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Biofouling-focused assessment of a novel, cellulose-based ionogel membrane applied in a microbial fuel cell

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ABSTRACT

In this work, a novel ionogel membrane was prepared on polyethersulfone physical support from the mixture of microcrystalline cellulose and [BMIM][Cl] (1-Butyl-3-methylimidazolium chloride) ionic liquid and used in a microbial fuel cell (MFC). The ionogel membrane was characterized in terms of its morphology, mass- (substrate, oxygen) and ion transfer features and compared to Nafion 115. The membranes were deployed in acetate-fed two-chamber MFC, where the MFC equipped with the ionogel membrane showed a Coulombic efficiency and peak current density of 49.4 % and 369 mA m^{-2}, respectively. Through three weeks of experiments, the electrode and membrane biofouling layers were studied by 16S amplicon metagenomics and correspondence analysis. It turned out that a cellulose-degrading species, *Clostridium termitidis* was present with a relatively large, 23.2 % relative abundance on the surface of the ionogel membrane, which may have caused its deterioration and the consequent colonization of the cathodic compartment.

1. Introduction

Recently, microbial fuel cells (MFC) have gained great interest, thanks to their hybrid potential in energy conversion and wastewater treatment (Bird et al., 2022; Palanisamy et al., 2019), including real household feedstock such as urine (You et al., 2021). However, despite the promising results, development of MFC at bigger scales is constrained by its total capital cost (Palanisamy et al., 2019). One of the major costs comes from the membrane used as electrode separator (Ge and He, 2016). It has been estimated that this cost could be above 40 % of the total capital cost at lab scale (Chakraborty et al., 2020; Hernández-Flores et al., 2016), and over 60 % at larger scales (Ge and He, 2016). MFC systems have been commonly studied using Nafion membranes (Dizge et al., 2019; Koók et al., 2020a), due to its high ion exchange capacity and proton conductivity (Palanisamy et al., 2019). However, beside its cost, oxygen leakages from the cathode chamber to the anode chamber have been identified as a particular disadvantage in this type of membranes (Chae et al., 2008; Huang et al., 2018). Due to these drawbacks, researchers have explored the possibility of replacing these membranes with other materials and their composites (Cheraghipoor et al., 2022; Daud et al., 2015; Patel et al., 2022), such as Zirfon, expanded polystyrene (Mathuriya and Pant, 2019; Pasupuleti et al., 2016) and even separators made with inorganic elements e.g. Fuller's earth-material, clay (Gunaseelan et al., 2022).

As previously shown by Koók et al. (Koók et al., 2020a), >20 different materials have been used as separators in MFC systems. Although many of these materials have shown good performance in comparison to the Nafion membranes, their development based on fossil-based materials does not fit with the goals of the 2030 Agenda for Sustainable Development. In this context, eco-friendly membranes derived from renewable resources, such as the biopolysaccharide cellulose, have gained notable relevance. So far, in MFC systems, mainly cellulose ester has been used as a separator material. For example, Tang et al. (Tang et al., 2010) reported that microfiltration cellulose ester membranes could have a similar average power density than Nafion ones, but at a 5.8 times higher power-to-cost ratio (Hernández-Flores

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et al., 2016). Kondaveeti et al. (Kondaveeti et al., 2018) also used a cellulose ester membrane obtaining a maximum power density comparable to Nafion and the oxygen mass transfer coefficient of the two membranes was similar ($k_o = 15 \times 10^{-5}$ cm s^{-1}). Wang and Lim (Wang and Lim, 2017) applied mixed cellulose ester filter as a separator achieving a maximum power density of 780.7 ± 18.7 mW m^{-2}, which was close to the performance of a Nafion membrane. However, more severe biofouling was observed on the latter one. Mashkour et al. (Mashkour et al., 2021) employed a bacterial cellulose membrane coated with conductive multi-walled carbon nanotubes and nano-zycosil as an air–cathode in a single-chamber MFC, leading to a pulse power density of 1790 mW m^{-2}, which was roughly twice as high as the pulse power density of a PTFE- based gas diffusion electrode. By contrast, Vilela et al. (Vilela et al., 2020) deployed a separator made of bacterial cellulose and fucoidan attaining a power density of 2.42 mW m^{-2} and a maximum protonic conductivity of 1.6 mS cm^{-1} at 94 °C, which was two orders of magnitude lower compared to Nafion membranes. As shown from the above examples, membranes based on cellulose can have the potential to compete with Nafion in MFCs. However, conventional processing methods for cellulose dissolution rely on chemical methods that could be harmful to the environment, or in the case of the N-Methyl morpholine N-oxide (NMMO) solvent, being prone to runaway reactions due to its instability (Felgueiras et al., 2021; Rieland and Love, 2020; Sayyed et al., 2019). Bacterial cellulose is an option that could overcome these drawbacks, but its production costs are still considered very high due to the low yields (Felgueiras et al., 2021).

Accordingly, a promising approach for producing membranes based on regenerated cellulose and ionic liquid could be proposed based on two-dimensional (plain) biomacromolecular self-assembly (Zhu et al., 2023). Ionic liquids (ILs), particularly [BMIM][Cl] have been used to dissolve cellulose since 2002 (Swatloski et al., 2002), showing good results in very different applications, such as air filtration (Zhu et al., 2020), oil-water separation (Kim et al., 2019), organic solvent nanofiltration (Sukma and Çulfaz-Emecen, 2018) and protein separation (Chen et al., 2012; Ma et al., 2013). The success of ionic liquids is based on their low melting points (<100 °C), negligible vapor pressures, and good thermal and chemical stability that contribute to the green synthesis, material recovery and reuse (Mai et al., 2014; Rieland and Love, 2020; Sayyed et al., 2019). Although the underlying mechanism is not fully understood, it is suggested that the disruption of hydrogen bonding by the ionic liquids takes part in the dissolution of cellulose (Felgueiras et al., 2021; Medronho and Lindman, 2015; Rieland and Love, 2020; Sayyed et al., 2019). Until now, ionic liquids have been used in MFCs as part of the electrolytic solution (Nunes et al., 2017) or as a coating/filler of the separators to improve their properties (Hernández-Fernández et al., 2016; Koók et al., 2017, 2019b; Thanganathan and Nogami, 2015).

