Improvement of microbial fuel cell performance using novel kaolin earthenware membrane coated with a polybenzimidazole layer

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Abstract
A proton exchange membrane (PEM) is one of the most critical and expensive components in a dual-chamber microbial fuel cell (MFC) that separates the anode and cathode chambers. The novel macroporous kaolin earthenware coated with polybenzimidazole (NKE-PBI) fabricated in this study could become an alternative to PEM membranes. Briefly, PBI powder was dissolved in dimethylacetamide. Thereafter, NKE was fabricated at different porosities (10%, 20%, and 30%) using different starch powder volumes, which acted as pore-forming agents. The NKE-PBI with 30 vol% starch powder content produced the highest power output of 2450 ± 25 mW m⁻² (10.50 A m⁻²) and internal resistance of 71 ± 19 Ω under batch mode operation. The MFC–PEM reactor generated the lowest power output at the highest internal resistance of up to 1300 ± 15 mW m⁻² (3.7 A m⁻²) and 313 ± 16 Ω, respectively. In this study, the nonselective porous NKE coated with PBI membranes improved proton conduction activity and displayed comparable power performance with that of Nafion 117 in a dual-chambered MFC. Therefore, a porous earthenware membrane coated with a proton conductor could become a potential separator in a scaled-up MFC system for commercialization.

KEYWORDS
microbial fuel cell technology, novel kaolin earthenware, polybenzimidazole, proton conductor, proton exchange membrane
1 | INTRODUCTION

Renewable energy sources are an alternative to fossil fuels that are facing depletion and causing adverse effects in the environment. Wastewater can be a renewable energy source owing to its organic contaminants and food for anaerobic bacteria. These anaerobic bacteria can generate electricity and produce hydrogen gas through various methods, such as fermentation and microbial electrochemical technologies (METs). A general MET design will have electrodes for the anode and cathode. Electrochemically active bacteria (EAB) enriched from anaerobic bacteria form biofilms at the anode electrode. The EAB oxidizes the organic contaminant (electron donors) and transfers the electrons to cathodes via an external circuit. At the cathode, the reduction process is catalyzed either abiotically or biologically. Oxygen and nitrate at the cathode become electron acceptors that consume electrons transferred from the anode. Several factors were identified to contribute to the performance of MET, such as type of electron donor, values of the external resistors, electron transport from the biofilm to the anode electrode, the type of electron acceptor, the efficiency of the cathode electrode performing the reduction process, and high proton transport.

In a dual-chamber MET, a membrane separates the electrodes to prevent microorganism crossover and oxygen from the cathode to the anode chamber. A typical separator used in MET and common in a chemical fuel cell is Nafion, which allows the crossing of protons. However, a pH imbalance has been reported in a microbial fuel cell (MFC) system between the anolyte and catholyte when Nafion is employed as the separator. As a result, the pH of the cathode increases and subsequently leads to high internal resistance and reduction in power output, which corresponds to the high concentration polarization loss and high ohmic losses. The pH imbalance is due to the lower affinity of protons than the cation species in the MFC system. Theoretically, the electrons transferred from the anode electrode via the outer circuit must be equivalent to the protons transferred to the cathode via the separator. However, in practice, the cation concentration in the anolyte is higher than that in protons.

Various ongoing studies have reported improvements in MET membranes. For instance, composite Nafion or sulfonated aromatic polymers for MET applications are cheaper and more efficient than Nafion. Poly(allylamine hydrochloride), poly(vinyl alcohol), poly(phenylene) sulfide, poly(-propylene), polystyrene, cellulose esters, and chitosan are also polymer types tested as separators in the MFC system. However, these membranes have disadvantages, such as fragility, susceptibility to pH change, degradation with time, low conduction, and biofouling. Singha et al fabricated a new polymer membrane based on polybenzimidazole (PBI) using various methods, such as the synthesis of nanocomposites to improve conductivity. PBIs are commonly known as one of the most promising polymeric materials used as proton exchange membranes (PEMs) in PEMFCs. The acid- or alkali-doped PBI membranes have outstanding properties that allow them to be used as high-temperature PEMs up to 200°C, without dehydration, owing to the presence of acid or alkaline groups as proton carriers. PEM is also a relatively low-cost non-perfluorinated polymer that exhibits excellent oxidative and thermal stabilities. The first study of the ionic conductivity of PBI was reported over 40 years ago, and various studies have been conducted using PEM membranes. The interest in fuel cells with PEM is caused by its proton conductor ability, good solubility, and flexible ether backbone, compared to other polymer membranes, such as PVA, chitosan, and polystyrene.

