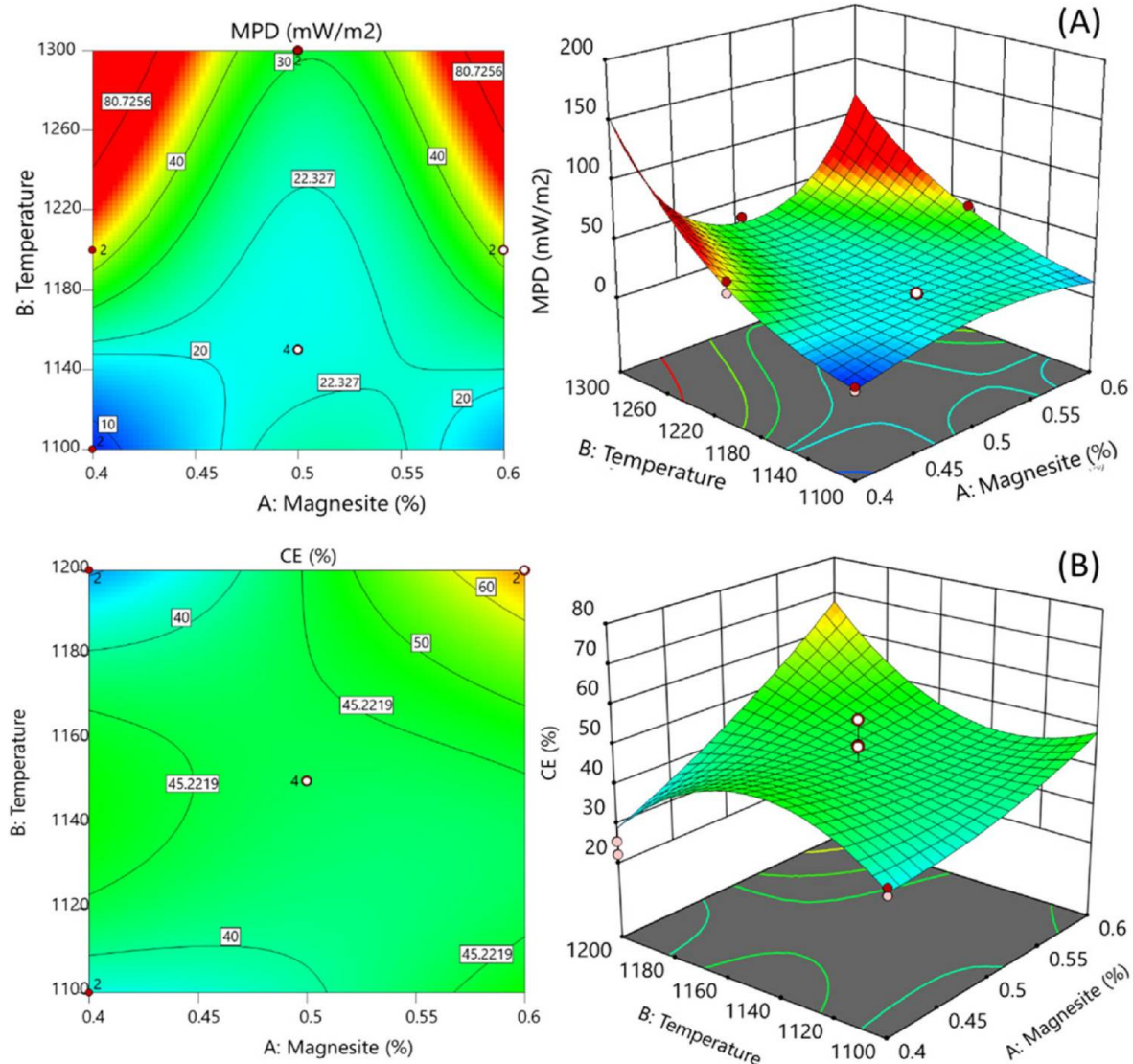


Fig. 7. Response surface and contour plots showing the interactive effects of magnesite percentage and ceramic sintering temperature on (A) MPD and (B) CE.

variables, while Eq. (7) is retained to emphasize factor effects and interactions.

3.4. The interactive effects of the variables

The ANOVA results show that the responses do not follow simple linear trends with respect to the individual factors; therefore, interpreting variables in isolation is insufficient. A clearer understanding is obtained by examining the interactive effects of magnesite content and sintering temperature and identifying the regions where their combined influence governs MPD and CE.