As a result, it turned out that membranes based on ionic liquids (ILs, liquid organic salts) are clearly among the emerging candidates as alternative separators in microbial electrochemical systems. In fact, it was shown that the immobilization of various ILs (including ones with alkyl- imidazolium cations and $[PF_6]^-$ and $[NTf_2]^-$ anions) in a microporous supporting layers and subsequent deployment of the so-obtained membranes in MFC led to enhanced charge and mass transfer processes and higher electrical performance compared to the reference material (e.g., Nafion PEM) (Hernández-Fernández et al., 2015; Koók et al., 2017, 2019b). So far, the main research directions for increasing the stability and performance of IL-membranes have been the entrapment/inclusion of IL in polymers (e.g., polymer inclusion membranes, PIM) and the self-polymerization of the IL. However, both approaches involve chemical- and energy-intensive steps in the fabrication, shading the attractiveness of the obtained separators. To overcome these issues, membrane synthesis based on bio-based, low-cost materials, such as the cellulose-based ionogels could be seen as a potential way forward.

Conceptually, the ionogel, is a material where the ionic liquid is confined in a polymer network (He et al., 2023; Néouze et al., 2006). These ionogels – under optimized preparation conditions – have good mechanical and electrochemical properties, which can be exploited in different electrochemical systems (Hopson et al., 2021; Rana et al., 2020; Sahrash et al., 2018). Nevertheless, to the authors knowledge, no reports on the performance of MFC working with an ionogel membrane (in particular, made of the biopolymer, cellulose and ionic liquid) are yet available. Therefore, the aim of this study was to combine cellulose and ionic liquid with the hypothesis that an efficient cellulose-[BMIM][Cl] ionogel membrane can be prepared on PES support (physical reinforcement) thus manufacturing a novel membrane that can act as a more cost-effective option for MFCs. The fabricated ionogel membrane was characterized via scanning electron microscopy, mass transfer (substrate, oxygen) measurements and ionic conductivity.

As a key-innovation to the already existing literature, a mixed culture, acetate-fed MFC equipped with the synthetized ionogel membrane was assessed with regard to the obtainable Coulombic efficiency, peak current density and energy production rate. The experiments involved Nafion 115 membrane for benchmarking purposes, as well. The assessment of the MFCs was strengthened by 16S amplicon metagenomics with regard to the electrode (anode, cathode) and membrane surface biofilms (biofouling layers) formed during the three weeks of experiments. As the last step, correspondence analysis was carried out for the qualitative (bacterial composition-based) comparison of the different biofilms samples for providing supportive and novel information towards the understanding of the supported cellulose-[BMIM][Cl] ionogel membrane behavior in the MFCs, as microbial electrochemical technology.

2. Materials and methods

2.1. Cellulose-[BMIM][Cl] ionogel membrane fabrication

In this study, the ionogel membrane was prepared from the mixture of microcrystalline cellulose (Molar Chemicals, Hungary) and [BMIM][Cl] (1-Butyl-3-methylimidazolium chloride) ionic liquid (IoLitec-Ionic Liquids Technologies GmbH, Germany) through phase inversion (sol-gel processing) technique. The ionogel synthesis scheme was adapted from the work of Kadokawa et al. (Kadokawa et al., 2008) and then, modified to some extent as the following, stepwise procedure to fabricate and obtain the supported cellulose-[BMIM][Cl] ionogel membrane (Fig. 1).

First, 4.35 g [BMIM][Cl] ionic liquid was preheated to 100 °C and then, 0.650 g microcrystalline cellulose was added slowly under constant mechanical stirring (120 rpm). After half an hour, an amber coloured, transparent and sticky (highly viscous) mixture containing dissolved cellulose was formed. The mixture was then poured onto a plastic mesh (as physical support) to improve the mechanical strength of the membrane. The plastic mesh had 0.6 mm lattice length and 0.15 mm average pore size, was made of polyethersulfone (PES) and manufactured in Oroszlány, Hungary by GE company (Fig. 1). Later, with a metal cylinder, approximately 1 mm thick sheet was cast towards obtaining the ionogel membrane. Following sheet manufacture, the product was immersed in room temperature (23 °C) 400 ml of distilled water as antisolvent bath for an hour to achieve cellulose regeneration and thus, the gelation (solidification) of the material. A plausible structure for a cellulose-[BMIM][Cl] ionogel was suggested by Takada et al. (Takada and Kadokawa, 2015) (right bottom corner in Fig. 1). Afterwards, the membrane with the necessary coin shape was cut out (4.6 cm diameter) and utilized in the MFC in addition to the 150 μm thick Nafion 115 (swollen state) as the reference material (Section 2.4.). Prior to application in MFCs, the Nafion 115 was pretreated according to Cardena et al. (Cardeña et al., 2021).