Studies on porous materials, particularly earthenware, have also been reported using MFC systems for cost reduction, scaling-up capability, and performance improvement. The porous separators applied in the MFC system, either built from organic or inorganic materials, showed better performance than PEM or other polymer membranes. Inorganic separators, such as glass fibers, have nonuniform structures. The nonuniformity in structures makes it unsuitable, especially in stacking several units of MFCs to obtain significant electricity. Stacking of the MFC units also results in uneven performance due to voltage reversal caused by fuel starvation. Loss of bacterial activity also occurs in the individual units. However, earthenware and ceramic are reported to possess positive performances in power production, COD removal, and reduction of internal resistance when installed as separators in MFCs.

Ceramic clay-based materials are promising alternative MFC membranes with low cost, natural availability, and functional long-term robustness. Ceramic materials are environmentally friendly, and their microstructure can be easily modified by either adding other compounds into their raw ceramic clay form or by varying the conditions during the sintering process. These modifications directly affect parameters, such as the overall effective porosity or pore size distribution, within the ceramic membranes (CM). The flux of ions through its structure is directly related to the power performance of MFCs. The fouling and clogging of membranes can severely shorten the lifetime of MFCs, which often build on cation exchange membranes (CEMs) after long-term operation. For the CEM, the cation-binding sites at the negatively charged sulfonate groups are the leading cause of fouling. Cations in the

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Electrolyte can bind these negatively charged sulfonate groups, causing an increase in the electrical resistance of the CEM. The CEM performance will eventually deteriorate, leading to a reduced MFC power performance in an extended continuous operation. A report on zirconia ceramic filters described a ceramic with a better shelf-life than CEM, resistance to aggressive solvents, and superior pressure and temperature tolerance than other membranes, such as nonwoven cloth, glass fiber, and natural rubber. The characteristics mentioned above make it suitable for the long-term operation of large-scale MFCs.

This study sought to describe the combined fabrication of novel kaolin earthenware with PBI (NKE-PBI) and its membrane performance compared to that of a Nafion 117 dual-chamber MFC. The morphological characteristics of NKE-PBI were observed using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). In this study, MFC performance and the suitability of NKE-PBI as an MFC separator were evaluated based on the power output, internal resistance, and ohmic resistance.

2 MATERIALS AND METHOD

2.1 In-house fabricated novel kaolin earthenware

The kaolin powder used in this study was purchased from a craft shop (Multifilla Sdn Bhd, Balakong, Selangor, Malaysia). Different compositions of kaolin (90%, 80%, and 70%) and starch powder (10%, 20%, and 30%; Table 1; Sigma Aldrich, USA) were mixed using a ball mill machine. After the starch forms pores in the ceramic body, a hydraulic system (Carver, USA) pressed the mixture samples at 7 atm (102.87 psi). A stainless-steel mold with a diameter of 23 mm and thickness of 4 mm was used to fabricate the body sample. The produced round-shape body samples were dried in a vacuum oven (Cole-Parmer, India) at 80°C for 24 hours. The purpose of drying the body samples was to obtain an equilibrium residue moisture content. The body samples were then sintered in a furnace at a maximum temperature of 1200°C, soaked for 3 hours at a heating rate of 5°C, and then cooled to 25°C.

2.2 Novel kaolin earthenware coating with PBI

PBI powder (0.6 g) was dissolved in 30 mL dimethylacetamide (DMAc) at 120°C for 5 hours. The PBI solution was then centrifuged to remove undissolved powder. The homogenous solution was placed in a petri dish and concentrated in a ventilated oven at 80-150°C for 12 hours. Thereafter, the PBI liquid was poured onto the surface of the fabricated NKE. The NKE coated with PBI was dried in a ventilated oven for 24 hours (Figure 1A,B).

2.3 Characterization of novel clay earthenware (NCE) and PBI

FESEM (Zeiss, Supra 55VP, Germany) and AFM (NT-NDT, Moscow, Russia) were used to characterize the NKE-PBI: surface, cross-section, and roughness, respectively. Fourier-transform infrared spectroscopy (FTIR; Perkin Elmer, Spectrum 400 FT-IR/NIR, USA) was also carried out to determine the chemical composition of PBI.