Fig. 7 presents the corresponding response surfaces. Because the formulation strategy linked magnesite and feldspar through a pre-defined linear scheme—where magnesite increases were proportionally matched with feldspar, and the remaining fraction was clay—the observed interaction surfaces represent the collective influence of all compositional changes together with thermal processing.

As indicated in Fig. 7A, two distinct high-MPD regions appear at elevated sintering temperatures (1200–1300 °C). The first occurs at low magnesite/feldspar levels (~20%), where the increased clay fraction enriches aluminosilicates and, upon partial melting at high temperature, forms a conductive glassy phase. The second optimum arises at high magnesite (~80%) and high temperature, where abundant magnesite and feldspar promote the formation of a dense, electrochemically favorable microstructure. Conversely, the lowest MPD values occur at low temperatures (1000–1100 °C) and low magnesite levels (20–30%), where insufficient melting of clay and feldspar yields an underdeveloped ceramic network and weak electrochemical performance. The overall response confirms a pronounced nonlinear behavior requiring high temperature and either low or high magnesite content for optimal MPD.

CE exhibits similarly distinct performance regions (Fig. 7B). High CE values appear at elevated temperatures (1200–1300 °C) and high magnesite/feldspar content (60–80%), where adequate feldspar melting and high magnesite levels jointly produce a dense, well-bonded microstructure. Poor CE occurs at low sintering temperatures (1000–1100 °C) and low magnesite contents, where insufficient melting increases porosity, facilitating oxygen and substrate crossover—major contributors to CE loss. Thus, optimal CE requires the synergistic combination of high temperature and high magnesite rather than either factor alone.

The desirability function was defined to maximize MPD and CE simultaneously. Although MPD can be high at low magnesite levels, CE drops substantially in that region. Based on the desirability function, the optimal operating window for strong overall MFC performance lies at high magnesite content and elevated sintering temperature, yet below ~1300 °C. This highlights the need for careful control of both formulation and sintering to achieve an appropriate microstructure and minimize oxygen leakage.

4. Discussion

The electrochemical performance of the ceramic membrane—expressed through MPD and CE—arises from the synergistic effects of magnesite loading, feldspar vitrification, and sintering temperature, which together govern phase evolution, pore structure, and proton-conduction pathways. Optimal behavior results from the formation of a dense, continuous aluminosilicate-MgO matrix rather than from any individual processing parameter.

Feldspar melting at elevated temperatures generates a glassy phase that infiltrates grain boundaries, reducing long-range porosity and blocking oxygen crossover—an effect directly aligned with improvements in CE and OCV stability. Simultaneously, the glass network provides non-bridging oxygens and hydroxylated sites capable of supporting proton hopping, consistent with proton conduction mechanisms reported in aluminosilicate-based membranes [34,35]. The parallel decrease in charge-transfer resistance (EIS) confirms enhanced boundary continuity and the emergence of stable conduction pathways.

Magnesite decomposition supplements this behavior by forming MgO, which introduces proton-active Mg–OH groups and regulates grain coarsening, yielding a more uniform and mechanically compact microstructure. The formation of Mg-silicate phases further restricts gas permeability and stabilizes the ceramic framework, reinforcing the suppressed oxygen crossover inferred from CE trends. These interactions explain the nonlinear response surface, in which magnesite improves CE only after sufficient vitrification has occurred.

Microstructural indicators—including reduced porosity, enhanced grain connectivity, and a more continuous ceramic–glass matrix—correlate directly with the electrochemical metrics. The combined improvements in conductivity, EIS resistance, and CV response reflect a strong structure–property–performance linkage where controlled densification and MgO-driven stabilization support selective proton transport.

This mechanistic interplay is consistent with the desirability optimization outcome, which identifies high magnesite content and high, yet sub-1300 °C, sintering temperatures as the most favorable processing window. Consistent with the MANCOVA results, the synergy between these parameters dictates the final performance, rather than the independent effect of porosity alone, confirming that the structural densification—as evidenced by the reduced porosity—is the primary driver for the observed electrochemical enhancement. Under these conditions, the membrane achieves an optimal balance between glass-phase continuity, microstructural compaction, low oxygen permeability, and efficient proton mobility, yielding superior MPD and CE.

