UNIVERSITY OF PANNONIA

CHEMICAL ENGINEERING AND MATERIAL SCIENCES DOCTORAL SCHOOL

INVESTIGATION OF BIOFOULING OF POLYMER- AND IONIC LIQUID MEMBRANES IN MICROBIAL FUEL CELLS

PH.D. THESES

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INTRODUCTION

Microbial fuel cells (MFC) are capable of processing and disposing of wastewater containing organic matter at a certain level. During their operation, electrons are released, which can be "collected" and utilized. Thus, they can be considered similar constructions as fuel cells in the traditional sense. There are several types of designs. During my work we used the H-shaped two-chamber system, which is divided by the membrane as a permselective wall. The function of the membrane is to physically separate the two chambers from each other, while allowing a certain level of material transport. The contents of the two chambers and thus some of their properties are significantly different. Thanks to the introduced/stored buffer solution containing wastewater, organic matter is present in the oxygen-poor anode space, which can be a source of inoculum and nutrients at the same time. The cathode space, in contrast to the anode space, is a medium saturated with oxygen thanks to the continuous flow of air. During their life processes, the electrochemically active microorganisms that settle on the surface of the anode use nutrients from the wastewater, and later from external feeding. During the processes that occur during utilization, electrons are released. As previously outlined, this type of system is capable of breaking down organic matter and, if adequately constructed, producing electricity.

MATERIALS AND METHODS

During my experiments, I conducted test procedures in two-chamber H-cells. In these cells, I tested externally developed PSEBS-SU22, commercially available Ralex® and self-developed ionogel membranes. I determined the most important (substrate and oxygen) material transfer coefficients and electrochemical characteristics in the previously mentioned H-cells. Important electrochemical characteristics: total internal cell resistance (LSV), monitoring of redox processes (CV) and determining the resistance/conductivity of membranes. Microbial consortium analysis of anode and membrane surface samples was also completed, based on which results I also performed PCA analysis. Where there was sufficient data, I also carried out a statistical evaluation.

NOVEL SCIENTIFIC ACHIEVEMENTS

1. **I determined the efficiency indicators of the microbial fuel cells equipped with the PSEBS-SU22 ion exchange membranes developed by the Czech Academy of Sciences (inoculated with mixed cultures, using acetate substrate), in comparison with the Nafion-115 membrane. Furthermore, I evaluated the microbial consortium level characteristics of the biofouling layers formed on the surfaces of each membrane with the help of principal component analysis.**

- The prominent values of MFCs equipped with Nafion-115 membranes ($CE_{10\ mM}$: 26.4 %, $v_{2.5\ mM}$: 190 J m^{-2} h^{-1}, $E_{10\ mM}$: 50 J) and the prominent values of MFCs equipped with PSEBS-SU22 membranes ($CE_{15\ mM}$: 26.2 %, v_{10mM}: 337 J m^{-2} h^{-1}, $E_{10\ mM}$: 79 J) encouraged me to conclude that the optimal acetate substrate concentration is achieved at 10 mM. In general, it can be said that the MFC with

PSEBS-SU22 membrane achieved a significantly higher extracted energy and specific energy output rate compared to the Nafion cell.

- After a metagenomic study the principal component analysis verified that the microbiological composition of membrane surface biofilms was more significantly influenced by the source of the inoculum than the effect of the membrane.

2. I investigated the electrochemical characteristics of the microbial fuel cells equipped with commercial (Ralex®) anion and cation exchange membranes - utilized mixed culture and acetate substrate - and the composition of the anode and membrane surface biofilms regarding the microbial consortium in the light of the mass transfer properties of the membranes, using principal component analysis.

- I showed that in terms of Coulombic efficiency in the presence of 2.15 mM acetate substrate concentration, in the case of MFC equipped with Ralex® membranes, a significant difference appeared between the anion and cation exchange membrane groups in the direction of MFC systems equipped with anion exchange membranes. In case of 4.3 mM acetate concentration, there was no significant difference between the CE values between the examined MFC systems.
- In terms of the specific energy output rate, I comparatively evaluated the MFCs equipped with Ralex® membranes in the presence of 2.15 mM acetate substrate. A significant difference was observed in favor of the MFC systems equipped with an anion exchange membrane. At the 4.3 mM acetate substrate concentration, no significant difference could be detected.
- Regarding the oxygen transfer properties, a significant difference was detected between the groups formed by CMHPES, AMHPP and AMHPES, CMHPP membranes, as membranes with "higher" and "lower" oxygen permeability groups. Furthermore, I found that the type of membrane, i.e. anion or cation exchanger (AMHPES, AMHPP vs. CMHPES-CMHPP) had a relatively greater effect on the microbial composition of the anodic biofilm than the polymer material used to make the given membrane (PP or PES).

3. Based on a method available in literature which is suitable for dissolving microcrystalline cellulose, I developed an ionogel membrane preparation method for use in microbial fuel cell, then tested its stability.