2.2. Scanning electron microscopy (SEM) of cellulose-[BMIM][Cl] ionogels

The samples of flat sheet cellulose-[BMIM][Cl] ionogel membranes –

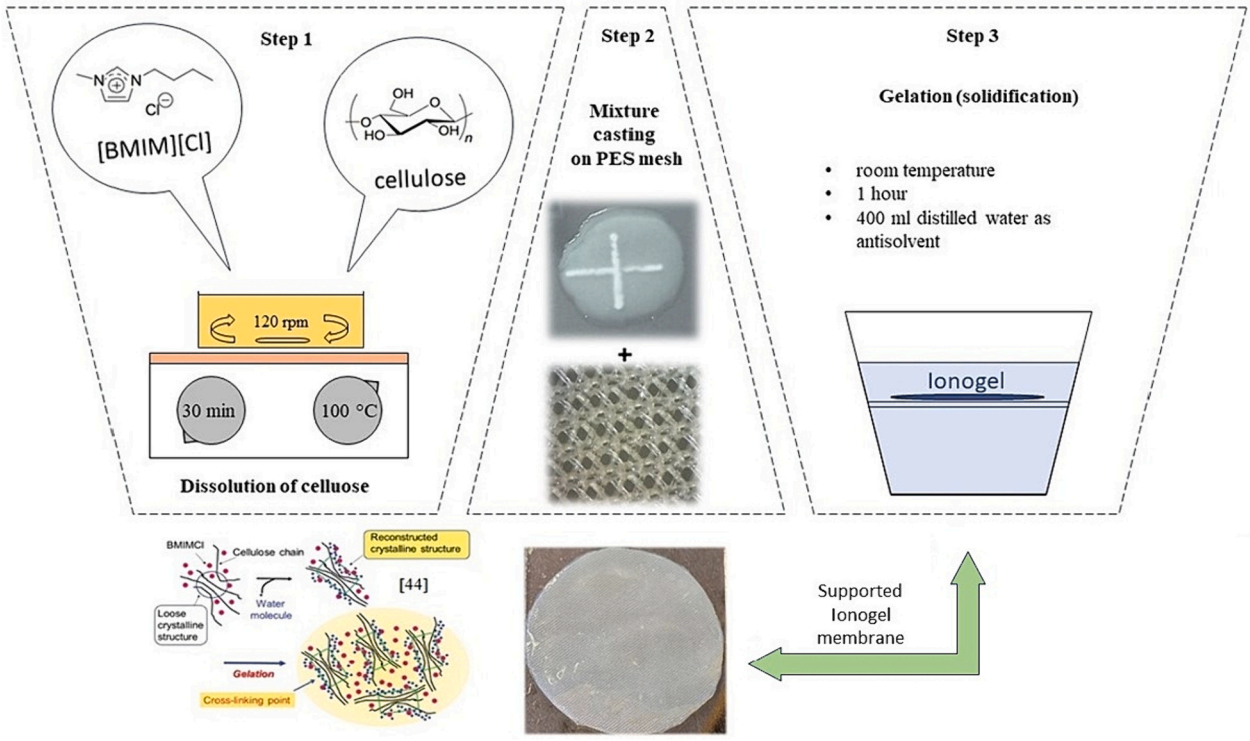

Fig. 1. Preparation scheme of the supported cellulose-[BMIM][Cl] ionogel membrane.

made as described in Section 2.1. – were examined in the swollen ("as prepared") state in both sides after freeze drying (lyophilization). Standard Scanning Electron Microscope Vega Plus TS 5135 (Tescan) was used for morphology analysis. To analyze the cross section, the samples were prepared under liquid nitrogen. The samples were coated with Platinum using a Vacuum sputter coaters SCD 050 (Balzers) platinum cover and were analyzed in different magnifications (Fig. 2).

2.3. Characterization of the physicochemical properties of the membranes

Both the cellulose-[BMIM][Cl] ionogel and Nafion 115 membranes were characterized in terms of their oxygen and substrate mass transfer coefficients (denoted onwards as k_O and k_S, respectively) following the methods reported by Kim et al. (Kim et al., 2007), while the ionic conductivity (S m^{-1}) of the two membranes were determined in 0.5 M NaCl electrolyte according to Geise et al. (Geise et al., 2013) (Fig. 3). The ionogel membrane was kept under water constantly and under these conditions, ionogel peeling off from the PES mesh was not noticed. Preliminary (UV spectroscopy) tests (Cao et al., 2014) confirmed the (abiotic) stability of the ionogel membrane as no leakage of the ionic liquid from the membrane matrix could be measured in the aqueous environment over a period of three months.

2.4. Microbial fuel cell setup

The two-chamber MFCs in this work were assembled as H-shaped glass reactors with 285 ml of working volume (each side). This type of

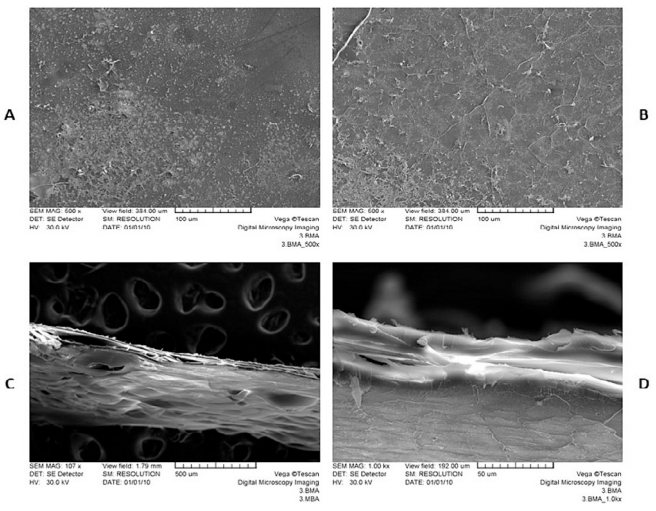

Fig. 2. SEM images for the cellulose-[BMIM][Cl] ionogel. A) Top section, B) bottom section, C) and D) cross section layers with different magnifications.