5. Economic perspective

The successful transition of microbial fuel cell (MFC) technology from laboratory-scale demonstrations to real-world applications is fundamentally dependent on its economic feasibility. Although MFCs offer several inherent advantages—including the use of wastewater and low-value waste materials as feedstocks, minimal operational costs, and the capability to generate clean and renewable energy—the technology has not yet achieved meaningful commercial adoption. As a consequence, MFC systems remain largely restricted to bench-scale investigations. Among the key barriers, the high cost of essential components, such as electrodes, noble-metal-based catalysts, and polymeric proton-exchange membranes, represents one of the most significant impediments to large-scale deployment. Notably, commercial ion-exchange membranes have been reported to account for more than 60% of the total material cost in pilot-scale MFC installations [36].

In this study, low-cost carbon cloth electrodes free of precious metal catalysts were employed, markedly reducing the initial construction cost of the MFC. More importantly, the proton-exchange membrane developed here is based on a ceramic composite composed of magnesite, pottery clay, and feldspar—materials that are naturally abundant, environmentally benign, and economically attractive. Through optimization of both composition and processing parameters, the ceramic membrane could be sintered at a moderate temperature range (1150–1200 °C), thereby substantially lowering the overall fabrication cost compared to conventional high-temperature ceramic processes. The simplicity of the preparation route further enhances the membrane's potential for scalable and industrial-level production.

A detailed cost assessment of the optimized membrane (C-0.8 Mg-1150, 12.56 cm²) indicates that the material expenditure—comprising 2 g of magnesite (35,000 IRR/kg) and 0.5 g of feldspar (28,000 IRR/kg)—amounts to 6.68 IRR/cm². Incorporating the sintering energy consumption (10 kWh per batch of 20 units) at an electricity tariff of 40,000 IRR/kWh and excluding labor expenses, the total fabrication cost is estimated to be 1599.04 IRR/cm², equivalent to 9.41 USD/m² based on an exchange rate of 1,700,000 IRR/USD.

Table 7 presents a comparative evaluation of the price and power-related performance of the magnesite-based ceramic membrane examined in this study relative to a range of proton-exchange membranes

Table 7

Comparison of the price and power density of the present magnesite-based membrane with other proton exchange membranes.

PEM	MFC type	Volume	MCD		MPD		CE	Power to price	Price	Ref.
		cm ³	mA/m ²	mA/m ³	mW/m ²	mW/m ³	%	mW/\$	\$/m ²	
Nafion 117	DC ^a	224	1750	n.r. ^d	602	12110	53	0.26	2300	[37]
UGWC ^f	DC ^a	224	1433.89	n.r. ^d	321.11 ± 2.2	6460	68	25.53	2.5	
7BL CHI/MMT over UGWC ^f	DC ^a	224	869.44 ± 27.49	n.r. ^d	119.58 ± 19.16	n.r. ^d	43.64 ± 0.44	34.16	3.5	[29]
CMMT-1/2 over UGWC ^g	DC ^a	224	1422.22 ± 41.2	n.r. ^d	229.12 ± 18.5	n.r. ^d	86.97 ± 13.2	65.46	3.5	[30]
MNC-BAC-M1000 ^e	SC ^b	70	n.r. ^d	32.15 ± 1.56	n.r. ^d	23.25 ± 2.14	n.r. ^d	n.r. ^d	1093.89 ^e	[38]
Ceramic-PVDF-OH/BS	SC ^b	26	2900	99200	398.7	13800	34.4	n.r. ^d	n.r. ^d	[39]
CMSA10 ^h	DC ^a	100	~1600	n.r. ^d	182.8	n.r. ^d	n.r. ^d	0.846	216.05 ^h	[40]
C-0.8 Mg-1150	DC ^a	40	1404.9 ± 165.05	36265 ± 1598.7	50.69 ± 0.05	1591.61 ± 284.48	64.74 ± 11.78	5.39	9.41	This study

ⁱ A cost of 3 Chinese yuan (¥3 CNY) is reported for each CMSA10 ceramic membrane, with an area of ca.19.625 cm². By converting the Chinese yuan to dollars at the current exchange rate and dividing by the ceramic area, a cost of 216.05 USD/m² is estimated here.

^a Double chamber.

^b Single chamber.

^c Clay-bituminous carbon modified with HSO₃Cl composite membrane.

^d Not reported.

^e The cost of 9.32 \$ was estimated for each cylindrical ceramic, by considering the outer surface of 85.20 cm² for the cylindrical ceramic membrane, the value of 1093.89 \$/m² is calculated here.

^f Seven bilayers of Chitosan-Montmorillonite over Unglazed Wall Ceramic membrane.