- I prepared a colloidal cellulose solution (sol) from a mixture of 87-13 m/m % microcrystalline cellulose - [BMIM][Cl] at 100 °C under continuous stirring (120 rpm). I spread the sol on a PES mesh, then immersed it in a certain amount of antisolvent at room temperature for 1 hour, after which the ionogel stiffened with a support layer.
- Through UV spectrometric test (after a preliminary calibration) for [BMIM][Cl], I showed that the ionogel membrane can be considered stable and thus suitable for use in MFC.

4. I evaluated the applicability of the self-developed ionogel membrane in a mixed-culture microbial fuel cell using acetate substrate, in comparison with the Nafion-115 membrane while considering the microbiological characteristics of the biofilms on the electrode and membrane surfaces.

- I measured that the values of the Coulombic efficiency of the MFC systems equipped with ionogel and Nafion-115 membranes at 2.5 mM acetate substrate concentration (47±6 % and 55±7 %) did not result in a statistically significant difference. Regarding the specific energy output rate, we found that there was a significant difference in the case of 2.5 mM acetate substrate concentration (respectively 608±176 $Jm^{-2}h^{-1}$ and 910±152 $Jm^{-2}h^{-1}$).
- Based on the energetic- and the mass transfer properties of the membranes (Ionogel, k_S: 1.17•10^{-4} cms^{-1}; k_O: 1.38•10^{-4} cms^{-1}, R_{int}: 303 Ω; Nafion-115, k_S: 8.52•10^{-6} cms^{-1}; k_O: 1.61•10^{-4} cms^{-1}, R_{int}: 242 Ω) it can be said that the higher cell resistance and also the ionogel membranes orders of magnitude higher substrate transfer coefficient is behind the lower efficiency of the MFC operated with ionogel. The high k_S value was presumably related to the fact that macroscopic biofilm formation also occurred on the cathode side of the system.
- According to the comparative analysis combined with the metagenomic study, the biofilms on the electrode and membrane surfaces differed sharply from the composition of the inoculum, indicating the completion of the adaptation process. One explanation for the proliferation on the cathode side (membrane and cathode surface) can be the presence of the bacterium Clostridium termitidis (23.2%) detected with a high relative abundance in the biofilm on the anode side of the ionogel membrane, which could have caused the possible degradation of the cellulose-containing membrane over time.

LIST OF PUBLICATIONS

1. **Szakács, S.**, Bakonyi, P. (2020). Considerations to Approach Membrane Biofouling in Microbial Fuel Cells, *Hungarian Journal of Industry and Chemistry,* 48, 51–53. https://doi.org/10.33927/hjic-2020-27.
2. **Szakács, S**., Koók, L., Nemestóthy, N., Bélafi-Bakó, K., & Bakonyi, P. (2022). Studying microbial fuel cells equipped with heterogeneous ion exchange membranes: Electrochemical performance and microbial community assessment of anodic and membrane-surface biofilms. *Bioresource Technology, 360*, 127628. https://doi.org/10.1016/j.biortech.2022.127628 **IF: 11.4**
3. Koók, L., Žitka, J., **Szakács, S**., Rózsenberszki, T., Otmar, M., Nemestóthy, N., Bélafi-Bakó, K., & Bakonyi, P. (2021). Efficiency, operational stability and biofouling of novel

sulfomethylated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene cation exchange membrane in microbial fuel cells. *Bioresource Technology*, *333*, 125153. https://doi.org/10.1016/j.biortech.2021.125153. **IF: 11.889**

4. **Szakács, S**., Martínez, E. O., Koók, L., Santos, G. M., Alarcon, J. T., Jeison, D., Pientka, Z., Nemestóthy, N., Bélafi-Bakó, K., & Bakonyi, P. (2024). Biofouling-focused assessment of a novel, cellulose-based ionogel membrane applied in a microbial fuel cell. *Bioresource Technology Reports*, *26*, 101817. https://doi.org/10.1016/j.biteb.2024.101817
5. 152. 4. (2021.04): Természet Világa; Lefolyóban a lehetőség; Szakács Szabolcs

POSTER AND ORAL PRESENTATION

1. 50. Műszaki Kémiai Napok, Veszprém, 2022. április 26-28., Cellulóz-alapú ionosfolyadék membrán, mint új típusú szeparátor mikrobiális üzemanyagcellában (Hungarian oral presentation)
2. 48th International Conference of the Slovak Society of Chemical Engineering & Membrance Conference PERMEA 2022, Slovakia, Tatranské Matliare, Hotel Hutník, 2022.may 23-26., Preparation of cellulose/ ionic liquid membrane and its application in microbial fuel cell (English oral presentation)
3. 51. Műszaki Kémiai Napok, Veszprém, 2023. április 18-20., : Cellulóz feldolgozhatósága és hasznosítása ionos folyadék felhasználásával (Hungarian oral presentation)
4. ICOM2023 13th International Conference on Membranes and Membrane Processes, Japán, Chiba, Makuhari Messe, Study of cellulose/ BMIMCl composite film as membrane in microbial fuel cell, 2023.07.11 (English oral presentation)
5. 39. European Membrane Society (EMS) Summer School, Belgium, Louvian-La-Neuve, 2024. Június 10-14. Fabrication and application of cellulose based ionogel membrane in microbial fuel cell (English poster)