Gazi Üniversitesi
Fen Bilimleri Dergisi
PART C: TASARIM VE TEKNOLOJİ

Gazi University
Journal of Science
PART C: DESIGN AND TECHNOLOGY

GU J Sci, Part C, 11(2): 685-694 (2023)

Cathode Materials for Microbial Fuel Cells

Işılay BİLGİÇ[1*]

[1]*Istanbul Okan University, Vocational School, Department of Electric and Energy, Istanbul, Turkey*

Article Info

Review article
Received: 07/05/2023
Revision: 07/06/2023
Accepted: 12/06/2023

Keywords

Microbial fuel cells
Oxygen reduction reaction
Cathode catalysts
Cost-effective catalysts

Makale Bilgisi

Derleme makale
Başvuru: 07/05/2023
Düzeltme: 07/06/2023
Kabul: 12/06/2023

Anahtar Kelimeler

Mikrobiyal yakıt hücreleri
Oksijen indirgeme reaksiyonu
Katot katalizörleri
Uygun maliyetli katalizörler

Graphical/Tabular Abstract (Grafik Özet)

Organic and inorganic contents in wastewater can be seen as potential energy sources. MFCs are the only systems that can convert the chemical energy in the organic and inorganic content of wastewater into electricity. In this study, cathode materials used in MFCs examined, and alternative materials were discussed. / Atık sulardaki organik ve inorganik içerikler potansiyel enerji kaynakları olarak görülebilir. MFC'ler atıksuyun organik ve inorganik içeriğindeki kimyasal enerjiyi elektriğe dönüştürebilen yegane sistemlerdir. Bu çalışmada MFC'lerde kullanılan katot malzemeleri incelenmiş ve alternatif malzemeler tartışılmıştır.

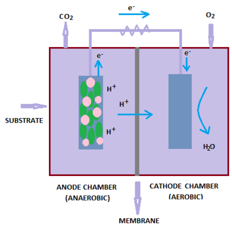

***Figure A**: Schematic Diagram of Microbial Fuel Cell / **Şekil A:** Mikrobiyal Yakıt Hücresinin Şematik Diyagramı*

Highlights (Önemli noktalar)

- *MFCs are unique systems in which microorganisms -instead of catalysts- and organic and inorganic molecules -instead of enzymes- at the anode are used to convert chemical energy to electrical energy. / MFC'ler, kimyasal enerjiyi elektrik enerjisine dönüştürmek için -katalizörler yerine- mikroorganizmaların ve anotta -enzimler yerine- organik ve inorganik moleküllerin kullanıldığı benzersiz sistemlerdir.*
- *MFC system is the most efficient method because of the bio-electrochemical design of this system which allows the purification of wastewater during the production of electricity. / MFC sistemi, elektrik üretimi sırasında atık suyun arıtılmasına olanak sağlayan biyo-elektrokimyasal tasarımı nedeniyle en verimli yöntemdir.*
- *The majority of the costs of MFCs are the catalyst materials used in the cathode. / MFC'lerin maliyetlerinin büyük bölümü katotta kullanılan katalizör malzemeleridir.*

Aim (Amaç): *In this study, the cathode materials used in MFCs were examined and alternative materials were discussed in terms of performance and cost. / Bu çalışmada MFC'lerde kullanılan katot malzemeleri incelenmiş, performans ve maliyet açısından alternatif malzemeler tartışılmıştır.*

Originality (Özgünlük): *By reviewing the literature, the effects of cathode materials used in MFCs on electrochemical performance are summarized. / Literatür incelenerek MFC'lerde kullanılan katot malzemelerinin elektrokimyasal performansa etkileri özetlenmiştir.*

Results (Bulgular): *Pt is a high-performance cathode material in terms of power density but it is an expensive material. For this reason, relatively cheaper materials such as graphite, carbon, Fe, Ni have been tested instead of Pt, and high power densities have been achieved. / Pt, güç yoğunluğu açısından yüksek performanslı bir katot malzemesidir ancak pahalı bir malzemedir. Bu nedenle Pt yerine grafit, karbon, Fe, Ni gibi nispeten daha ucuz malzemeler test edilmiş ve yüksek güç yoğunlukları elde edilmiştir.*