^g Self-assembled Chitosan -Montmorillonite nanocomposite, by 1/2 (% w/w) CHI/MMT, over Unglazed Wall Ceramic membrane.

^h The membrane CMSA10 contains 70 wt% Natural clay, 10 wt% Al₂O₃, 10 wt% SiO₂ and 10 wt% Wheat flour.

previously reported in the literature, including both ceramic composites and the commercial Nafion membrane. It is important to note that the comparison with the Nafion-based system cited in Ref. [37] is particularly robust, as the experimental configuration, reactor architecture, and operational conditions in that study are highly consistent with our current methodology, ensuring a reliable benchmark for our performance evaluation.

As shown, the magnesite membrane demonstrates a well-balanced performance profile across multiple metrics, positioning it as a viable alternative to more sophisticated and higher-cost membranes. Despite its exceptionally low fabrication cost of 9.41 USD/m² under laboratory-scale conditions, the magnesite membrane achieves a power-to-price ratio of 5.39 mW/USD—significantly outperforming the commercial Nafion membrane (0.26 mW/USD). This metric clearly highlights the economic advantage of the magnesite composition and underscores its suitability for cost-sensitive applications. Although the areal maximum power density obtained with the magnesite membrane (50.69 ± 9.05 mW/m²) is lower than that reported for certain advanced polymeric or nanocomposite membranes, its current density (1404.9 ± 165.05 mA/m²) lies within the operational range of Nafion-based (up to 1750 mA/m²), indicating effective ionic transport through the ceramic matrix. This modest power output should be interpreted in light of the intentionally simplified, low-cost electrode configuration used in this study, including plain granular graphite cathodes without ORR catalysts and non-optimized carbon cloth anodes, which impose cathodic kinetic limitations. Accordingly, the present work focuses on demonstrating a cost-effective and locally sourced membrane platform whose performance can be further improved through future electrode optimization.

Furthermore, the membrane exhibits a coulombic efficiency of 64.74 ± 11.78%, exceeding that of Nafion baseline (53%) as well as several nanocomposite-coated ceramic membranes (e.g., 43.64%). This improvement reflects the favorable electrochemical properties achieved through optimized ceramic formulation and processing. When combined with its strong volumetric performance metrics, the magnesite membrane demonstrates a compelling balance between cost efficiency and functional performance.

Overall, the comparative analysis indicates that the magnesite-based

membrane, despite its markedly low production cost, delivers competitive electrochemical performance relative to more expensive commercial and composite proton-exchange membranes. These findings highlight the promise of naturally abundant and inexpensive minerals such as magnesite and feldspar for the development of cost-effective MFC membranes at the laboratory scale. However, the present conclusions are based on small-scale systems, and further work is required to assess long-term stability, batch-to-batch fabrication consistency, and techno-economic feasibility before practical scale-up can be reliably evaluated.

6. Conclusions

This work demonstrates that magnesite-based ceramic membranes have the potential to be engineered as efficient, low-cost alternatives for MFC applications. Response Surface Methodology identified the coupled influence of magnesite content and sintering temperature, showing that membranes sintered at 1150–1200 °C achieve the optimal balance between functional porosity, shrinkage control, and structural stability. Among all samples, the C-0.8 Mg-1150 membrane exhibited the highest electrochemical performance, reaching the maximum power density and current density while maintaining low internal resistance.

Wastewater treatment performance remained consistently high across all membranes, with COD and BOD₅ removal above 89%, confirming their simultaneous suitability for bioenergy production and pollutant mitigation. MANOVA and ANOVA results verified that both magnesite fraction and sintering temperature significantly and non-linearly influence MPD and CE, while porosity alone was not a predictive parameter.

Overall, the findings highlight magnesite-rich ceramics—processed below 1250 °C—as promising and cost-effective proton conductive membrane materials for MFC systems. Future investigations should focus on elucidating the underlying ion transport mechanisms and proton-selective pathways within the optimized mineral microstructures.

CRediT authorship contribution statement

Vajihe Yousefi: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Fatemeh Najafi-Rad:** , Methodology. **Hosein Shokuhi-Far:** , Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research was financially supported by the University of Sistan and Baluchestan and the Kalateh Araban Magnesite Mine Company under research project No. 1402/154. The authors also express their appreciation to Niloufar Tile Factory for kindly providing the feldspar sample used in this study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2026.156992>.