2.4 MFC reactor

The fabricated NKE-PBI membranes with three different porosities (Table 1) and Nafion 117 were installed in dual-chambered MFC reactors, with Nafion 117 as the control. Pretreatment of the Nafion 117 membrane (DuPont Co., USA) was performed according to the method described by Chae et al. Both the anode and cathode chambers were round, with each chamber having a volume of 16 mL. Plain graphite felt (GEFC Co., China) with a projected area of 4.9 cm² became the anode electrode, while the cathode was derived from plain graphite felt coated with 0.5 mg Pt cm⁻² catalyst. The anode and cathode electrodes were placed 1-1.5 cm apart. Each separator was...
analyzed in three replicates of the MFCs, and a t-test was used for statistical analysis.

### 2.5 Microbial inoculation and operation

A 1:1 mixed ratio of phosphate-buffer basal medium and sludge was prepared for inoculation in the anode chamber. The sludge originated from anaerobic digestion provided by the National Sewerage Company, the Indah Water Konsortium. The anolyte was composed of 0.41 g L$^{-1}$ sodium acetate, 0.75 g L$^{-1}$ NH$_4$Cl, 0.11 g L$^{-1}$ KCl, 1.0 mL L$^{-1}$ yeast extract, trace metals, and 150 mmol/L phosphate buffer solution. Anode feeding was performed in the fed-batch mode using a syringe. The catholyte contained 150 mmol/L phosphate buffer solution with continuous aeration. All systems were operated at a temperature of 28°C and pH of 7.0. Both the anode and cathode electrodes were joined using external circuit wires connected to a 100 Ω external resistor after 24 hours of inoculation.

### 2.6 Data logging

A multimeter (Model 2700, Keithley, USA) was used to record the data reading of the closed-circuit system voltage every 5 minutes. The current $I$ of the system was calculated using Ohm’s law: $I = V/R$, where $V$ is the voltage and $R$ is the external resistance (Ω).

### 2.7 Polarization experiment

An AUTOLAB potentiostat (PGSTAT128N, Utrecht, The Netherlands) was used to plot the linear forward and reverse sweep voltammograms. The analysis started with an open-circuit voltage (OCV) of zero and zero to the OCV at a scan rate of 1 mV s$^{-1}$. The voltage was plotted against the power density and current density to obtain the power density and polarization curves. Both power and current were normalized by the anode with a projected area of 4.9 cm$^2$. 
2.8 | Electrochemical impedance spectroscopy (EIS)

The impedance of the system was measured using the EIS technique was integrated into an AUTOLAB potentiostat. The ohmic resistance \( R_{oh} \) value was obtained during the open voltage within the frequency range of 0-10 kHz. The data were then used for the Nyquist plot \( (Z''-Z' \) graph) reported by Logan et al.\(^{45} \) The linear part of the polarization graphs was used to analyze the internal resistance \( R_{in} \) of the overall systems.

3 | RESULTS AND DISCUSSIONS

3.1 | Enrichment of EAB biofilm

Enrichment was performed in the anode chamber to obtain the EAB biofilm. The low external resistance applied (100 Ω) facilitates the crossing of the electron transfer. The EAB biofilm formation on the anode increased the maximum power generation, as reported by Lefebvre et al.\(^{46} \) Further, the MET voltage increased with time. At day-10, after start-up, the closed-circuit voltage increased from 5 mV (0.05 mA) to 10 mV (0.1 mA) on day-15. The closed circuit allowed electron transfer from the anode to the cathode. From day-16 to 19, EAB enrichment showed an 88% inclination improvement, with a rapid increase from 10 mV (0.1 mA) to 35 mV (0.35 mA). A stable voltage was detected from day-15 to 50 of operation (Figure 2A). SEM morphology analysis substantiated EAB enrichment on the anode surface (Figure 2B).

3.2 | Sample compound identification

The presence of PBI on NKE was detected by FTIR spectroscopy. The characteristic peaks of PBI synthesized from PBI powder and DMAc solution were observed from 3500 to 500 cm\(^{-1}\): 3185 cm\(^{-1}\) and 1611 cm\(^{-1}\) for the N–H bond and the C=N bond, respectively (Figure 2). The PBI stretching bands of typical C=C and C=N appeared at 1611 cm\(^{-1}\), and the breathing mode of the imidazole ring appeared at 1286 cm\(^{-1}\) for polymer.\(^{47} \) The C=C and C=N stretching bands appeared in the region of 1630-1500 cm\(^{-1}\).\(^{48} \) The plane deformation of benzimidazole rings could be due to the large band at 1536-1286 cm\(^{-1}\) (Figure 3).