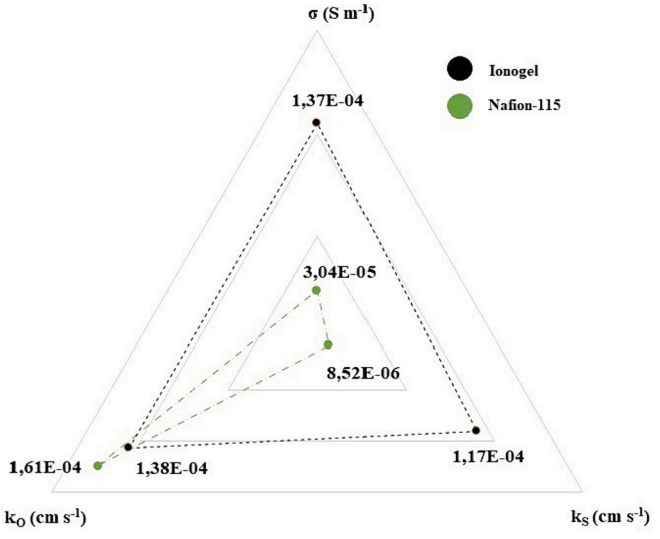

Fig. 3. Comparative radar diagram of Nafion 115 and cellulose-[BMIM][Cl] ionogel membranes with regard to their physico-chemical features.

MFC, as a first approach, is suitable to conduct fundamental research where for instance it is aimed to evaluate the effect of certain MFC components, such the membrane (Kim et al., 2007). The membrane separating the anodic chamber from the cathodic was placed in the middle of the glass cylinder that connects the chambers (the membrane-electrode and anode-cathode distancing was 5 cm and 10 cm, respectively). The anode was carbon felt (Zoltek PX35, Zoltek Corp., USA) with the surface area of 27 cm^2, while the cathode was a Pt/carbon paper (0.3 mg cm^{-2}, surface area: 10 cm^2, FuelCellsEtc, USA).

The electrodes connections and the external circuit were Ti wiring (Merck, Germany). The anode chamber contained 285 ml of anolyte solution which consisted of 256.5 ml phosphate buffer solution (PBS, pH = 7.2, 50 mM) and 28.5 ml of wastewater sludge inoculum (Szakács et al., 2022) supplemented with 100 µl −100 µl of vitamin and mineral solution (according to DSMZ 141 medium). The catholyte consisted of 50 mM PBS (pH = 7.2) and was constantly purged with air. The catholyte was exchanged weekly, while the anolyte was replenished once (on the 13th day) with 50 mM PBS (pH = 7.2) to manage pH imbalances. As substrate, sodium acetate (Merck, Germany) was used to ensure three different concentrations of acetate in the anolyte (c_{Ac}): 5.0 and 10.0 mM in the consecutive order of 5–10-5 mM during the start-up phase (0-14th days) and then, 2.5 mM under the steady-state conditions (15th-23rd day) (Fig. 4). The anolyte was stirred at 500 rpm. The MFCs were temperature controlled at 37 °C, and the voltage signal was recorded using a data acquisition card (USB-2404-10, Measurement Computing, USA). For closed-circuit operation mode, external resistor of 470 Ω was utilized thoroughly. All reactor parameters were identical apart from the applied membrane with an active surface area of 8 cm^2 (either the cellulose-[BMIM][Cl] ionogel or Nafion 115). The membranes were sandwiched between two O-rings to ensure proper sealing and avoid the leakage of MFC content. The two half-cells were tightly connected with a membrane in-between using metal clamp. All chemicals used in the experiments were at least of analytical grade.

The electrochemical performance of MFCs in terms of maximal peak current density (j_{max}; mA m^{-2}), Coulombic efficiency (CE*; %), energy production rate (ν, J m^{-2} h^{-1}) and total internal resistance (R_{int}, Ω) were computed and determined according to our earlier papers (Koók et al., 2018, 2021; Szakács et al., 2022) (Fig. 5).

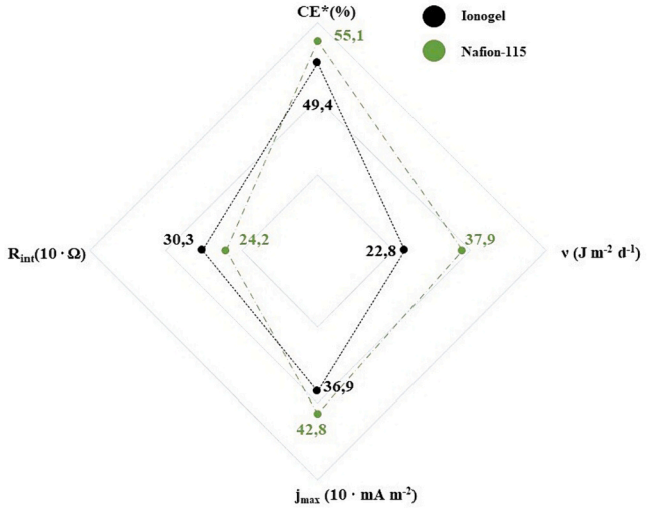

Fig. 5. Comparative radar diagram of MFC performances installed with Nafion 115 and cellulose-[BMIM][Cl] ionogel membranes.

2.5. 16S amplicon metagenomics: extraction of DNA, PCR amplification, sequencing, bioinformatics

The 16S rRNA gene- and Illumina sequencing-based metagenomic analysis of microbial communities located either on the electrode (anode, cathode) or on the membrane used in the MFCs was performed following the methods/protocol published in our recent paper regarding DNA extraction, PCR amplification, sequencing and bioinformatics analysis (Szakács et al., 2022).

Subsequently, the obtained relative abundance data of the inoculum and the samples (as objects) scratched and taken from the anode, membrane and cathode surfaces at the end point of MFC operation (22nd-23rd days in Fig. 4) were used to perform Correspondence Analysis (CA) type I at the families (as variables) level (>2.0 %) (Fig. 6).