Conclusion (Sonuç): *Studies on MFC have focused on reducing the use of expensive catalysts such as Pt, thus reducing system cost. It is possible to achieve high power densities in MFCs by using lower-cost cathode catalysts such as carbon and graphite-based materials or Fe and Mn. Further development of metal-carbon hybrid catalysts will provide high-performance and low-cost MFCs. / MFC ile ilgili çalışmalar, Pt gibi pahalı katalizörlerin kullanımının azaltılmasına ve dolayısıyla sistem maliyetinin düşürülmesine odaklanmıştır. Karbon ve grafit bazlı malzemeler veya Fe ve Mn gibi daha düşük maliyetli katot katalizörleri kullanarak MFC'lerde yüksek güç yoğunlukları elde etmek mümkündür. Metal-karbon hibrit katalizörlerinin daha da geliştirilmesi, yüksek performanslı ve düşük maliyetli MFC'ler sağlayacaktır.*

*Corresponding author, e-mail: isilayulusoy@gmail.com
DOI: 10.29109/gujsc.1293678

GU J Sci, Part C, 11(2): 685-694 (2023)

Gazi Üniversitesi
Fen Bilimleri Dergisi
PART C: TASARIM VE TEKNOLOJİ

Gazi University
Journal of Science
PART C: DESIGN AND TECHNOLOGY

http://dergipark.gov.tr/gujsc

Cathode Materials for Microbial Fuel Cells

Işılay BİLGİÇ[1*]

[1]*Istanbul Okan University, Vocational School, Department of Electric and Energy, Istanbul, Turkey*

Article Info

Review article
Received: 07/05/2023
Revision: 07/06/2023
Accepted: 12/06/2023

Keywords

Microbial fuel cells
Oxygen reduction reaction
Cathode catalysts
Cost-effective catalysts

Abstract

Titanium alloys are one of the materials that are difficult to process due to their high strength, The most important problems of today are meeting the increasing energy needs and avoiding environmental pollution caused by fossil resources usage for energy production. In addition, the decrease in usable water in the world has become a threat to human health and the population. Microbial fuel cells (MFC) have become more interesting in recent years because of their potential to solve these three important problems. Organic and inorganic contents in wastewater can be seen as potential energy sources. MFCs are the only systems that can convert the chemical energy in the organic and inorganic content of wastewater into electricity. While this transformation is realized, the process of cleaning the wastewater can be done. Reducing the costs of these systems is the most important parameter to accelerate the use of the system. In particular, studies on reducing the cost and increasing the efficiency of the catalysts used in the cathode compartment where the oxygen reduction reaction takes place are predominant. In this study, cathode materials used in MFCs examined, and alternative materials were discussed.

Mikrobiyal Yakıt Hücreleri İçin Katot Malzemeleri

Makale Bilgisi

Derleme makale
Başvuru: 07/05/2023
Düzeltme: 07/06/2023
Kabul: 12/06/2023

Anahtar Kelimeler

Mikrobiyal yakıt hücreleri
Oksijen indirgeme reaksiyonu
Katot katalizörleri
Uygun maliyetli katalizörler

Öz

Günümüzün en önemli sorunları arasında artan enerji ihtiyacını karşılamak ve fosil kaynakların enerji üretimi için kullanımından kaynaklanan çevre kirliliğinin önlenmesi yer almaktadır. Ayrıca, dünyadaki kullanılabilir sudaki azalma insan sağlığı ve nüfusu için bir tehdit haline gelmiştir. Mikrobiyolojik yakıt hücreleri (MYH) bu üç önemli sorunu çözme potansiyeli sebebiyle son yıllarda daha ilgi çekici bir konu haline gelmiştir. Atık sulardaki organik ve inorganik içerikler potansiyel bir enerji kaynağı olarak görülebilir. MYH'ler, atık suyun organik ve inorganik içeriğindeki kimyasal enerjiyi elektriğe dönüştürebilen tek sistemdir. Bu dönüşüm gerçekleştirilirken, atık suyun temizlenmesi işlemi yapılabilir. Bu sistemlerin maliyetlerini azaltmak, sistemin kullanımını hızlandırmak için en önemli parametredir. Son zamanlarda özellikle, oksijen indirgeme reaksiyonunun gerçekleştiği katot bölmesinde kullanılan katalizörlerin maliyetinin düşürülmesi ve verimliliğinin arttırılması üzerine yapılan araştırmalar hız kazanmıştır. Bu çalışmada, MYH 'lerde kullanılan katot malzemeleri incelenecek ve alternatif malzemeler tartışılacaktır.

