University of Pannonia
Chemical Engineering and Material Sciences Doctoral School

THE ROLE OF IONIC LIQUID-BASED MEMBRANES ON THE EFFICIENCY ENHANCEMENT OF BIOELECTROCHEMICAL SYSTEMS

DOCTORAL (Ph.D.) THESIS

Author:

László Koók
Chemical Engineer

Supervisor:

Dr. Péter Bakonyi
Senior Research Fellow

University of Pannonia
Research Group on Bioengineering, Membrane Technology and Energetics

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Introduction

Nowadays, we can witness the continuously increasing influence of renewable energy sources in various industrial sectors. Electric energy industry is one of the highest contributor to the emission of different environmental pollutants, such as CO_2, and its effect – together with the growing need for energy in general – on our everyday life is getting more and more significant.

Bioelectrochemical systems (BES) offer a sustainable alternative platform for energy- and value-added component production based on renewable sources. The future of BES technology relies heavily on the engineering of efficient and economic reactors. The BES efficiency is directly determined by the mass transfer processes through the membrane, which separates the anode- and cathode chambers. However, due to their intrinsic properties and the special nature of BES electrolyte solutions, the widely used proton selective membranes limit the systems' performance. Among other directions of development, significant attention has been paid towards ionic liquid membranes (ILM), which may act as excellent charge transfer media due to their chemical composition.

The goal of this work was to prepare and use alternative membrane materials in microbial fuel cells (MFC) in order to enhance their operational efficiency. In the experiments, supported ionic liquid membranes were prepared based on hydrophobic ionic liquids, and they were employed in microbial fuel cells. The aim was to investigate the applicability of ILM for BES, as well as to study the relationship between the MFC efficiency and various transport characteristics of the ILM.

Experimental

ILMs were prepared by using [bmim][NTf_2], [bmim][PF_6] and [hmim][PF_6] hydrophobic ionic liquids, and PVDF microporous supporting membrane. The ILMs were emloyed in dual-chamber microbial fuel cells. In the experimental work, a wide variety of tools were used to study and evaluate the systems, including the determination of efficiency measures, mass transport properties as well as different electrochemical techniques

Thesis Statements

I. I have demonstrated that the using ionic liquid membranes containing [bmim][NTf_2] and [bmim][PF_6] enhanced the MFC performance at limiting acetate concentrations (c_{Ac} ≤ 5 mM), resulting in higher energy yield, energy production rate and charge recovery efficiency. At the optimal c_{Ac} = 5 mM concentration:

(i) The energy yield exceeded the value obtained in the MFC operated with Nafion membrane by 50% and 178 % by using ionic liquid membranes based on [bmim][NTf_2] and [bmim][PF_6], respectively,

(ii) Compared to Nafion-MFC, the energy production rate was 66 % and 3-fold higher in case of [bmim][NTf_2] and [bmim][PF_6] ionic liquid membranes, respectively,

(iii) The charge recovery efficiency was fairly equal for Nafion and [bmim][NTf_2], while it exceeded Nafion's CE^* by 75% in case of [bmim][PF_6].

II. Using direct metabolic activity (dehydrogenase enzyme activity) and indirect cyclic voltammetric bioelectrochemical activity assays, I demonstrated that the use of ionic liquid membranes does not affect the course of biofilm formation nor the activity of the biological apparatus. Uniform redox characteristics of the biofilms formed on the anode surface was shown, regardless of the membrane type. Thus, it could be concluded that the performance enhancement observed by using ionic liquid membrane, did not originate from differences in biological aspects.

(i) The increase of the metabolic activity at the electrode surface, as well as its decrease in the bulk liquid phase could be unambiguously concluded from dehydrogenase enzyme activity tests.

(ii) The time course of cyclic voltamograms – in good agreement with enzyme activity data – followed an increasing trend, indicating the increasing redox activity at the electrode surface. Moreover, I have concluded based on the formal potentials related to the obtained current peaks, that regardless of the membrane type, uniform redox systems could form in the biofilm.