3. Results and discussions

3.1. Observation of the cellulose-[BMIM][Cl] ionogel membranes by SEM

Fig. 2A-D illustrate the morphology of the top, bottom, and cross

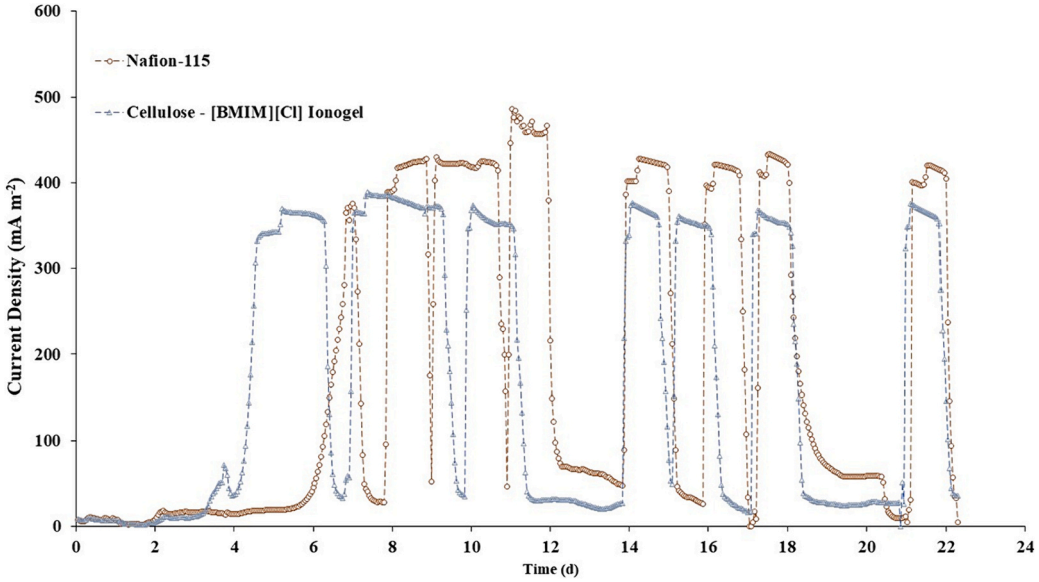

Fig. 4. Current density profile of the MFCs operated with Nafion 115 and cellulose-[BMIM][Cl] ionogel membranes.

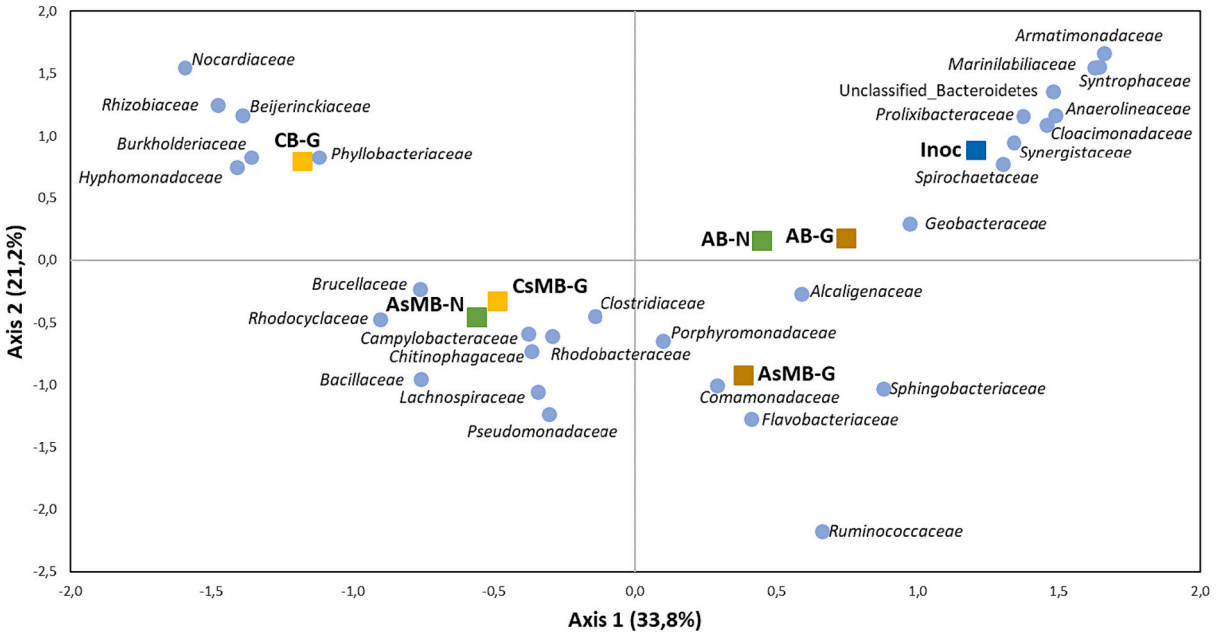

Fig. 6. Correspondence analysis (type I) of the microbial communities of the samples comparing cellulose-[BMIM][Cl] ionogel and Nafion membranes.

section layer of the cellulose-[BMIM][Cl] ionogel membranes, respectively. The top section and bottom sections present a homogenous surface. The cross section exhibits some hills and big voids, which could have presumably formed due to the penetration of air microbubbles into the continuously stirred solution of the ionic liquid-cellulose during the cellulose dissolution process, before the actual film for membrane formation was cast over the PES mesh as physical support. Although imidazolium type ILs with halide ions such as [BMIM][Cl] have shown the best performance in terms of cellulose solubility (Swatloski et al., 2002), its high viscosity can cause technical difficulties with the dissolution of cellulose and the further processing of the resulting solution (Gericke et al., 2012; Isik et al., 2014) where air bubbles may be present due to agitation. For instance, Xia et al. (Xia et al., 2014) obtained more homogeneous structures by using a kneading machine rather than stirring the cellulose/ionic liquid mixture.

3.2. Comparison of cellulose-[BMIM][Cl] ionogel and Nafion 115 membranes based on their physico-chemical features

Prior to deployment in MFCs, the Nafion 115 and the cellulose-[BMIM][Cl] ionogel membranes were studied with regard to various pristine-state material properties, such as the oxygen and acetate mass transfer coefficients and specific conductivity (Fig. 3). Dissolved oxygen passing through the actual membrane can be toxic/inhibitory to the anode-surface electro-active bacteria and/or divert their metabolism. Thus, it is crucial to know the k_O of the membranes used, which should be minimized to evade the loss of working efficiency in the MFC. Similarly, the substrate crossover (the leakage of the substrate from the anolyte to the catholyte through the membrane) can increase the threat of microbial proliferation in the cathode chamber and concurrently cause adverse effects linked for instance to the biological fouling of the cathode (Pasternak et al., 2016). The phenomenon was experienced during MFC operation only in the reactor equipped with the cellulose-[BMIM][Cl] ionogel membrane, as it will be elaborated in Section 3.4.