1. INTRODUCTION (GİRİŞ)

Fossil fuels used as energy sources are the main causes of global warming as well as important environmental problems. The increase in energy demand encourages fossil fuels to gradually disappear, the development of environmental consciousness, and researchers to find renewable and sustainable energy sources. Recently microbial fuel cell (MFC) systems have emerged that can use organic substances as fuel. MFC transforms biochemical energy, which is formed by the breakdown of organic substances, into electricity by the catalytic reactions of microorganisms. In particular, the high organic content of sludges from domestic wastewater treatment plants has led to the use of MFC for sludge treatment and energy production.

MFCs can be described briefly; as systems to convert biochemical energy to electrical energy. MFCs are unique systems in which microorganisms -instead of catalysts- and organic and inorganic molecules -instead of enzymes- at the anode are used to convert chemical energy to electrical energy. MFC system is the most efficient method because of the bio-electrochemical design of this system which allows the purification of wastewater

*Corresponding author, e-mail: isilayulusoy@gmail.com
DOI: 10.29109/gujsc.1293678

during the production of electricity. MFCs generally consist of two chambers, an anode, and a cathode. Figure 1 shows a schematic diagram of a microbial fuel cell. These chambers are generally separated from each other by a membrane. The anode chamber contains microorganisms that oxidize the existing nutrients. The cathode chamber is generally designed as an open ambient air chamber.

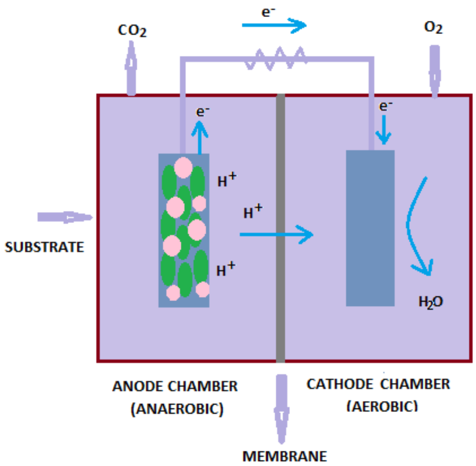

Figure 1. Schematic Diagram of Microbial Fuel Cell (Mikrobiyal Yakıt Hücresinin Şematik Diyagramı)

By utilizing microbial metabolism, MFCs generate electrons and protons in the anodic chamber from the oxidation of organic matter present in the wastewater, which is then donated to the extracellular acceptor i.e. anode [1]. The protons, thus generated, migrate to the cathode chamber via the proton exchange membrane and help O_2 to get reduced to H_2O, thus producing electricity [2-3].

Although MFCs have many advantages, it is not preferred as an alternative energy production system due to their high costs and low energy production efficiency. The majority of the costs of MFCs are the catalyst materials used in the cathode.

The investment cost of MFC systems can be seen as the biggest obstacle to its common usage and increase in the percentage of usage among renewable energy sources. The average cost of MFC is 30 times higher than the cost of conventional wastewater treatment systems [4]. The cost of MFC's cathode material is 70.42% of the total cost [5-6].