References

- [1] Renju Singh R. (Bio)electrochemical system: a systematic approach from agricultural waste to sewage wastewater treatment with nutrients and hydrogen recovery. *J Clean Prod* 2024;457:142387.
- [2] Kovalev AA, Kovalev DA, Panchenko VA, Vivekanand V, Zhuravleva EA, Littl Y. Bioelectrochemical system for green energy production in a circular bioeconomy: conversion of solar energy and organic waste into hydrogen carrier gases. *Int J Hydrogen Energy* 2025;152:150206.
- [3] Adeptan OL, Alabi OO, Gbadeyan OJ, Deenadayalu N. Bioelectrochemical systems for waste treatment and valorization: a review of applications and benefits. *Biofuel Bioprod Biorefining* 2025;19:2700–11.
- [4] Kwofie M, Amanful B, Gamor S, Kaku F. Comprehensive analysis of clean energy generation mechanisms in microbial fuel cells. *Int J Energy Res* 2024;2024:5866657.
- [5] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, et al. Microbial fuel cells: methodology and technology. *Environ Sci Technol* 2006;40:5181–92.
- [6] Rezaei F, Yousefi V, Mohebbi-Kalhari D, Samimi A. Performance evaluation of novel ml-scale microbial fuel cells using different polymeric hollow-fiber membranes. *J Water Proc Eng* 2023;55:104064.
- [7] Sharma A, Đelević L, Herkendell K. Next-generation proton-exchange membranes in microbial fuel cells: overcoming nafion's limitations. *Energy Technol* 2024;12:2301346.
- [8] Yousefi V, Mohebbi-Kalhari D, Samimi A, Salari M. Effect of separator electrode assembly (SEA) design and mode of operation on the performance of continuous tubular microbial fuel cells (MFCs). *Int J Hydrogen Energy* 2016;41:597–606.
- [9] Bakhshi A, Yousefi V, Mohebbi-Kalhari D, Samimi A. Implementation of Chitosan modified ultrafiltration hollow fiber as proton exchange membrane of ml-scale microbial fuel cells. *Hydrogen, Fuel Cell Energy Storage* 2023;10:299–310.
- [10] Ahmad ST, Ahmad R, Shaukat H, Rout PR, Fazal T, Dumfort A. Bioenergy production from wastewater using cost-effective ceramic membranes: a review. *Environ Chem Lett* 2025;23:463–90.
- [11] Yousefi V, Mohebbi-Kalhari D, Samimi A. Ceramic-based microbial fuel cells (MFCs): a review. *Int J Hydrogen Energy* 2017;42:1672–90.
- [12] Daud SM, Noor ZZ, Mutamim NSA, Baharuddin NH, Aris A, Faizal ANM, et al. A critical review of ceramic microbial fuel cell: economics, long-term operation, scale-up, performances and challenges. *Fuel* 2024;365:131150.
- [13] Yousefi V. Statistical investigation of pivotal physical and chemical factors on the performance of ceramic-based microbial fuel cells. *Energy Harvesting Syst* 2022;9:239–52.
- [14] Pradhan P, Rathod AP, Rai SB, Mohapatra SS. An overview of research progress on ceramic-based membranes. *Mater Today Proc* 2024;102:88–96.
- [15] Kyrii S. Materials and methods for ceramic membrane synthesis. Short Review. *Water & Water Purification Technologies. Scientific and Technical News* 2023;35(1):26–45.
- [16] Lee HJ, Ha J-H, Lee J, Song I-H. Current research trends and prospects on manufacturing and development of porous ceramic membranes. *J Korean Ceram Soc* 2023;60:760–80.
- [17] Christian Reichl MS. World mining data 2025. Vienna: Federal Ministry of Finance, Republic of Austria. 2025. p. 266.
- [18] Yu J, Tan W, Tian N, Huang Y, Zheng J, Luo Y, et al. Enhanced performance of ZnO/NiO bulk heterojunction based low-temperature solid oxide fuel cells realized by the addition of MgO insulator. *J Alloys Compd* 2023;969:172508.
- [19] Wang F, Ye J, He G, Liu G, Xie Z, Li J. Preparation and characterization of porous MgAl₂O₄ spinel ceramic supports from bauxite and magnesite. *Ceram Int* 2015;41:7374–80.
- [20] Aşkın A, Tatar İ, Kılınc Ş, Tezel Ö. The utilization of waste magnesite in the production of the cordierite ceramic. *Energy Proc* 2017;107:137–43.