The specific conductivity (σ) and mass transfer coefficient (k_O and k_S) values are shown in Fig. 3 and it can be inferred that the Nafion 115 had a 16 % higher k_O than that of the cellulose-[BMIM][Cl] ionogel membrane (1.61×10^{-4} cm s^{-1} and 1.38×10^{-4} cm s^{-1}, respectively). Previously, papers such as Koók et el. (Koók et al., 2017)and Bakonyi et al. (Bakonyi et al., 2018) thoroughly worked on the issue created by the oxygen crossover and it would appear that membranes having $k_O < 10^{-3}$ (favorably at least in the order of 10^{-4} cm s^{-1}) could be more adequate choices in MFCs. Accordingly, in this aspect, both membranes could be seen viable for MFC applications.

As for the substrate crossover, however, there is a big difference between the two membranes. The cellulose-[BMIM][Cl] ionogel membrane, compared to Nafion 115, could be characterized by a significantly higher k_S (1.17×10^{-4} cm s^{-1} and 8.52×10^{-6} cm s^{-1}, respectively), meaning that the ionogel membrane lets the substrate pass through by two orders of magnitude faster. Nonetheless, regarding the specific conductivity, it turned out that the cellulose-[BMIM][Cl] ionogel membrane (1.37×10^{-4} S m^{-1}) was 4–5 times greater than it was measured for the Nafion 115 (3.04×10^{-5} S m^{-1}) and refers hence to a better ionic conductor.

3.3. Evaluation of MFC working efficiency

In Fig. 4, the current density time profile of the MFCs is demonstrated. The MFCs were maintained in total for slightly more than three weeks of operation time, which was split into two phases. The first period following the inoculation of the systems (0-14th days) was considered as the start-up phase, while the additional experiments were carried out under steady-state conditions in the already established systems.

In both cases, the current generation was assessed through 7 substrate feeding cycles: from left to right in Fig. 4, three in the start-up with 5, 10, 5 mM and four another in the steady-state with 2.5 mM of acetate in the anolyte. In Fig. 5, the radar diagram summarizes the peak current density, Coulombic efficiency, energy production rate and total internal resistance data pertaining to the steady-state of the MFCs. It is to note that the j_{max}, CE^* and ν values in Fig. 5 are averages calculated from the four consecutive substrate feeding cycles ($c_{Ac} = 2.5$ mM), while the R_{int} was measured right before the MFCs were shut down (22nd day) under the peak current density conditions. Basically, the MFC installed with the Nafion 115 membrane performed better than the one applying the cellulose-[BMIM][Cl] ionogel membrane: higher CE^*, j_{max} and ν could be realized along the lower R_{int}.

As the R_{int} was measured at the end of MFC operation, the results obtained could have been influenced by the acetate crossover and the formation of the biofilms on the membrane and the cathode. Although

the original ("before use") specific conductivity (1.37×10^{-4} S m^{-1}) of the ionogel membrane was better than Nafion 115 (3.04×10^{-5} S m^{-1}) and thus promising, it was more prone to biofouling due to the significantly higher k_S value (1.17×10^{-4} cm s^{-1}). The (cathodic and cathode-side membrane) biofouling – discussed in details in Section 3.4. – could have caused the notable increase of R_{int} and a concurrently lower electrochemical performance in comparison with the MFC equipped with the Nafion 115 membrane.

3.4. Assessment of electrode biofilms and membrane biofouling layers

The suitable membrane candidates for MFCs should tend to resist biological fouling in order for maintaining the (favorable) ion- and mass transfer characteristics leading simultaneously to expectedly enhanced electrochemical efficiency and system stability (Koók et al., 2019a). Hence, the changes occurring at the level of the membrane, e.g. due to biofouling will likely have an impact on the global working traits of MFCs in the longer-term, both in economic and technological senses (Koók et al., 2020b; Noori et al., 2019). Therefore, given such importance of the membrane biofouling issue, we have analyzed the microbiological composition of the biofilms grown over the surfaces of the Nafion 115 and cellulose-[BMIM][Cl] ionogel membranes at the endpoint of the of MFC operation (22nd – 23rd days, Fig. 4) and made a comparison with those biofilms existed on the electrode surfaces. It is noteworthy that in case of the Nafion 115, biofilms were only found on the anode electrode and the physically anode-oriented side of the membrane. Nevertheless, in case of the cellulose-[BMIM][Cl] ionogel membrane, additional biofilms were formed on the cathode-facing side of the membrane as well as on the cathode. As discussed in Section 3.1., the cross section of the cellulose-[BMIM][Cl] ionogel membrane (Fig. 2C) could be characterized by a hilly-structure consisting of relatively larger-size cavities, which may refer to the presence of air microbubbles in the membrane. In our hypothesis, these thin-wall voids may have collapsed and/or got disintegrated in the course of MFC operation and the so-formed defects, such as pinholes in the material could make it more and more permeable. This idea about the presumed degradation of the cellulose-[BMIM][Cl] ionogel membrane over time seems to be supported by the species level relative abundance data obtained from the 16S metagenomics. As a matter of fact, the anode-facing biofouling layer on the cellulose-[BMIM][Cl] ionogel membrane comprised of 23.2 % *Clostridium termitidis*, which was recognized for its cellulose-degrading capability (Gomez-Flores et al., 2017; Hethener et al., 1992). This particular bacterium, however, was not detected at all over the Nafion 115 membrane and it appears as a realistic explanation that the cellulose-based ionogel membrane was attacked by the cellulolytic *C. termitidis*, leading up to morphological changes, altered mass transport features and an undermined performance in comparison to Nafion 115 in MFCs (Figs. 4 and 5). This possible, microbiology-routed mechanism is definitely a peculiar phenomenon that will need to be further investigated and confirmed (or discarded) in the future.