3.3 | Surface morphology and pore size

Figure 4A,B display the surface and cross-section of Nafion 117, respectively, with no evidence of pore distribution. Generally, PEMs, including Nafion 117, have sulfonate groups \( (SO_3^-) \) that contribute to a high cation conductivity level.\(^{49} \) Figure 4C-H illustrates the FESEM images with pore distribution for NKE-PBI. The nonselective porous membrane can transfer ions (protons or cations) without using an ion selection transport mechanism, such as the PEM, Nafion 117.\(^{33,34} \) A previous study comparing the performance of nylon mesh and glass fiber filters in an MFC system\(^{32} \) reported that the increasing power density corresponded with the improvement in pore size of these filters. Three types of glass fiber filters used with pore sizes of 0.7 µm (GF0.7), 1.0 µm (GF1), and 2.0 µm (GF2) generated maximum power densities that did not exceed 800 mW m\(^{-2}\) (GF0.7, 732 ± 48 mW m\(^{-2}\), GF1, 716 ± 60 mW m\(^{-2}\), and

**FIGURE 3** Fourier transform infrared spectral of PBI
GF2, 779 ± 43 mW m⁻²). However, the nylon separator MFCs with the largest pore size of 160 µm generated a maximum power density of up to 941 ± 47 mW m⁻². Such finding indicates that a large pore size, similar to that of the nylon mesh when used as a separator in MFC, will significantly increase the power density.

Recently, Merino-Jimenez et al. tested six types of fine fire clay (FFC) for water absorption. They applied two types of treatments to the FFC: varying firing temperatures (1206°C, 1205°C, and 1150°C) (FFC1, FFC2, and FFC3), and adjusting the chemical composition of alkaline and earth before manufacturing with varying firing temperatures (FFC4, FFC5, and FFC6). The FFC from varying firing cycles showed smaller ceramic granules, leading to a more porous structure than the treatment involving no adjustment to the FFC chemical composition. The porous structure improved the water absorption properties of the ceramics, thereby increasing the power output of the MFCs by 64%. However, the pore sizes were not uniform, with pores ranging from 200 nm (FFC5) up to 5 µm (FFC6), generating powers of 1068 µW and 960 µW, respectively.

Another factor affecting MFC power performance is oxygen diffusion from the cathode chamber to the anode chamber. The separators with large pore sizes enable more transport of chemical species, including protons. The ease of ion transport across the separator assisted the MFC in high performance with low ohmic losses compared to Nafion, as reported by Choi et al.

3.4 | Surface roughness and porosity

Several factors are involved in power generation, such as the porosity, thickness, and roughness of the separators
Figure 4 shows the surface roughness of NKE10-PBI, NKE20-PBI, and NKE30-PBI observed using AFM at 10^2 scanned areas. NKE30-PBI had a higher average roughness of up to 56% than NKE20-PBI (18.75 nm) and up to 52% compared to NKE10 (20.59 nm). This study revealed a markedly lower surface roughness than a previous study on NCE without PBI application by Daud et al. According to these researchers, their NCE30 separator exhibited up to 232-fold more roughness than PEM, while concurrently generating a higher power density than PEM. In this study, the NKE30-PBI only had a 41-fold higher roughness than PEM. The other NKE-PBIs were markedly less: up to 17-fold rougher than PEM for NKE20-PBI and 19-fold more roughness than PEM for NKE10-PBI. The power performance of NKE30-PBI in this study was 8% higher than that of NCE30 without PBI, which was studied by Daud et al. The advantage of PBI coating of NKE is its ability to reduce the surface roughness and improve proton conductivity (Figure 5 and Table 2).

The porosity of NKE30-PBI was 33.3% and 66.7% higher than that of NKE20-PBI and NKE10-PBI, respectively. The existence of porosity allows high proton transfer via the separators and increases the power output due to NKE30-PBI, with up to 2450 ± 25 mW m⁻² (Table 2 and Figure 2). However, increased porosity reduced the strength of the fabricated ceramic, as stated by Eom and Kim (2008). According to these researchers, both the compressive and flexural strengths increased with decreasing porosity, and both the flexural and compressive strengths increased with decreasing template size, such as pore size, owing to an increase in strut strength and a decrease in the critical flow size. The typical compressive and flexural strengths were 600 and 105 MPa, respectively, at a porosity of 30%. Sengphet et al reported that their fabricated porous clay ceramics with porosity between 11.86% and 45.64% had a decrease in tensile strength from 24.05 to 9.06 MPa. This decrease in tensile strength was attributed to the increase in porosity.