2. MATERIALS AND METHODS (MATERYAL VE METOD)

In this study, the tested cathode materials used in MFCs in the literature and the obtained power values were compared and the materials with the highest power values were determined. In the selection of cathode materials, which is the most decisive parameter in the costs of MFCs, the selection of materials that are both cheaper and with the highest power value is very important. For this reason, researches are mostly in the direction of cathode material development. Metal-based, carbon-based, hybrid, and biocathode materials using these two materials together are the most widely researched today. While providing optimum conditions in MFC systems, expanding usage areas, and ensuring waste disposal, these studies are of great importance in order to produce electricity at the same time.

3. CATHODE CATALYSTS USED IN MFC (MFC'DE KULLANILAN KATOT KATALİZÖRLERİ)

Due to the decrease of oxygen in the environment, the poor kinetics of the Oxygen Reduction Reaction (ORR) at the cathode is one of the important factors limiting the performance of MFC. Therefore, need for a catalyst at the cathode to avoid reduced performance in a low oxygen environment for the MFC system. Pt is generally used as a catalyst at the cathode [7]. However, Pt has disadvantages that include high cost, propensity for biofouling, and low surface poisoning tolerance in wastewater [8]. Even though oxygen has been considered the most suitable oxidant in the cathode compartment to enhance MFC performance during ORR, oxidants used as electron acceptors such as ferricyanide and permanganate have been used to influence the ORR process [6-9-10-11-12].

Because of the high cost of Pt, it has been necessitated the search for alternative catalysts. Non-precious metal catalysts are extensively investigated as Pt alternatives in fuel cells. It has been reported that catalysts without Pt group metals prepared by supporting transition metals such as Fe, Co, Zr, and N-doped carbon are used as cathode catalysts in MFCs to obtain equivalent electrochemical performance [13].

Various inexpensive, high catalytic activity and biofouling-resistant cathode electrode materials have been explored to enhance the power output from MFCs. These materials include carbon structures, metal complexes, metal oxides, conducting polymers, N-doped carbon, and others. Among the various electrode materials tested as cathode electrodes, carbon-based materials provided promising performance. For example, the bio-derived, heteroatom-doped carbon obtained from Alfalfa plant leaves provided higher cathodic catalyst activity and high power output of 1328.9 $mW.m^{-2}$ which was equivalent to the typical Pt/C cathodic catalyst provided 1337.7 $mW.m^{-2}$ power output [6-14]. Graphite materials used as cathode catalysts, chemically treated with H_3PO_4 and HNO_3 exhibited improved ORR properties in MFC and generated higher power densities of 7.9 Wm^{-3} and 6.5 Wm^{-3}, respectively [6-15].

The kinetic rate of the ORR is low because of the high activation energy required to break the O=O bond (498 $kJmol^{-1}$) [16]. The ORR catalysts can follow two different pathways. One of them reduces oxygen through one step four-electron pathway which has a higher reduction potential. The second pathway is which less efficient two-electron pathway that generates highly reactive hydrogen peroxide and leads to damaged membranes and electrodes [17-18].

1. pathway: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (E^0 = 1.229 V vs. NHE) (1)

2. pathway: $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ (E^0 = - 0.065 V vs. NHE) (2)

The second pathway followed by the reduction of HO_2^-

$HO_2^- + H_2O + 2e^- \rightarrow 3\,OH^-$ (E^0 = 0.867 V vs. NHE) (3)

or r by the more rapid disproportionation of HO_2^-

$$2\,HO_2^- \rightarrow 2\,OH^- + O_2 \quad (4)$$

According to the Nernst equation, the ORR potential at pH 7 can be calculated by using Equation (5):

$$E'_0=E_0−RTnFln1[O_2][H^+]^4 \quad (5)$$

in which R (8.314 $JK^{-1}mol^{-1}$) is the universal gas constant, T is the thermodynamic temperature, n is the number of electrons transferred, and F (9.648x104 $Cmol^{-1}$) is the Faraday constant. Therefore, if T=298.15 K, pH 7.0, and $[O_2]$=0.2 mol L^{-1}, E'_0 is determined to be 0.805 V for the four-electron pathway [16].