- [21] Manni A, Achiou B, Karim A, Harrati A, Sadik C, Ouammou M, et al. New low-cost ceramic microfiltration membrane made from natural magnesite for industrial wastewater treatment. *J Environ Chem Eng* 2020;8:103906.
- [22] Ren X, Ma B, Wang L, Liu G, Yu J. From magnesite directly to lightweight closed-pore MgO ceramics: the role of Si and Si/SiC. *Ceram Int* 2021;47:31130–7.
- [23] Ren X, Ma B, Fu G, Qian F, Liu G, Yu J, et al. Facile synthesis of MgO-Mg₂SiO₄ composite ceramics with high strength and low thermal conductivity. *Ceram Int* 2021;47:19959–69.
- [24] Ma B, Zan W, Liu K, Mu X, Deng C, Huang A. Preparation and properties of porous MgO based ceramics from magnesite tailings and fused magnesia. *Ceram Int* 2023;49:19072–82.
- [25] Cao R, Ma B, Zan W, Mu X, Zhou Z, Yu C, et al. Preparation and properties of lightweight aggregates and corundum-spinel castables with used alumina refractories and magnesite tailings. *Constr Build Mater* 2025;478:141398.
- [26] Schiavo LS, Mantas PQ, Segadaes AM, Cruz RC. From dry pressing to plastic forming of ceramics: assessing the workability window. *Constr Build Mater* 2018;189:594–600.
- [27] ASTM C373-88. Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products. ASTM international; 2006.
- [28] Falamaki C, Afarani MS, Aghaie A. Initial sintering stage pore growth mechanism applied to the manufacture of ceramic membrane supports. *J Eur Ceram Soc* 2004;24:2285–92.
- [29] Yousefi V, Mohebbi-Kalhari D, Samimi A. Application of layer-by-layer assembled chitosan/montmorillonite nanocomposite as oxygen barrier film over the ceramic separator of the microbial fuel cell. *Electrochim Acta* 2018;283:234–47.
- [30] Yousefi V, Mohebbi-Kalhari D, Samimi A. Start-up investigation of the self-assembled chitosan/montmorillonite nanocomposite over the ceramic support as a low-cost membrane for microbial fuel cell application. *Int J Hydrogen Energy* 2020;45:4804–20.
- [31] Yousefi V, Mohebbi-Kalhari D, Samimi A. Equivalent electrical circuit modeling of ceramic-based microbial fuel cells using the electrochemical impedance spectroscopy (EIS) analysis. *J Renew Energy Environ* 2019;6:21–8.
- [32] Orazem ME, Tribollet B. *Electrochemical Impedance Spectroscopy*. New Jersey: John Wiley & Sons; 2011.
- [33] Brug GJ, van den Eeden ALG, Sluyters-Rehbach M, Sluyters JH. The analysis of electrode impedances complicated by the presence of a constant phase element. *J Electroanal Chem Interfacial Electrochem* 1984;176:275–95.
- [34] Norby T. Solid-state protonic conductors: principles, properties, progress and prospects. *Solid State Ionics* 1999;125:1–11.
- [35] Georgolamprou X, Ritucci I, Pirou S, Kiebach R. Development of glass sealants for proton conducting ceramic cells: materials, concepts and challenges. *J Mater Sci: Mater Eng* 2024;19:36.
- [36] Ge Z, He Z. Long-term performance of a 200 liter modularized microbial fuel cell system treating municipal wastewater: treatment, energy, and cost. *Environ Sci Water Res Technol* 2016;2:274–81.
- [37] Khalili H-B, Mohebbi-Kalhari D, Afarani MS. Microbial fuel cell (MFC) using commercially available unglazed ceramic wares: low-cost ceramic separators suitable for scale-up. *Int J Hydrogen Energy* 2017;42:8233–41.
- [38] Sabina-Delgado A, Kumar Kamaraj S, Hernández-Montoya V, Valdés-Valadez JO, Prieto-Muñoz R, Cervantes FJ, et al. Optimization of the microbial fuel cells operation for wastewater treatment by using cylindrical ceramic membranes. *Int J Hydrogen Energy* 2024;72:400–11.
- [39] de Rosset A, Yalcinkaya F, Wolska J, Waclawek S, Pasternak G. Enhancing performance and durability of PVDF-ceramic composite membranes in microbial fuel cells using natural rhamnolipids. *J Power Sources* 2024;621:235257.
- [40] Gong K, Zhang X, Tan B, Tang J, Wang L. Development and characterization of clay based ceramic membrane with high proton conductivity and low cost for application in microbial fuel cell. *Mater Res Bull* 2025;184:113278.