Overall, it is assumed that an open-pore membrane structure developing with time could have led to microbial migration from the anode side of the MFC (where the inoculum is loaded) towards the cathode chamber, causing the rise of bacterial colonies on the cathode and on the cathode-facing side of the membrane, as well. It is however to note that as the experiments were not carried out in a sterile environment, it is also hypothetically possible that some strains already present (at very low concentrations) in the assays may have proliferated utilizing the acetate substrate passing through the membrane over time. Nevertheless, the comparison of the inoculum (Inoc, Table 1) and the cathodic side biofilms' (CB-G and CsMB-G, Table 1) compositions indicates that there were numerous common species in the three samples and therefore, the above-proposed microbiological crossover seems to be a well-supported idea. Additionally, though it is not clear from our SEM images in Fig. 2, ionogels consisting of [BMIM][Cl] and cellulose – depending greatly on the preparation method – can inherently have a porous structure and notable porosity (Peng et al., 2018; Sun et al., 2019). Accordingly, in other words, pores may have also been present in the material without any microbiological phenomenon. If this was the case, it is still not known (i) to what extent those pores could have been communicating or not communicating and hence, (ii) how they played a role in the above-discussed migration of bacteria from one side of the

Table 1
Relative abundance (%) of microbial communities at the family level.

Family Taxonomic level	Inoc	AB-G	AB-N	AsMB-G	AsMB-N	CB-G	CsMB-G
Rhodocyclaceae	0.65	1.04	6.00	1.53	45.44	13.50	13.31
Nocardiaceae	0.49	0.93	1.39	1.15	1.84	33.88	3.61
Alcaligenaceae	0.09	29.98	13.66	18.39	2.59	5.82	3.77
Ruminococcaceae	0.90	0.39	0.98	26.16	0.16	0.01	0.82
Campylobacteraceae	0.38	4.74	0.61	0.40	0.01	0.17	21.31
Phyllobacteriaceae	0.24	0.24	4.43	1.01	3.74	14.91	4.22
Porphyromonadaceae	3.33	4.26	8.09	8.66	7.50	0.28	14.33
Anaerolineaceae	13.81	4.05	5.91	2.51	0.28	0.00	0.01
Geobacteraceae	0.05	8.44	10.59	1.01	0.08	0.01	0.02
Pseudomonadaceae	0.12	1.16	1.57	5.90	10.32	0.43	3.82
Burkholderiaceae	0.05	0.30	0.54	0.45	0.02	10.17	6.89
Cloacimonadaceae	9.07	9.76	3.68	0.87	0.19	0.01	0.01
Clostridiaceae	1.08	0.70	3.71	0.28	6.98	0.01	1.88
Rhizobiaceae	0.12	0.04	0.17	0.77	0.05	6.37	1.27
Comamonadaceae	0.74	2.24	1.48	6.31	1.60	0.53	2.96
Flavobacteriaceae	1.15	0.41	0.53	6.15	0.12	0.26	2.55
Spirochaetaceae	2.32	5.85	2.05	0.36	0.11	0.01	0.02
Synergistaceae	5.75	4.24	3.85	1.03	0.35	0.04	0.04
Brucellaceae	0.08	0.36	0.60	0.65	0.25	1.90	5.51
Prolixibacteraceae	4.52	1.76	2.08	0.40	0.59	0.00	0.00
Marinilabiliaceae	4.38	1.08	0.82	0.26	0.22	0.00	0.01
unclassified_Bacteroidetes	4.15	1.17	1.49	0.25	0.38	0.00	0.00
Armatimonadaceae	3.85	0.69	1.08	0.12	0.08	0.00	0.00
Bacillaceae	0.04	0.06	0.37	0.02	3.44	0.10	0.00
Beijerinckiaceae	0.09	0.04	0.25	0.15	0.13	3.00	0.97
Others[a] (<3.0)	42.55	16.07	24.07	15.20	13.54	8.60	12.68

Inoc: Inoculum; **AB-G**: Anode biofilm – ionogel membrane; **AB-N**: Anode biofilm – Nafion; **AsMB-G**: Anode-side membrane biofilm – ionogel membrane; **AsMB-N**: Anode-side membrane biofilm – Nafion; **CB-G**: Cathode biofilm – ionogel membrane; **CsMB-G**: Cathode-side membrane biofilm – ionogel membrane.

[a] Families with a relative abundance <3.0 % were classified as Others.

MFC to another. This will need to be a subject of further investigation. With regard to the rise of the biofouling layer on the cathode, to the naked eye, microbial proliferation became first visible somewhere between the 7th and 14th days of MFC operation (the second half of the start-up period) and was keep on existing afterwards till the end of the experiment (22nd-23rd days). Moreover, it is to keep in mind that the pristine cellulose-[BMIM][Cl] ionogel membrane displayed a quite high substrate (acetate) mass transfer coefficient (1.17×10^{-4} cm s^{-1}), which might also have promoted the growth of microbes at the cathode-side located environment of the MFC and contributed consequently to the lower electrochemical performance achieved with this membrane (Figs. 4 and 5) (Pasternak et al., 2016). From the Correspondence Analysis of the microbial communities (Fig. 6), it can be noticed that the inoculum microbial community (Inoc, Table 1) is quite distant from the other samples, which is expected as the initial populations usually adapt themselves and change therefore during the MFC operation.

