Performance evaluation of microbial electrochemical systems operated with Nafion and supported ionic liquid membranes

László Koók[1,*], Nándor Nemestóthy[1], Péter Bakonyi[1], Guangyin Zhen[2], Gopalakrishnan Kumar[3,4], Xueqin Lu[5], Lianghu Su[6], Ganesh Dattatraya Saratale[7], Sang-Hyoun Kim[3,4], László Gubicza[1]

[1]Research Institute on Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem ut 10, 8200 Veszprém, Hungary

[2]School of Ecological and Environmental Sciences, East China Normal University, Shanghai 200241, China

[3]Department of Environmental Engineering, Daegu University, Gyeongsan, Gyeongbuk 712-714, Republic of Korea

[4]Sustainable Environmental Process Research Institute, Daegu University, Jillyang, Gyeongsan, Gyeongbuk 38453, Republic of Korea

[5]Department of Civil and Environmental Engineering, Graduate School of Engineering, Tohoku University, Sendai, Miyagi 980-8579, Japan

[6]Nanjing Institute of Environmental Sciences of the Ministry of Environmental Protection, 210046, Nanjing, PR China

[7]Department of Food Science & Biotechnology, Dongguk University, Ilsandong-gu, Goyang-si, Gyeonggido, 410-820, Republic of Korea

[*]Corresponding Author: László Koók

Tel: +3688624385

Fax: +3688624292

E-mail: kook@almos.uni-pannon.hu

Abstract

In this work, the performance of dual-chamber microbial fuel cells (MFCs) constructed either with commonly used Nafion® proton exchange membrane or supported ionic liquid membranes (SILMs) was assessed. The behavior of MFCs was followed and analyzed by taking the polarization curves and besides, their efficiency was characterized by measuring the electricity generation using various substrates such as acetate and glucose. By using the SILMs containing either $[C_6mim][PF_6]$ or $[Bmim][NTf_2]$ ionic liquids, the energy production of these MFCs from glucose was comparable to that obtained with the MFC employing polymeric Nafion® and the same substrate. Furthermore, the MFC operated with $[Bmim][NTf_2]$-based SILM demonstrated higher energy yield in case of low acetate loading (80.1 J g^{-1} COD_{in} m^{-2} h^{-1}) than the one with the polymeric Nafion® N115 (59 J g^{-1} COD_{in} m^{-2} h^{-1}). Significant difference was observed between the two SILM-MFCs, however, the characteristics of the system was similar based on the cell polarization measurements. The results suggest that membrane-engineering applying ionic liquids can be an interesting subject field for bioelectrochemical system research.

Keywords: bioelectrochemical system, microbial fuel cell, membrane, ionic liquid, electricity generation, polarization

1. Introduction

Microbial fuel cells (MFCs) are considered as newfangled and environmental friendly renewable energy-producing systems that are able to directly convert waste-bound chemical energy into electricity by the assistance of electrochemically-active microorganisms (Logan et al., 2006; Lovley, 2006). A classical microbial electrochemical system consists of three main structural components, such as (i) an anaerobic anode, (ii) an aerobic cathode chamber and (iii) a separator in-between them, in most cases a membrane with ion-exchange capacity (Kumar et al., 2017). The membrane, besides its role in physically separating the two half-cells, is supposed to facilitate the selective transport of protons from the anode to the cathode chamber (Winfield et al., 2016). So far, a significant number of studies have dealt with the development of bioelectrochemical cells and it has been proven that they can be operated with different type of membranes (e.g. proton exchange (PEM), anion-selective, bipolar, ultra- and microfiltration or composite, etc.) (Li et al., 2011). Thus, it can be concluded that their features can notably affect the performance of these applications (Gildemyn et al., 2017) i.e. due to their different contribution to the overall internal resistance of the system (Kumar et al., 2017). Though there is a range of membranes to choose from, PEMs are the most routinely used by far (Rahimnejad et al., 2014). However, their price is a factor that can limit scale-up and thus drive the research to develop alternative, potential replacement materials.

Recently, novel membranes prepared with ionic liquids were reported as promising competitors to conventional polymers such as Nafion® in MFCs

(Hernández-Fernández et al., 2015). Ionic liquids (ILs) have been recognized as novel and green solvents, many of which – depending on their chemical structure – are liquids even at room temperature and can be immobilized in a porous matrices to form a so-called supported ionic liquid membrane (SILM) (Bakonyi et al., 2013; Bednár et al., 2016; Cserjési et al., 2010). Moreover, there is a possibility to process the ionic liquid into polymers where no porous supports are required (Yuan et al., 2013). Recent findings of Hernández-Fernández et al. (2015) and Hernández-Fernández et al. (2016) indicated that ionic liquids can actively participate in the proton transport taking place between the anode and cathode chambers of bioelectrochemical system and additionally, it was concluded that the amount of ionic liquid immobilized in the membrane is able to influence the actual power output in microbial fuel cells. The same research group demonstrated the role of ionic liquids in MFCs by using different ionic liquid-polymer inclusion membranes (PIM) as well as ionic liquid-type membrane-cathode assembly (Salar-García et al., 2015; 2016). In an interesting study, Sood and co-workers (2015) communicated the successful combination of Nafion® and proton conductive ionic liquids, where increasing conductivities of the doped membranes along with higher ionic liquid loadings were observed. More recently, an approach to prepare ionic liquid/imidazoledicarboxylic acid modified poly(vinylalcohol) polyelectrolyte membranes was introduced by Gohil and Karamanev (2016), where MFC set-ups with these blended membranes provided salient current as well as power densities. Further applications of ionic liquid in MFCs include (i) the functionalization of carbon nanotubes to obtain anodes with improved

interfacial electron transfer (Wei et al., 2016) and (ii) the modification of cathodes for enhanced MFC performance (Ortiz-Martínez et al., 2016).