3.1. Metal-Based Catalysts (Metal Bazlı Katalizörler)

Studies on MFC catalysts have been concentrated on Pt for a long time as it is an active catalyst. However, because Pt is an expensive metal, many studies have been performed to obtain high energy output in different catalyst combinations. Among them, Fe-based catalysts were the most prominent in terms of their high activity. In a study using a Fe-N-C catalyst 2437 ± 55 $mW.m^{-2}$ power output was obtained [19-20]. In addition, Ni [21], Fe-Mn [22], Co-Fe [23], and V-based catalysts [24] have come to the forefront due to their high power output. One of the biggest challenges in metal catalysts is their low stability. Leaching problems have been observed in alloy catalysts such as Pt-Co and Pt-Fe [25].

In addition, carbon-supported non-precious metal-based catalysts have been studied as alternative cathode catalysts for MFC, because of their low costs, high natural abundance, apparent catalytic activity, and good mechanical strength. In a study, MFC using Fe, N-codoped carbon as the cathode catalyst has been found to deliver a maximum power density (P_{max}) of 3118.9 mWm^{-2}. In another study in which nitrogen-doped carbon nanotubes (Co / NCNT) were used as a catalyst, a power density of 1260 $mW.m^{-2}$ was reached [8-26]. A study focused on sodium cobalt oxide (NaCo2O4) as a cathode catalyst reached 0.6 $W.m^{-2}$ [27]. Wu et al. (2019) developed and employed reduced graphene oxide (rGO) as a cathode catalyst in a membrane-less microbial fuel cell (MFC) [28]. rGO-based cathode exhibited better characterizations in structure and electron transfer than graphene oxide (GO)-based cathode [28].

Majidi et al. (2019), in their study, synthesized low-cost α-MnO_2 nanowires and α-MnO_2 nanowires supported on carbon Vulcan [29]. They reached 180 $mW.m^{-2}$ power density in their air cathode MFC (α-MnO_2/C as an ORR). However, Chiodoni et al. (2019), by using the Mn_xO_y as a cathode catalyst in MFC, achieved competitiviable catalytic efficiency results with Pt-based catalysts [30].

3.2. Carbon-Based Catalysts (Karbon Bazlı Katalizörler)

Carbon black is widely used as the support material for metal catalysts due to its large specific surface area and high stability. At the same time, simple chemical modification and/or the introduction of functional groups can create active sites that make carbon black a metal-free ORR catalyst. Also carbon black is a very economic material as the catalyst, but its durability is still unknown for MFC systems [25].

Among the commonly used electrode materials, the majority are preferred activated carbon because of its low cost and large surface area [31]. Due to its electrochemical properties, activated carbon is a good support material for catalysts. While the current density of a Pt/C cathode dropped by 73% after 7 h of the chronoamperometry test, a nitrogen-doped AC cathode showed only 30% decrease. However, biofouling on the AC cathode and degenerated MFC performance were still observed [25].

Carbon nanotubes are more resistant than Pt/C as cathode catalysts. The reason for this is that graphitic-N in the carbon plane is thought to be less sensitive to protonation [25].

In addition, graphite and graphene-based catalysts were also used in MFCs. Zheng et al. (2015) in their study using graphite plates have been obtained 3215 ± 80 $mW.m^{-2}$ as a very high power density value [30-32].

3.3. Metal-Carbon Hybrid Catalysts (Metal-Karbon Hibrit Katalizörler)

Pt catalysts are generally used in fuel cells as carbon-supported. This increases the durability and surface area. High power densities were obtained in several MFC systems using Pt/C as cathode catalysts. In addition, non-precious metal catalysts are used, while active carbon, graphene, and graphite materials are also used as support. Metal and carbon-based catalysts can be used as catalysts in one-by-one MFCs and can be synthesized together to form a suitable cathode catalyst material.

Although activated carbon has a low cost and wide surface area, it has a low catalytic activity. Various metals can be doped to enhance the electrocatalytic properties of the activated carbon in the ORR reaction. Lv et al. (2019) synthesized activated carbon-supported Fe-Ag-N multi-doped graphene as the air cathode catalyst in MFC [31]. They obtained the highest maximum power density up to 1956.45 $mW.m^{-2}$ [31]. Santoro et al. (2019) in their study using Fe-N-C cathode catalysts have reached a maximum power density of 36.9 $W.m^{-3}$ [33].