A positive outcome has been reported in studies of other materials modified with PBI. For instance, Choi et al introduced poly(2,5-benzimidazole) (ABPBI) into a nonwoven fabric (NWF) membrane electrode. The power density of the 50 mg ABPBI cm⁻² MFC was 766 ± 20 mW m⁻², while that of the control sample with NWF was 413 ± 97 mW m⁻².

### 3.5 Factors affecting the electrochemical performance of the MFC system

The performance of the MFCs was analyzed in batch mode operation (Table 3). The OCV obtained for all systems in this study was almost similar, with values of 805 ± 7 mV for PEM, 802 ± 4 mV for NKE10-PBI, 798 ± 3 mV for NKE20-PBI, and 801 ± 6 mV for NKE30-PBI (Table 3). In this study, the internal resistance affected the electrochemical performance. NKE30-PBI obtained the highest power density of up to 2450 ± 25 mW m⁻² (10.5 A m⁻²), which was 46.9% higher than that of Nafion 117 (3.7 A m⁻²; Figure 6A,B). The other NKE-PBIs also produced a higher power density than the PEM: 41.7% (10 A m⁻²) less than NKE20-PBI and 27.7% (7.8 A m⁻²) less than NKE10-PBI. The internal resistance calculated from the polarization graph for the MFC-PEM (313 ± 16 Ω) was 4.4-fold higher than those with NKE30-PBI and almost 2.8- and 1.6-fold higher than those of NKE10-PBI and NKE20-PBI, respectively. Figure 7 shows the abundance of EABs in the anode chamber after 3 months of MFC operation, which corresponds to the correlation between the electroactive biofilm’s power output and microbial behavior.

The power density, current density, and internal resistance are mainly affected by the difference in porosity, which directly increases the transportation of protons or cations. Pasternak et al reported that porosity in their earthenware (above 2.0%) and pyrophyllite (between 1.0% and 2.0%) separators produced volumetric power densities of 6930 mW m⁻³ and 6860 mW m⁻³, respectively, which were the highest performances. The lowest power density of 2.63 W m⁻³ was obtained for alumina with low porosity (below 1%), which resulted in poor proton transport. Daud et al reported that NCE30 (30% porosity) generated the highest power density (2250 ± 21 mW m⁻²), followed by NCE20 (20% porosity) (2000 ± 23 mW m⁻²) and NCE10 (10% porosity) (1550 ± 28 mW m⁻²). In addition,
Salar-García and Ieropoulos\textsuperscript{50} reported that the porosity of the membranes was affected by the sintering temperatures, where high temperatures reduced the porosity and power output. The same trend of ionic conductivity (%) as well as MFC power output corresponding to the sintering temperature was found: 1140°C (87.38%) < 1030°C (92.24%) < 860°C (94.05%).

The clay and kaolin powders are similar based on their characteristics and properties.\textsuperscript{52,53} In this study, NKE30 coated with PBI generated an 8.16\% improvement in power density compared to NCE30 without PBI. The ionic functional group in PBI leads to a membrane with lower internal and ohmic resistances, which increases the maximum power density.\textsuperscript{49} The overall performance of the MFCs is proportionally related to the ionic mass transfer through the separators. The ionic mass balance sheet of the MET system was elaborated in detail by Daud et al.\textsuperscript{54} Materials with nonion selective charge transfer or macroporous separators without ion selection preference include earthenware, ceramic, nonwoven fabric, and NKE-PBI. Compared