In this research work, the characteristics of SILM-based MFCs (membranes prepared with [C_6mim][PF_6] and [Bmim][NTf_2] ionic liquids) were investigated in terms of their main energetical traits along with behavior analysis using the polarization curve technique. The results were compared to MFCs operating with Nafion® proton exchange membrane in order to evaluate the feasibility of MFCs with new generation membrane separators and attempt to deliver a better comprehension of the membrane-related effects.

2. Materials and Methods

2.1. Preparation of SILMs

To prepare the SILMs, water immiscible 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide ([Bmim][NTf_2]) and 1-hexyl-3-methylimidazoluim hexafluorophosphate ([C_6mim][PF_6]) ionic liquids (IoLiTec, Germany) were chosen. The main aspect was to use ionic liquids with near the same hydrophobicity, thus, the effect of the hydrophobicity on the observed differences can be avoided. Since the anions possess disparate hydrophobicity values, the differences can be compensated through selecting the cation chain length properly. As supporting layer for ionic liquid immobilization, hydrophobic porous Durapore® PVDF membrane was used, ~~each~~ having a diameter of 4.5 cm, a pore size of 0.22 μm and a

thickness of 125 μm (Millipore Corp., USA). The SILM fabrication procedure had been described in details in our previous paper (Cserjési et al., 2010). After IL immobilization, the membrane surface was cleaned carefully (to remove excess ionic liquid). Subsequently, the weight and thickness of the SILMs were measured and the amount of IL embedded in the PVDF matrix was determined.

2.2. MFC setup

Mesophilic anaerobic sludge (with initial COD and pH of 17 g L^{-1} and 7.5, respectively) collected from a local biogas plant was used for the inoculation of the plexi-made MFCs which were constructed with a total working volume of 60 mL of each chamber (Koók et al., 2016, Rózsenberszki et al., 2015). ~~The schematic diagram of the MFC can be seen in **Fig. 1**.~~ The MFC chambers were separated by Nafion® N115 (Sigma-Aldrich, USA) PEM or the different SILMs. Prior to use, the Nafion® was pretreated by following the method described in the work of Ghasemi et al. (2013) and Rahimnejad et al. (2012). Carbon cloth fixed on a titanium wire with a total projected surface area of 64 cm^2 was used as electrode (both anode and cathode). The cathode chamber contained 60 mL, 50 mM phosphate buffer (pH = 7), which was continuously aerated. Initially, the anode chamber was filled with 45 mL of the same buffer, 14 mL of the anaerobic sludge as seed source and substrates were injected in 1 mL volume to achieve the desired initial substrate concentration in 60 mL for the experiments (see in Section 3.1.). A 100 Ω resistor was inserted in the external circuit to record the potential difference between the two electrodes. More details regarding

the MFC set-up can be found in our earlier publications (Koók et al., 2016, Rózsenberszki et al., 2015, 2017). The start-up experiences with various substrate (sodium acetate, glucose) feedings is discussed in Section 3.1.

2.3. Analysis and Calculations

The cell voltage was continuously measured and acquired by using a data logger device (National Instruments). According to Ohm's law, current (I) and thus other electrical data (such as current density, I or power density, P_d) could be calculated based on the voltage recorded and the external resistance I. Cumulative energy data I is the product of integrating the time-dependent power curve. The time-specific (Y_t) and substrate-specific energy yields (Y_S) were computed according to Eqs. 1 and 2, respectively (specified relationships based on Koók et al., 2016; Rózsenberszki et al., 2015):

$$Y_t = \frac{\int_0^\tau P(t)dt}{A\,\tau} \quad (1)$$

$$Y_S = \frac{\int_0^\tau P(t)dt}{m(COD_{in})\,A\,\tau} \quad (2)$$

where P is the power (W), A is the apparent anode surface area (m^{-2}), τ is the operation time (h) for a batch feeding cycle and $m_{(CODin)}$ is the amount of COD added (grams) by the different substrate feedings. COD was determined in accordance with the Standard Methods (APHA, 1995). The operation time was defined as the time elapsed between

the substrate addition and the point when the voltage peak was returned to the initial value.

In order to measure the polarization curves (Section 3.2.), an external circuit with variable resistor and a digital multimeter were applied. Based on the slope of the linear region of the polarization curves, the internal cell resistance (R_i) could be estimated.

3. Results and Discussion

3.1. Comparing the performance of MFCs with different membrane separators and substrates

The SILMs were prepared successfully, having final masses of 299 mg and 296 mg and thicknesses of 117 μm and 115 μm in case of $[C_6mim][PF_6]$ and $[Bmim][NTf_2]$ ionic liquids, respectively. The PVDF membrane pores were considered saturated with the particular ionic liquid, the surface specific ionic liquid contents were 11.37 ± 0.1 mg cm^{-2}. This value is fairly comparable with those reported by Hernández-Fernández et al. (2015), who manufactured SILMs with ~18 mg cm^{-2} ionic liquid content in nylon supporting layer.