In addition, metal nitrogen carbon complex catalysts have also been tested. Among them Ni/N–CNFs [33], Fe–N–C [33-35], Co/Fe–N–C [36] catalysts are prominent.

3.4. Biocathodes (Biyokatotlar)

Biological cathodes, after the initial investment, can be much lower cost than other cathodes. Compared with platinum-catalyzed cathodes, they have higher resistance to poisoning [37]. In addition to catalyzing the ORR, some catalysts help to improve the biological treatment of wastewater by performing further processes such as the reduction of nitrates, sulfates, and dyes [38-39-40].

Santoro et al. (2016) [41] in a study by using bilirubin oxidase as a cathode catalyst, obtained a power density of 2 $W.m^{-2}$ [42]. Christwardana et al. (2016), in their studies using laccase as enzymatic biocatalysts, have reached a power density of 102 ± 5.1 $\mu W\ cm^{-2}$ [43]. In another study by using laccase-producing white-rot fungus on the cathode, the maximum power density of 13.38 $mW.m^{-2}$ was reached [44].

4. RESULTS (BULGULAR)

When the studies on the development of MFC cathode materials and increasing the power density values obtained from these systems are summarized, it is seen that the cathode material with the highest power density value is graphite plate. Zheng et al. (2015) obtained a power density of 3215 mw/m^2 in their study using a graphite plate cathode [32]. This is followed by the study by Tang et al. (2016) in which 3D porous Fe-N-C on carbon paper cathode material was used and a high power density value of 3118.9 mw/m^2 was obtained [34].

Although Pt is a high-performance cathode material in terms of power density, it is an expensive material. For this reason, relatively cheaper materials such as graphite, carbon, Fe, Ni have been tested instead of Pt, and high power densities have been achieved. In particular, carbon-based materials are the optimum materials used as cathode materials in MFCs in terms of both cost and power density.

When we examined the alternative biocathodes used, the study by Breheny et al. (2019), in which bilirubin oxidase is used as the cathode material, stands out with the power density value obtained [42]. Breheny et al. (2019) were able to reach a high power density value of 2000 mW/m^2 in their study [42]. This result showed that high power densities can be achieved by using alternative biocathodes in MFCs, giving hope for further studies.

Table 1. shows cathode catalysts used in MFCs in recent years and their power density values.

Table 1. Cathode Catalysts in MFC and Power Density Values (MFC'de Katot Katalizörleri ve Güç Yoğunluğu Değerleri)

Cathode	**Power density (mW.m^{-2})**	**Reference**
Graphite plate	3215 ± 80	[32]
3D porous Fe-N-C on carbon paper	3118.9	[26]
Carbon brush	2777.7	[45]
Fe-N-C	2437 ± 55	[20]
Carbon cloth	2420	[46]
Pt and carbon cloth	2400	[47]
Carbon felt	2142	[48]
Carbon cloth	2110 ± 68	[49]
Carbon paper with Pt catalyst	2066	[50]
$NiCo_2S_4$/AC	2000 ± 59	[21]
Activated carbon-supported multi-doped graphene	1956.45	[31]
Fe-Mn	1940 ± 31	[51]
Graphite plates	1771	[52]
$CoFe_2O_4$@N-AC	1770.8 ± 15.0	[23]
Carbon cloth with three PDMS/carbon layers and Pt catalysts	1635 ± 62	[53]
Pt rod	1624	[54]
N and P dual-doped carbon derived from chitosan catalyst	1603	[53]
Cobalt oxide supported on N-doped CNT	1.260	[55]
V_2O_5	1.073	[24]
Pseudomas biofilm	1056	[56]
Co/N/C based catalyst	931.1	[57]
Fe-containing N-doped carbon	900	[19]
MnO_x	48.4 ± 10.16	[58]

5. CONCLUSIONS (SONUÇLAR)

The increasing population of the world brings with it an increase in the waste generated by consumption. Utilizing these wastes and their bio-electrochemical energy content in MFC systems can be reduced environmental pollution and increased the amount of clean, renewable energy production. Therefore, active use of MFCs is very important for a future clean and sustainable world.