(iii) Based on the voltamograms, each systems' anodic reaction rate was limited by the diffusion of redox mediator shuttle molecules synthetized by the electrochemically active microbes.

III. By determining the individual electrode potential values in the maximal substrate-degrading phase of MFC operation, I have demonstrated that the overall performance of the MFC is proportional to the value of the cathode potential drop. It turned out that the ionic liquid membranes (based on [bmim][PF_6]) was more advantageous in this aspect. The differences in the cathode potentials originate in the differing losses due to distinct mass transport characteristics through the membranes. This conclusion was further supported by electrochemical impedance spectroscopy data.

(i) It turned out from the electrode potential measurements, that the anode potentials developed towards the same value regardless of the membrane type, while the differences in the cathode potential values increased over time. The cathode potential was 345 mV lower than the expected theoretical value for the [bmim][PF_6]-MFC, while the potential drop was singificantly higher in case of Nafion-MFC (502 mV).

(ii) The differences between the cathode potentials where proportional to the actual MFC performance. Since there were no qualitative difference in the biological aspects of the MFCs operating with the two membrane types, the performance enhancement observed with ionic liquid membrane can be explained by the specific mass transport features of the membrane.

(iii) I have concluded based on whole cell electrochemical impedance spectroscopy measurements that regardless of the membrane, the total internal resistance was dominated by its diffusion resistance component. Moreover, the diffusion resistance was lower in case of the MFC equipped with ionic liquid membrane.

IV. I have concluded based on the mass transfer coefficients of the reactants, that the substrate loss due to the permeation of acetate through the membrane could be significantly lowered by using ionic liquid membranes with both [hmim][PF_6] and [bmim][NTf_2]. The oxygen tranfer, which reduces the charge recovery efficiency in MFCs, could be moderated by using [bmim][NTf_2] compared to Nafion's k_O and D_O, while [hmim][PF_6] showed higher oxygen transfer coefficient. I have described the relationship between oxygen mass transfer coefficients and MFC charge recovery efficiency, incorporating literature data, as well. The relationship could be presented by two regions, a kinetic and a saturated k_O interval.

(i) Compared to Nafion, the ionic liquid membranes showed 13.4-times ([bmim][NTf_2]) and 9.3-times ([hmim][PF_6]) lower acetate transfer coefficient. Thus, the substrate loss can be minimized by using ionic liquid membranes.

(ii) [bmim][NTf_2] presented lower oxygen permeation compared to Nafion, which directly affects the charge recovery efficiency of the MFC. The oxygen transfer was, however, more pronounced in case of [hmim][PF_6], which could be due to the higher miscibility of this ionic liquid with water, and thus, the permeating water microclasters could dissolve more oxygen, and deliver it through the ionic liquid phase.

(iii) The role of k_O on the charge recovery (and Coulombic) efficiency of an MFC can be highly significant within a relatively narrow kinetic k_O range (up to $k_O \approx 1{,}8\text{-}2^{*}10^{-4}$ cm s^{-1}), while its effect decreases through a saturation range with increasing k_O values.

V. Based on the proton mass transfer coefficients and diffusivities, I have concluded that the membranes based on both [bmim][NTf_2] and [hmim][PF_6] ionionic liquids serve as a better proton transfer medium than Nafion. The electric mobility value for protons, derived from diffusivity values by using the Einstein-equation, supported the assumption that proton transfer occurs with the permeating water microclasters through the [hmim][PF_6] ionic liquid. However, it does not seem to be the valid mechanism in case of [bmim][NTf_2] ionic liquid, thus, actual proton-ionic liquid interactions can be presumed.

(i) The [bmim][NTf_2] ionic liquid showed 2-times higher proton transfer coefficient and 80 % higher proton diffusivity compared to Nafion. In this ionic liquid, actual proton-ionic liquid interactions can be presumed, as the measured proton diffusivities are two orders of magnitude higher than the water diffusuvity in [bmim][NTf_2]. This confutes the proton transfer mechanism with permeating water through the ionic liquid phase.