In the first period of the MFC operation, considered as the biofilm acclimation period, glucose (5 mM) as adaptation substrate was used in several consecutive cycles, until stabilized current density time profiles were reached (Carmona-Martínez et al., 2015). Afterwards, the main goal of the investigation was to reveal how the various

membrane types affect the performance of the MFC. To do so, the MFCs were installed with the Nafion and SILMs and put to work with sequential feedings of 25 mg Na-acetate and 25 mg glucose in all cases. The main, process efficiency-related parameters measured and calculated are listed in **Table 1** for comparison. From **Table 1**, it can be inferred that the MFC behavior was quite determined by the sort of membrane employed, resulting in notable performance differences in case of the same amount and quality of substrate. Applying acetate, the [C_6mim][PF_6]-MFC produced the least attractive outputs along with the longest operation time. In summary, it can be concluded that the use of [C_6mim][PF_6]-containing SILM caused 50 % lower maximal voltage and current density in comparison with the Nafion®-MFC. In contrast, as response to the same dose of acetate, the [Bmim][NTf_2]-MFC was able to exceed the voltage, current and power density values of the Nafion®-MFC. In fact, the maximal power density was 28 % higher than for Nafion®-MFC. Regarding glucose feeding, although the [Bmim][NTf_2]-MFC was the more efficient among the two SILM-MFCs, both were found to be relatively less efficient than the Nafion®-MFC, as both were characterized with approximately 35 % lower voltage and current density outputs as well as roughly 60 % less maximal power densities.

These achievements for the Nafion®-MFC coincide well with the previous literature, where for instance, Ieropoulos et al. (2005) tested different types of MFCs with pure cultures, applying Nafion® as separator. In case of 5 mM acetate injection and absence of added mediators, the *G. sulfurreducens*-inoculated MFCs produced current density values between 1.17 – 5.93 mA m^{-2} and power density of 0.257 – 1.175 mW m^{-2}, meanwhile 28.5 mA m^{-2} and 0.52 mW m^{-2} could be achieved in our present

experimentation for Nafion® membrane. In another paper, Chaudhuri and Lovley (2003) operated mediator-less Nafion®-MFCs fed with 10 mM glucose, using different types of graphite anodes. They reported current densities of 28 – 74 28.5 mA m^{-2}, which are in the same order or magnitude with those with glucose in our present Nafion®-MFC (36.4 mA m^{-2}). In addition, Zhang et al. (2006) investigated MFCs with perfluorinated ion membrane fed with different substrates. They reported 140 mA m^{-2} current density and 59 mW m^{-2} power density in case of 20 mM acetate, while these values were 110 mA m^{-2} and 43 mW m^{-2} for 10 mM glucose, respectively. Glucose and acetate were also tested in our earlier work for energy generation in MFCs (chambers separated by Nafion® membrane) inoculated with mesophilic sludge (Bélafi-Bakó et al., 2011). As a response to the addition of 0.1 – 0.5 mM glucose, the MFCs produced 200 – 320 mA m^{-2} current and 2 – 5.1 mW m^{-2} power density (glucose), while after the supplementation of 0.25 – 1 mM acetate, 170 mA m^{-2} and 1.45 mW m^{-2} could be achieved (Bélafi-Bakó et al., 2011).

Lately, Hernández-Fernández et al. (2015) demonstrated that 115 mW m^{-3} volume specific power density could be attained by treating wastewater substrate in Nafion®-MFC, while in contrast, the MFCs operated with [Omim][NTf_2] and [Omim][PF_6]-containing nylon membranes provided 61 and 200 mW m^{-3}, respectively. In the light of our results with Nafion® (power density of 60.2 mW m^{-3} for acetate and 98.7 mW m^{-3} for glucose) and [Bmim][NTf_2]-based SILMs (77.2 mW m^{-3} for acetate and 42.6 mW m^{-3} for glucose), it can be deduced that despite certain differences in the experimental conditions (i.e. the type of cation in the ionic liquids, the support material

231 and the substrate used) the results of the current investigation agree more or less with
232 the already published literature (Hernández-Fernández et al., 2015).

233 Further description of the experiences with the various MFCs can be ensured
234 based on the energy parameters (E and Y_S). As a matter of fact, the [Bmim][NTf_2]-
235 MFC appeared to be the most reliable in the view of the obtainable (i) cumulated
236 energy and (ii) energy yield by feeding acetate. In particular, its cumulative energy
237 production was 50 % and nearly 3-fold higher than for the Nafion®–MFC and
238 [C_6mim][PF_6]-MFC, respectively. During the experiments, this cumulative energy
239 value was 0.41 J, while the highest energy yield of 80.1 J g^{-1} COD_{in} m^{-2} h^{-1} could be
240 noticed. The glucose addition led to approximately the same cumulative energy values
241 for the SILM-MFCs, while the Nafion®-MFC produced the highest value with more
242 than 0.34 J in this part of the experiments.

243 The time course of the energy production (**Fig. 1**) suggests considerable
244 differences for the MFCs, reflecting distinguishable features between the energy
245 production kinetics of the two SILM-MFCs. The acetate-utilizing [Bmim][NTf_2]-MFC
246 was capable of reaching the peak value of the obtainable energy in 37 hours, while this
247 point could be achieved only after 100 hours of operation with the [C_6mim][PF_6]-
248 MFC. Furthermore, the [Bmim][NTf_2]-MFC significantly exceeded the performance
249 of Nafion®-MFC. For this latter system, the operation time was 36 hours, however, its
250 initial energy production rate gradually decreased after the 20th hour.

251 After glucose addition, the Nafion®-MFC was able to reach higher energy
252 values than the SILM-MFCs. Noteworthy, the [Bmim][NTf_2]-MFC showed a stable
253 energy production over 38 hours, which started to stagnate around 40 J m^{-2}. On the

other hand, stable production was followed by a slower increase after the 25th hour in case of [C_6mim][PF_6]-MFC, and after 80 hours, it exceeded barely the value of maximal cumulated energy produced by the [Bmim][NTf_2]-MFC at the 45th hour. It is noteworthy that the MFCs were stable for more than two months (until disassembling), meaning that that the membranes containing ionic liquids had no negative effect on the system stability in the operational time range of this research.