Nonetheless, the AB-N and AB-G were found as similar communities and it would mean that – considering the taxonomic level of family – the membrane type does have not a big impact on the microbial community selected on anode biofilms. These samples (AB-N and AB-G, Table 1) are related to *Geobacteriaceae* and *Alcaligenaceae,* which are bacterial families normally identified in bioelectrochemical systems as a part of a diverse underlying microflora and can contribute to organic matter decomposition (Cristiani et al., 2013; Meylani et al., 2023). Furthermore, independently of the type of the membrane, the biofilms formed on the membranes are different from those taken from the anode surfaces. For instance, AsMB-G and AsMB-N are distant from AB-G and AB-N, respectively (Table 1). The same observation goes for the cathodic biofilm sample (CB-G, Table 1).

Overall, to sum up, it is indicated by the two-dimensional map in Fig. 6 that the samples standing for the anode-, cathode- and membrane-surface biofilms (Table 1) could be properly differentiated. This means that the adaptation of bacteria – in line also with their possible roles in the bioreactors – to the various conditions representing the anode, the membrane and the cathode would require different strategies and abilities for survival. We would here argue that one possible, microbial selection factor could have been the availability of dissolved oxygen gas at the physically distant spots of the MFC. The anode is basically under anaerobic conditions, the cathode is continuously aerated, while the membrane is placed at the interface of the two. In this context, similar findings have been communicated in our recent paper, where MFCs equipped with polymeric, ion (anion- and cation) exchange membranes demonstrating varying k_O values were studied (Szakács et al., 2022).

As a matter of fact, the top five (most abundant) classified species on the anode of the MFC equipped with the Nafion 115 membrane (AB-N) were *Geobacter anodireducens* (10.3 %), *Kerstersia gyiorum* (6.1 %), *Levilinea saccharolytica* (4.8 %), *Proteiniborus ethanoligenes* (3.7 %) and *Proteiniphilum acetatigenes* (3.7 %). As for the MFC equipped with the cellulose-[BMIM][Cl] ionogel membrane, *Advenella faeciporci* (27.9 %), *Cloacamonas acidaminovorans* (9.5 %), *Geobacter anodireducens* (8 %), *Treponema medium* (4.7 %) and *Arcobacter cryaerophilus* (4.3 %) could be listed among the five most significant, classified species on the anode (AB-G). *Geobacter anodireducens,* detected in both anodic biofilms, is a well-known electro-active bacterium commonly enriched in bioelectrochemical systems (Sun et al., 2014).

Meanwhile, the bacteria in the cathode biofouling layer in the case of the MFC installed with the cellulose-[BMIM][Cl] ionogel membrane (CB-G) were found as *Gordonia cholesterolivorans* (19 %), *Azoarcus indigens* (13.3 %), *Gordonia polyisoprenivorans* (8 %), *Aquamicrobium terrae* (5.6 %) and *Aquamicrobium lusatiense* (4.5 %). On the anode-facing side of the Nafion 115 membrane (AsMB-N), *Pseudomonas stutzeri* (8.4 %), *Proteiniphilum acetatigenes* (6.7 %), *Proteiniborus ethanoligenes* (5.3 %), *Bacillus horti* (3.4 %) and *Aquamicrobium aestuarii* (2.5 %) were the most abundant, classified species. Regarding the top five, classified species on the anode- and cathode-facing sides of the cellulose-[BMIM][Cl] ionogel membrane (AsMB-G and CsMB-G), *Clostridium termitidis* (23.3 %), *Advenella faeciporci* (17.1 %), *Hydrogenophaga temperata* (5.9 %), *Dysgonomonas oryzarvi* (4.7 %), *Pseudomonas aeruginosa* (4.6 %) and *Arcobacter lanthieri* (20.4 %), *Dysgonomonas oryzarvi* (12.3 %), *Azoarcus indigens* (12 %), *Niabella yanshanensis* (2.7 %), *Clostridium celerecrescens* (2.2 %) were recognized, respectively. Interestingly, among the membrane-surface samples, *Campylobacterales* to larger extents (21.2 %) was only found on the cathode-facing biofouling layer of the cellulose-[BMIM][Cl] ionogel membrane. In the case of the cathodic chamber side samples (CB-G and CsMB-G) it will be interesting to evaluate whether there was consumption of acetate that may have appeared due to the crossover effect in accordance with the previous discussion. Moreover, the potentiality of the cathodic biofilm (CB-G) towards electroactivity, particularly to consume (take up) electrons from the cathode should be investigated.

As final remarks, the applicability of ionogel membrane for real wastewater treatment remains an open question and the effect of certain components (e.g. ions) on its behavior can be sought to understand its long-term stability. These in-depth future studies should also involve electrochemical analysis such as linear sweep voltammetry, cyclic voltammetry and impedance spectroscopy.

4. Conclusions

The behavior of MFCs was assessed in this study applying Nafion 115 (for benchmarking) and a cellulose-based ionogel membrane prepared with [BMIM][Cl] ionic liquid on PES mesh. The remarkable acetate crossover in the course of MFC operation was appointed as a potential contributory factor of severe biological fouling occurring on the cathode side of the system installed with the ionogel membrane. The assessment of microbial communities showed that the ionogel membrane promoted a cellulose-degrading microorganism (*Clostridium termitidis*) on its surface. To conclude on the positive note, an optimized recipe and a technically improved ionogel synthesis could apparently lead to a better membrane formation strategy with an expectedly higher performance in MFC.

CRediT authorship contribution statement

Szabolcs Szakács: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Eduardo Ortega Martínez:** Writing – original draft, Visualization, Investigation. **László Koók:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Gabriela Medeiros Santos:** Writing – original draft, Visualization, Investigation. **Javiera Toledo Alarcon:** Writing – original draft, Visualization, Funding acquisition, Data curation. **David Jeison:** Writing – review & editing, Project administration, Funding acquisition. **Zbynek Pientka:** Visualization, Supervision, Investigation. **Nándor Nemestóthy:** Supervision, Resources, Project administration, Investigation. **Katalin Bélafi-Bakó:** Writing – review & editing, Writing – original draft, Supervision. **Péter Bakonyi:** Writing – review & editing, Writing – original draft, Resources, Investigation, Funding acquisition, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

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