(ii) The significantly higher proton transfer coefficient and proton diffusivity in case of [hmim][PF_6] could be explained by the proton transfer mechanism driven by water microclasters permeating through the ionic liquid phase. This was supported by the proton electric mobility data (conformity with literature data obtained from measurements in water).

Related publications

Theses-related publiactions in international journals:

[1] **L Koók**, P Takács, P Bakonyi, K Bélafi-Bakó, N Nemestóthy. Investigating the proton and ion transfer properties of supported ionic liquid membranes prepared for bioelectrochemical applications using hydrophobic imidazolium-type ionic liquids. *Membranes* 2021 (11) 359. **(IF: 4,106)**

[2] P Bakonyi, **L Koók**, T Rózsenberszki, G Tóth, K Bélafi-Bakó, N Nemestóthy. Development and Application of Supported Ionic Liquid Membranes in Microbial Fuel Cell Technology: A Concise Overview. *Membranes* 2020 (10) 16. **(IF: 4,106)**

[3] **L Koók**, B Kaufer, P Bakonyi, T Rózsenberszki, I Rivera, G Buitrón et al. Supported ionic liquid membrane based on [bmim][PF_6] can be a promising separator to replace Nafion in microbial fuel cells and improve energy recovery: A comparative process evaluation. *Journal of Membrane Science* 2019 (570-571) 215-225. **(IF: 7,183)**

[4] **L Koók**, N Nemestóthy, P Bakonyi, A Göllei, T Rózsenberszki, P Takács, et al. On the efficiency of dual-chamber biocatalytic electrochemical cells applying membrane separators prepared with imidazolium-type ionic liquids containing $[NTf_2]^-$ and $[PF_6]^-$ anions. *Chemical Engineering Journal* 2017 (324) 296-302. (**IF: 6,735)**

[5] **L Koók**✉, N Nemestóthy, P Bakonyi, G Zhen, G Kumar, X Lu, et al. Performance evaluation of microbial electrochemical systems operated with Nafion and supported ionic liquid membranes. *Chemosphere* 2017 (175) 350-355. **(IF: 4,432)**

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- **Koók L**, Nemestóthy N. „Mikrobiális üzemanyagcellák" c. magyar nyelvű könyv, 8. Fejezet: Bioelektrokémiai rendszerek és méréstechnikájuk. Pannon Egyetemi Kiadó, Veszprém, 2016.

Conference presentations and posters

- **L Koók**, J Zitka, R Cardena, P Bakonyi. Case studies on the application of new ion exchange membrane materials for bioelectrochemistry. Melpro 2020 (Czech Republic), online oral presentation
- **L Koók**, P Bakonyi, G Tóth, K Bélafi-Bakó, N Nemestóthy. The Interrelation Between Ion-Exchange Membranes and the Efficiency of Microbial Electrochemical Systems. XXV International Symposium on Bioelectrochemistry and Bioenergetics 2019 (Ireland), poster presentation
- **L Koók**, P Bakonyi, T Rózsenberszki, J Žitka, K Bélafi-Bakó, N Nemestóthy. Study on microbial electrochemical systems operating with fabricated ion exchange membranes as competitive separators to Nafion. EU-ISMET 2018 (United Kingdom), poster presentation
- **L Koók**, B Kaufer, T Rózsenberszki, P Bakonyi, K Bélafi-Bakó, N Nemestóthy. Study on the effect of supported [bmim][PF6] ionic liquid and Nafion membranes used in microbial electrochemical cells. Melpro 2018 (Czech Republic), poster presentation
- **L Koók**, N Nemestóthy, P Bakonyi, A Göllei, T Rózsenberszki, P Takács, et al. On the relationship of energy generation and ionic liquid-based membrane properties in biocatalytic electrochemical systems. ISMET 6 2017 (Portugal), poster presentation