Based on the actual efficiency obtained from g of COD fed (either in the form of acetate or glucose), it can be said that the Nafion®-MFC produced nearly the same value for the two substrates (14.3 J g^{-1} and 13.1 J g^{-1}), while these values were 7.2 J g^{-1} and 10.9 J g^{-1} for the [C_6mim][PF_6]-MFC and 21 J g^{-1} and 10.9 J g^{-1} for the [Bmim][NTf_2]-MFC, respectively. Accordingly, the MFC with the [Bmim][NTf_2]-containing membrane possessed the highest specific energy yield for acetate (21 J g^{-1} vs. 14.3 and 7.2 J g^{-1}), while nearly the same values (13.1, 10.9 and 10.9 J g^{-1}) were obtained with glucose, regardless of the membrane applied.

Thus, it can be assumed that the [Bmim][NTf_2]-MFC had a property which resulted in a more efficient acetate utilization capacity. The results cannot be explained by the possible differences in the degradation capacity of the biofilms, since the same cell was used in the experiments with the various membranes sequentially. Therefore, the observed differences should have a relation with other intrinsic properties of the biological fuel cells e.g. internal resistance, which can be influenced by the particular membrane acting as an Ohmic resistance (Kumar et al., 2017). Therefore, Section 3.2. presents the results of polarization curves, which were taken to see whether the change of MFC internal resistances can be correlated with the membrane actually used.

3.2. Determination of the system-specific parameters: MFC internal resistance vs. membrane-type

The determination of the polarization curves (**Fig. 2**) was carried out once steady-state conditions in the MFCs (reaching the stabilized, maximum voltages) were noted with acetate substrate. Speaking generally, the Nafion®-MFC produced the highest current and power densities, while the results for SILM-MFCs were far below these data. The Ohmic range of the curves was twice as narrow for the SILM-operating MFCs as for Nafion® (up to 38 mA m^{-2}), numerically up to 16 mA m^{-2} for $[C_6mim][PF_6]$-MFC and 18 mA m^{-2} for $[Bmim][NTf_2]$-MFC.

The maximal power density was obtained at ~ 1.5 kΩ external resistance in case case of Nafion®-MFC, while for the SILM-MFCs, this point was reached at ~3 kΩ. The use of Nafion® membrane resulted in P_d value of 4.2 mW m^{-2}, while the $[C_6mim][PF_6]$-MFC produced 1.1 mW m^{-2} and $[Bmim][NTf_2]$-MFC exceeded 1.4 mW m^{-2}. Based on the slope of the linear region of the polarization curves (derived from the average of at least 3 repetitions), the internal cell resistances (R_i) could be estimated (Logan et al., 2006). The R_i values for Nafion®-MFC, $[C_6mim][PF_6]$-MFC and $[Bmim][NTf_2]$-MFC were found as 1.3 kΩ, 2.7 kΩ and 2.5 kΩ, respectively. In case of Nafion®, the R_i is comparable with literature data, for example, Ieropoulos et al. (2005) demonstrated acetate-utilizing (5 mM) Nafion®–MFC with 1.1 kΩ internal resistance. In another paper, Oh and Logan (2006) obtained R_i in the range of 89 Ω – 1.1 kΩ for acetate-utilizing Nafion®-MFCs, depending on the membrane size, which

seemed to play a defining role in the actual internal resistance of the bioelectrochemical set-up.

Overall, it has turned out from our data that there was no significant difference between the internal cell resistance of the two SILM-MFC and both of them had about two times higher R_i value than the Nafion®-MFC. Consequently, these results imply that the performance of MFCs with different membranes was not primarily associated the alterations of internal resistances and it can be proposed that only a deeper study on (i) properties of the individual ionic liquids as well as (ii) those of the membranes prepared with them will enhance the level of understanding about the underlying phenomena. This will be targeted in our next work, where parameters such as gas permeability (i.e. O_2 transfer), substrate (such as acetate) transport, etc. can be useful to further elaborate the MFC behaviors.

3.3. Effect of the substrate quantity on MFC performance with supported ionic liquid and Nafion® membranes

Since the [Bmim][NTf_2]-based SILM was the most efficient with acetate, further experiments were conducted using this membrane and Nafion® as a benchmark. The effect of the amount of COD added by the substrate on the energy output was studied by varying the Na-acetate loading. **Fig. 3** illustrates the tendency of the cumulated energy as a function of COD added. It can be seen in the chart that *E* values, for both membranes, were in nearly direct proportionality with the dose of organic matter.

Fig. 4 indicates the specific energy yields as a function of the COD input. Considering the time-specific energy yield (**Fig. 4A**), it could be observed that Y_t was increased by higher COD inputs using Nafion®-MFC. However, the [Bmim][NTf_2]-MFC demonstrated a completely different tendency, as reflected by the profile developed in the whole COD range studied. This stagnation may have occurred due to achieving the maximal rate of the whole cell reaction, caused by possibly limited (proton) transport process across the membrane and the losses related. **Fig. 4B** depicts that higher energy yield could be realized at the lowest substrate loading by applying the [Bmim][NTf_2]-based SILM as separator, in comparison with Nafion®-MFC. However, this advantage rapidly disappears as the amount of substrate is increased (**Fig. 4B**). Thus, it can be drawn from **Fig. 4** that in the lower substrate (acetate) loading regions, SILM based on [Bmim][NTf_2] can be competitive with the widely-used Nafion®.Nevertheless, it is an important conclusion for both the Nafion®-MFC and the [Bmim][NTf_2]-MFC that making a trade-off between the time-specific (**Fig. 4A**) and substrate dose-specific energy yield (**Fig. 4B**) is required, since higher time-specific values were manageable only at the expense of decreased substrate-specific one. The observation that Y_S was in reverse relationship with substrate concentration is in agreement with our previous findings on MFC operated with the liquid fraction of pressed solid waste (Koók et al., 2016).