| Type of membrane | PEM | NKE10-PBI | NKE20-PBI | NKE30-PBI |
|------------------|-----|-----------|-----------|-----------|
| OCV (mV)         | 805 ± 7 | 802 ± 4 | 798 ± 3 | 801 ± 6 |
| Max. power density (mW m\(^{-2}\)) | 1300 ± 15 | 1800 ± 22 | 2230 ± 23 | 2450 ± 25 |
| Internal resistance (Ω) | 313 ± 16 | 201 ± 23 | 117 ± 21 | 71 ± 19 |
| Ohmic resistance (Ω) | 67.6 ± 8 | 29.8 ± 5 | 12.6 ± 9 | 9.62 ± 7 |
to PEMs, these materials can exhibit high performance owing to an existing barrier within the PEM membrane. The barrier reduces the proton transport and eventually, the power performance during long-term operation, unlike the macroporous separator. The increase in pore size and porosity in the macroporous separators decreased this barrier effect. The oxidation process at the anode electrode by EAB produces protons, and the reduction process consumes protons at the cathode electrode to produce water. Figure 8 shows other ions in the anolyte, such as Na⁺, NH₄⁺, Ca²⁺, and Mg²⁺, including protons directly involved in ion transportation via diffusion or migration. An imbalance in the pH environment in both the anode and cathode compartments only developed when selected cations could cross the PEM separators. This condition reduced the pH in the anode compartment while increasing the pH of the cathode. In this study, the MFC-PEM agrees with the ionic mass balance sheet’s pH theory, producing the lowest performance compared to the macroporous NKE-PBIs. In an interesting study by Daud et al., a zirconia CM was compared to Nafion 117 in an ionic gradient concentration improvement using a dual-chamber MFC system. Based on their results, a high concentration of cation species was present in the catholyte: 35% of Na⁺, 7% of NH₄⁺, 19% of Ca²⁺, and 25% of Mg²⁺ when using a porous CM separator compared to PEM. The CM MFCs resulted in a slight change in the anolyte pH to maintain a neutral pH compared to the PEM MFCs. The nonion selective charge transfer provided a pH balance and electroneutrality, corresponding to increased power output.

The thickness of the earthenware is another parameter that affects the MFC performance according to Behera and Ghangrekar. These researchers reported that the thickness reduction of the earthen pot wall that functions as the separator reduced the internal resistance of the MFCs. However, in this study, the following thickness was obtained: NKE = 23-25 mm and Nafion 117 = 0.18 mm; thickness was not the main factor contributing to the maximum power density (Table 2). Although Nafion 117 was thinner than...
NKE-PBI, it produced a higher internal resistance, resulting in a lower power density (Table 3). PBI is a proton conductor that improves the overall performance of MFCs, including ohmic resistance, internal resistance, and power. Regardless of the thickness, in this study, the NKE-PBI showed the highest power density of the MFC systems resulting from efficient proton transfer via the membrane.

### 3.6 Impedance of the system

Three months after startup, the MFCs with NKE30-PBI showed the lowest $R_{oh}$ of $9.62 \pm 7 \Omega$, which was 42% and 34% lower than those of NKE10-PBI and NKE20-PBI, respectively (Figure 9 and Table 3). The MFCs with PEM generated the lowest power density with the highest $R_{oh}$ ($1350 \pm 17 \text{ mW m}^{-2}, 67.6 \pm 8 \Omega$) from the EIS measurement, which was 85% higher than the NKE30-PBI membrane ($2450 \pm 25 \text{ mW m}^{-2}, 9.62 \pm 7 \Omega$), followed by the NKE20-PBI membrane ($2230 \pm 23 \text{ mW m}^{-2}, 12.6 \pm 9 \Omega$), which was 23% higher than both NKE30-PBI and NKE10-PBI membranes ($1800 \pm 22 \text{ mW m}^{-2}, 29.8 \pm 5 \Omega$), and 68% higher than the NKE30-PBI membrane. Polyphenylene sulfide was tested in another study and nonwoven fabric (NWF80) was found to produce a low $R_{oh}$ of ~41 $\Omega$ ($231 \text{ mW m}^{-2}$) and 36 $\Omega$ ($280 \text{ mW m}^{-2}$), respectively, as reported by Kondaveeti et al.\textsuperscript{31} This study proved that a high $R_{oh}$ corresponds to a low power density and MFC performance.

## 4 CONCLUSIONS

The difference in porosity of in-house-fabricated NKEs coated with PBI (NKE10-PBI, NKE20-PBI, and NKE30-PBI) revealed suitability separators in MFCs. The PEM, Naftion 117, was employed as a control in this study to enable performance comparison. Based on the results, NKE30-PBI with the highest porosity (30%) generated the highest power density ($2450 \pm 25 \text{ mW m}^{-2}$) and the lowest internal resistance (71 $\Omega$). The power density and internal resistance of the MFC-PEM were $1300 \pm 15 \text{ mW m}^{-2}$ and 313 $\Omega$, respectively. The low proton transport via the PEM separator decreased the overall performance of the MFC system. However, the in-house fabricated macroporous NKE-PBIs enable a high transfer of protons, including other ions. The ease of ion transfer can generate the highest overall performance in the MFC system. This study agrees with the previous study regarding ceramic and earthenware, where low-cost fabricated NKE membranes and earthenware materials were identified as suitable candidates for separators, leading to the commercialization and large-scale production of MFC systems.

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## CONFLICT OF INTEREST

The authors declare that is no conflict of interests regarding the publication of this paper.

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