4. Conclusions

Supported ionic liquid membranes (SILMs) could be successfully prepared using water immiscible ionic liquids and PVDF as supporting layer. Two-chamber MFCs were built and operated steadily in longer-terms with Nafion® proton selective membrane, $[C_6mim][PF_6]$ and $[Bmim][NTf_2]$-based SILMs. The highest energy output could be achieved with the $[Bmim][NTf_2]$-MFC using acetate, while the lowest one was produced by the $[C_6mim][PF_6]$-MFC on the same substrate. In case of glucose addition, the Nafion®-MFC was found to be the most efficient, whilst the SILM-MFCs could be characterized with comparable energy generation. The assessment of polarization curves led to the conclusion that the different behaviors of the two SILM-MFCs (with acetate) could not be explained by the change of internal resistance (R_i) values, creating a need for future study to elaborate the correlation of ionic liquid properties with the actual MFC performance. The experiments on the substrate loading-dependency applying acetate have shown that the $[Bmim][NTf_2]$-MFC could be competitive with the Nafion®-MFC at low substrate inputs.

Acknowledgement

Péter Bakonyi acknowledges the support received from National Research, Development and Innovation Office (Hungary) under grant number PD 115640. The "GINOP-2.3.2-15 – Excellence of strategic R+D workshops (Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary (2016-2020))" is thanked for supporting this work. Nándor Nemestóthy was supported by the ÚNKP-2016-4-04 "New National Excellence Program of the Ministry of Human Capacities".

References

APHA: Standard Methods for the Examination of Water and Wastewater, 19th edn. American Public Health Association, New York, 1995.

Bakonyi, P., Nemestóthy, N., Bélafi-Bakó, K., 2013. Biohydrogen purification by membranes: An overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes. Int. J. Hydrogen Energy 38, 9673-9687.

Bednár, A., Nemestóthy, N., Bakonyi, P., Fülöp, L., Zhen, G., Lu, X., et al., 2016. Enzymatically-boosted ionic liquid gas separation membranes using carbonic anhydrase of biomass origin. Chem. Eng. J. 303, 621-626.

381 Bélafi-Bako, K., Vajda, B., Nemestothy, N., 2011. Study on operation of a microbial
382 fuel cell using mesophilic anaerobic sludge. Desalin. Water Treat. 35, 222-226.

383 Carmona-Martínez, A.A., Trably, E., Milferstedt, K., Lacroix, R., Etcheverry, L.,
384 Bernet, N., 2015. Long-term continuous operation of H_2 in microbial electrolysis cell
385 (MEC) treating saline wastewater. Water Res. 81, 149-156.

386 Chaudhuri, S.K., Lovley, D.R., 2003. Electricity generation by direct oxidation of
387 glucose in mediatorless microbial fuel cells. Nat. Biotechnol. 21, 1229-1232.

388 Cserjési, P., Nemestóthy, N., Bélafi-Bakó, K., 2010. Gas separation properties of
389 supported liquid membranes prepared with unconventional ionic liquids. J. Membr.
390 Sci. 349, 6-11.

391 Ghasemi, M., Daud, W.R.W., Ismail., M., Rahimnejad, M., Ismail, A.F., Leong, J.X.,
392 et al., 2013. Effect of pre-treatment and biofouling of proton exchange membrane on
393 microbial fuel cell performance. Int. J. Hydrogen Energy 38, 5480-5484.

394 Gildemyn, S., Verbeeck, K., Jansen, R., Rabaey, K., 2017. The type of ion selective
395 membrane determines stability and production levels of microbial electrosynthesis.
396 Bioresour. Technol. 224, 358-364.

397 Gohil, J.M., Karamanev, D.G., 2016. Novel approach for the preparation of ionic
398 liquid/imidazoledicarboxylic acid modified poly(vinylalcohol) polyelectrolyte
399 membranes. J.Membr. Sci. 513, 33-39.

400 Hernández-Fernández, F.J., de los Ríos, A.P., Mateo-Ramírez, F., Godínez, C.,
401 Lozano-Blanco, L.J., Moreno, J.I., et al., 2015. New application of supported ionic

liquids membranes as proton exchange membranes in microbial fuel cell for waste water treatment. Chem. Eng. J. 279, 115-119.

Hernández-Fernández, F.J., de los Ríos, A.P., Mateo-Ramírez, F., Juarez, M.D., Lozano-Blanco, L.J., Godínez, C., 2016. New application of polymer inclusion membrane based on ionic liquids as proton exchange membrane in microbial fuel cell. Sep. Purif. Technol. 160, 51-58.

Ieropoulos, I.A., Greenman, J., Melhuish, C., Hart, J., 2005. Comparative study of three types of microbial fuel cell. Enzyme Microb. Technol 37, 238-245.

Koók, L., Rózsenberszki, T., Nemestóthy, N., Bélafi-Bakó, K., Bakonyi, P., 2016. Bioelectrochemical treatment of municipal waste liquor in microbial fuel cells for energy valorization. J. Clean. Prod. 112, 4406-4412.

Kumar, G., Bakonyi, P., Zhen, G, Sivagurunathan, P., Koók, L., Kim, S.H., et al., 2016. Microbial electrochemical systems for sustainable biohydrogen production: Surveying the experiences from a start-up viewpoint. Renew. Sustain. Energy Rev., http://dx.doi.org/10.1016/j.rser.2016.11.107

Li, W.W., Sheng, G.P., Liu, X.W., Yu, H.Q., 2011. Recent advances in the separators for microbial fuel cells. Bioresour. Technol. 102, 244-252.

Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., et al., 2006. Microbial fuel cells: Methodology and technology. Environ. Sci. Technol. 40, 5181-5192.

Lovley, D.R., 2006. Microbial fuel cells: novel microbial physiologies and engineering approaches. Curr. Opin. Biotechnol. 17, 327-332.

Oh, S.E., Logan, B.E., 2006. Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells. Appl. Microbiol. Biotechnol. 70, 162-169.

Ortiz-Martínez, V.M., Gajda, I., Salar-García, M.J., Greenman, J., Hernández-Fernández, F.J., Ieropoulos, I., 2016. Study of the effects of ionic liquid-modified cathodes and ceramic separators on MFC performance. Chem. Eng. J. 291, 317-324.

Rahimnejad, M, Bakeri, G., Ghasemi, M., Zirepour, A., 2014. A review on the role of proton exchange membrane on the performance of microbial fuel cell. Polym. Adv. Technol. 25, 1426-1432.

Rahimnejad, M., Ghasemi, M., Najafpour, G.D., Ismail., M., Mohammad, A.V., Ghoreyshi, A.A., et al., 2012. Synthesis, characterization and application studies of self-made Fe_3O_4/PES nanocomposite membranes in microbial fuel cell. Electrochim. Acta 85, 700-706.

Rózsenberszki, T., Koók, L., Bakonyi, P., Nemestóthy, N., Logrono, W., Pérez, M., et al., 2017. Municipal waste liquor treatment via bioelectrochemical and fermentation (H_2 + CH_4) processes: Assessment of various technological sequences. Chemosphere 171, 692-701.

Rózsenberszki, T., Koók, L., Hutvágner, D., Nemestóthy, N., Bélafi-Bakó, K., Bakonyi, P., et al., 2015. Comparison of anaerobic degradation processes for bioenergy generation from liquid fraction of pressed solid waste. Waste Biomass Valor. 6, 465-473.

445 Salar-García, M.J., Ortiz-Martínez, V.M., Baicha, Z., de los Ríos, A.P., Hernández-
446 Fernández, F.J., 2016. Scaled-up continuous up-flow microbial fuel cell based on
447 novel embedded ionic liquid-type membrane-cathode assembly. Energy 101, 113-120.

448 Salar-García, M.J., Ortiz-Martínez, V.M., de los Ríos, A.P., Hernández-Fernández,
449 F.J., 2015. A method based on impedance spectroscopy for predicting the behavior of
450 novel ionic liquid-polymer inclusion membranes in microbial fuel cells. Energy 89,
451 648-654.

452 Sood, R., Iojoiu, C., Espuche, E., Gouanvé, F., Mendil-Jakani, H., Lyonnard, S., 2015.
453 Influence of different perfluorinated anion based Ionic liquids on the intrinsic
454 properties of Nafion®. J. Membr. Sci. 495, 445-456.

455 Wei, H., Wu, X.S., Zou, L., Wen, G.Y., Liu, D.Y., Qiao, Y., 2016. Amine-terminated
456 ionic liquid functionalized carbon nanotubes for enhanced interfacial electron
457 transfer of Shewanella putrefaciens anode in microbial fuel cells. J. Power Sources
458 315, 192-198.

459 Winfield, J., Gajda, I., Greenman, J., Ieropoulos, I., 2016. A review into the use of
460 ceramics in microbial fuel cells. Bioresour. Technol. 215, 296-303.

461 Yuan, J., Mecerreyes, D., Antonietti, M., 2013. Poly(ionic liquid)s: An update. Prog.
462 Polym. Sci. 38, 1009-1036.

463 Zhang, E., Xu, W., Diao, G., Shuang, C., 2006. Electricity generation from acetate and
464 glucose by sedimentary bacterium attached to electrode in microbial-anode fuel
465 cells. J. Power Sources 161, 820-825.

466

Figure Legend

~~**Fig. 1 – Schematic diagram of a dual-chamber MFC**~~

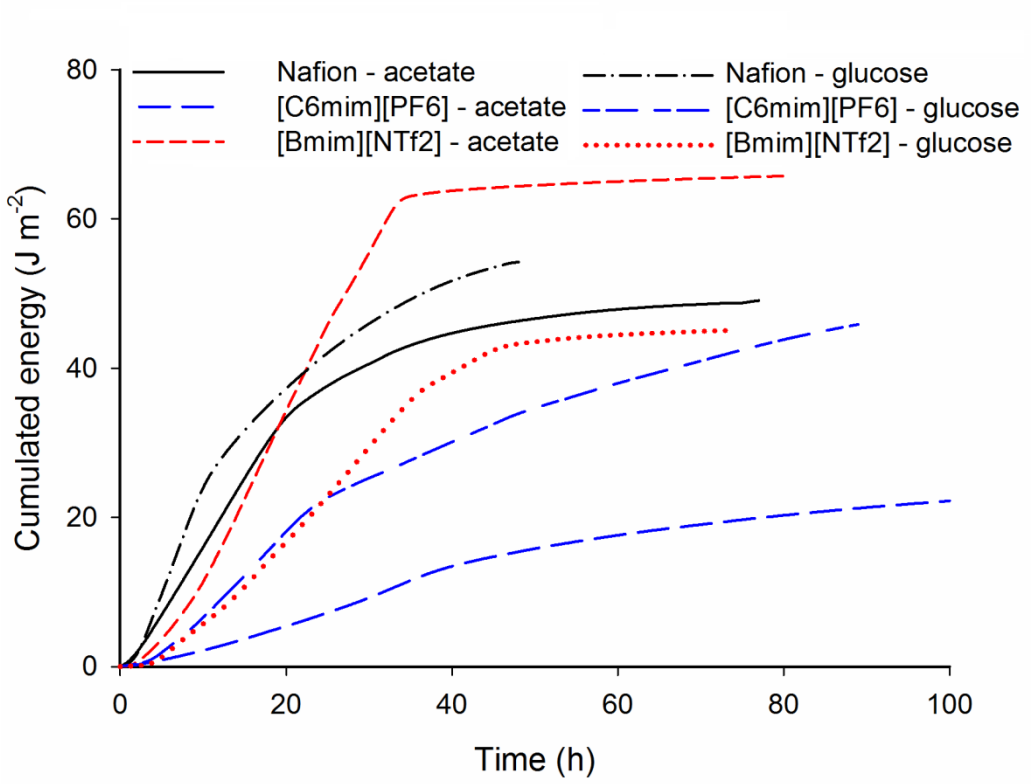
Fig. 1 – Time course of the energy production with different membranes and substrates

Fig. 2 – Results of polarization curve measurements on MFCs with various membrane separators in the presence of acetate substrate

Fig. 3 – Cumulated energy data with different acetate feedings

Fig. 4 – A: Time-specific energy yield; B: substrate-specific energy yield as a function of COD input

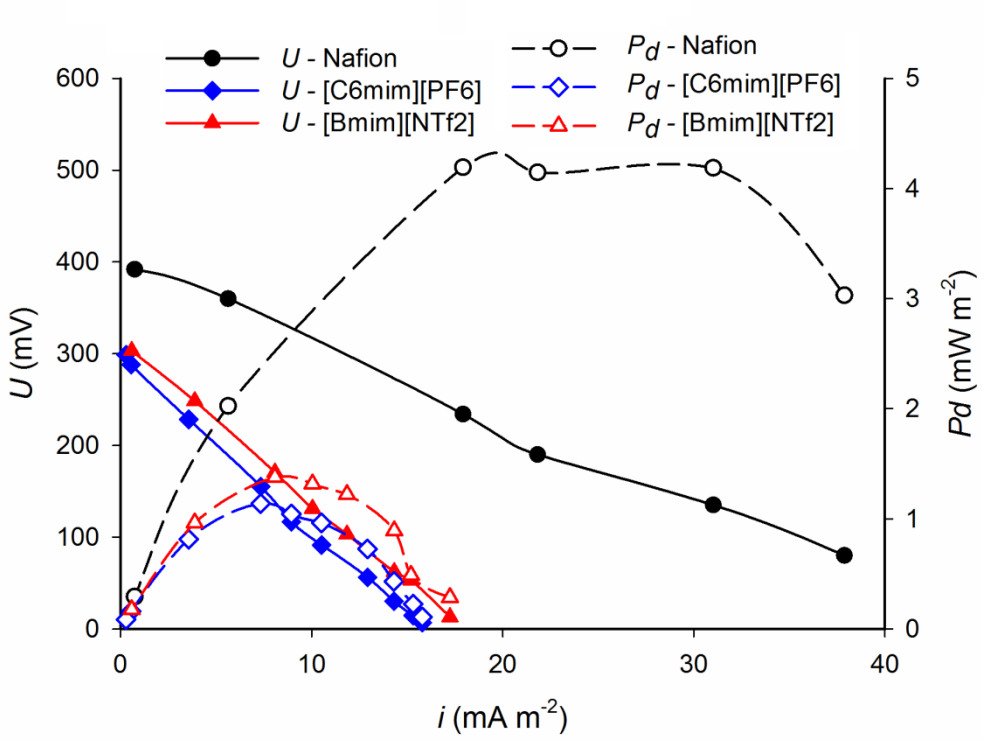
481 Fig. 1



482

483

484 Fig. 2



485

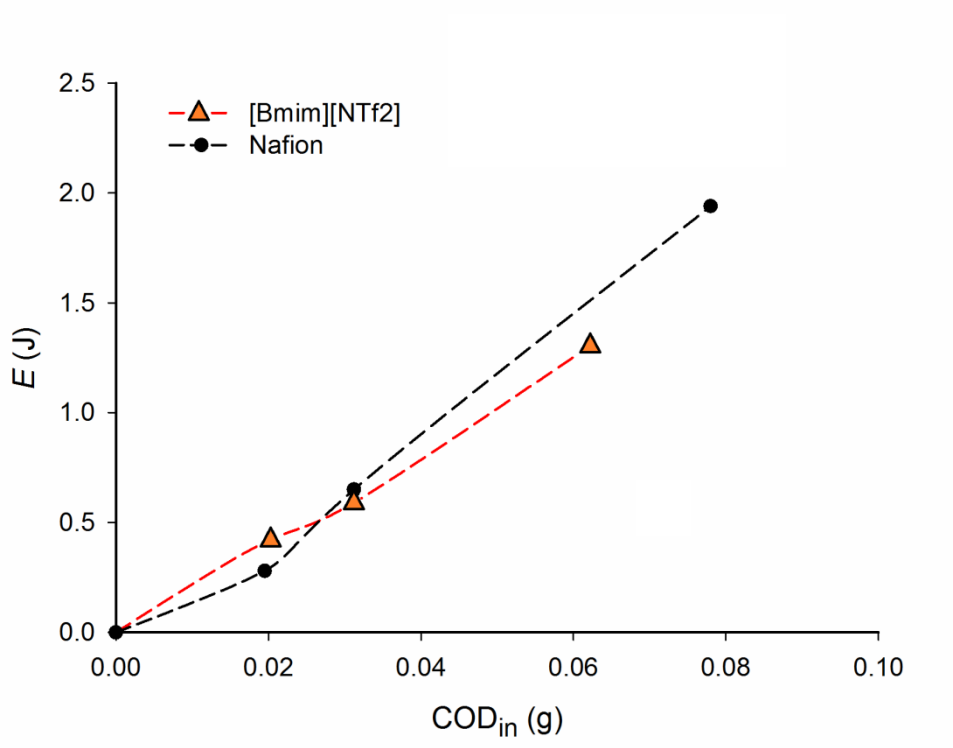
486

487

488

489

490 Fig. 3



491

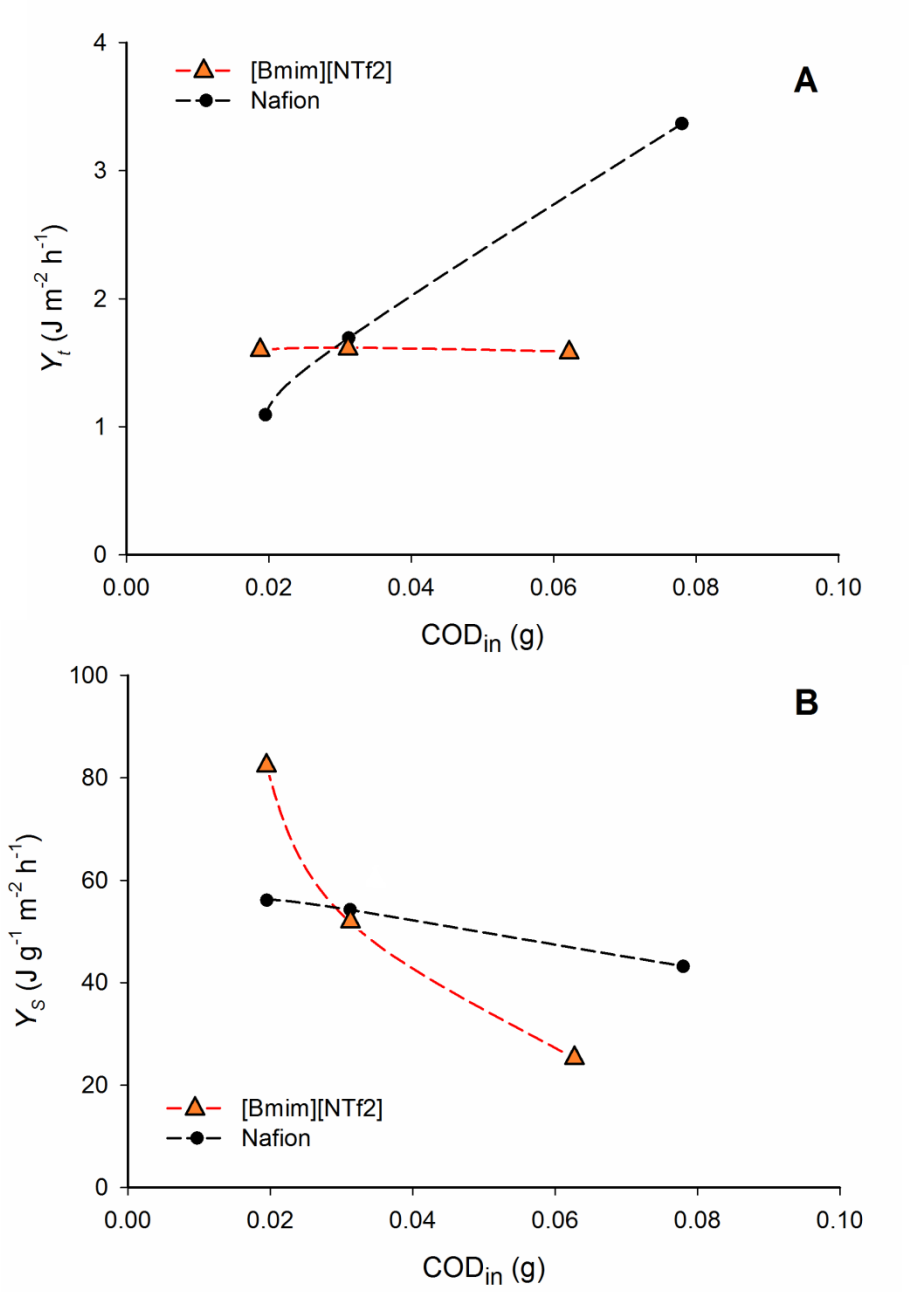
492

493

494

495

Fig. 4


A
[Bmim][NTf2]
Nafion
Y_t (J m^{-2} h^{-1})
COD_{in} (g)
B
Y_S (J g^{-1} m^{-2} h^{-1})
[Bmim][NTf2]
Nafion
COD_{in} (g)

504 **Table 1 – Electric outputs and operation time of substrate feedings for the**

505 **different MFCs**

506

	Na-acetate			Glucose		
	Nafion®	$[C_6mim][PF_6]$	$[Bmim][NTf_2]$	Nafion®	$[C_6mim][PF_6]$	$[Bmim][NTf_2]$
U_{max} [mV]	18.2	9.1	20.6	23.3	14.6	15.3
i_{max} [mA m^{-2}]	28.5	14.3	32.3	36.4	22.9	23.9
$P_{d,max}$ [mW m^{-2}]	0.52	0.13	0.67	0.85	0.33	0.37
$P^*_{d,max}$ [mW m^{-3}]	60.2	15.1	77.2	98.7	38.8	42.6
τ [h]	36	97	37	42	88	41
E [J]	0.28	0.14	0.41	0.35	0.29	0.29
Y_S [J g^{-1} COD_{in} m^{-2} h^{-1}]	59.0	11.4	80.1	42.2	19.2	29.5

$P_{d,max}$ and $P^*_{d,max}$ values were calculated relative to the anode surface area and the anolyte volume, respectively.

507