As seen in this study, in recent years, studies on MFC have focused on reducing the use of expensive catalysts such as Pt, thus reducing system cost. The studies show that it is possible to achieve high power densities in MFCs by using lower-cost cathode catalysts such as carbon and graphite-based materials or Fe and Mn. Again, further development of metal-carbon hybrid catalysts will provide high-performance and low-cost MFCs.

DECLARATION OF ETHICAL STANDARDS (ETİK STANDARTLARIN BEYANI)

The author of this article declares that the materials and methods they use in their work do not require ethical committee approval and/or legal-specific permission.

Bu makalenin yazarı çalışmalarında kullandıkları materyal ve yöntemlerin etik kurul izni ve/veya yasal-özel bir izin gerektirmediğini beyan ederler.

AUTHORS' CONTRIBUTIONS (YAZARLARIN KATKILARI)

***Işılay BİLGİÇ*:** She conducted the research, analyzed the results and performed the writing process.

Araştırmayı yapmış, sonuçlarını analiz etmiş ve maklenin yazım işlemini gerçekleştirmiştir.

CONFLICT OF INTEREST (ÇIKAR ÇATIŞMASI)

There is no conflict of interest in this study.

Bu çalışmada herhangi bir çıkar çatışması yoktur.

REFERENCES (KAYNAKLAR)

[1] Logan, B. E., Hamelers, B., Rozendal, R. A., Schr€order, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., & Rabaey, K. (2006). Microbial fuel cells: Methodology and technology. Environmental Science & Technology, 40, 5181-5192. https://doi.org/10.1021/es0605016

[1] Kannan, M. V., & Kumar, G. G. (2016). Current status, key challenges and its solutions in the design and development of graphene based ORR catalysts for the microbial fuel cell applications. Biosensors and Bioelectronics, 77, 1208-1220. https://doi.org/10.1016/j.bios.2015.10.018

[2] Turk, K. K., Kruusenberg, I., Kibena, P. E., Bhowmick, G. D., Kook, M., Tammeveski, K., Matisen, L., Merisalu, M., Sammelselg, V., Ghangrekar, M. M., Mitra, A., & Banerjee, R. (2018). Novel multi walled carbon nanotube based nitrogen impregnated Co and Fe cathode catalysts for improved microbial fuel cell performance. International Journal of Hydrogen Energy, 43(51), 23027-23035. https://doi.org/10.1016/j.ijhydene.2018.10.143

[3] He, L., Du, P., Chen, Y., Lu, H., Cheng, X., Chang, B., & Wang, Z. (2017). Advances in microbial fuel cells for wastewater treatment. Renewable and Sustainable Energy Reviews, 71, 388-403. https://doi.org/10.1016/j.rser.2016.12.069

[4] Abourached, C., English, M. J., & Liu, H. (2016). Wastewater Treatment by Microbial Fuel Cell (MFC) prior irrigation water reuse. Journal of Cleaner Production, 137, 144-149. https://doi.org/10.1016/j.jclepro.2016.07.048

[5] Palanisamy, G., Jung, H. Y., Sadhasivam, T., Kurkuri, M. D., Kim, S. C., & Roh, S. H. (2019). A comprehensive review on microbial fuel cell technologies: Processes, utilization, and advanced developments in electrodes and membranes. Journal of Cleaner Production, 221, 598-621. https://doi.org/10.1016/j.jclepro.2019.02.172

[6] Huang, D., Li, M. J., Song, B.Y., & Liu Z. B. (2019). Structure and dynamics of microbial fuel cell catalyst layer. Electrochimica Acta, 300, 404-416. https://doi.org/10.1016/j.electacta.2019.01.111

[7] Wei X.Y., Liu, M., Yang, J., Du, W.N., Sun, X., Huang, Y.P., Zhang, X., Khalil, S.K., Lou, D.M., Zhou, Y.D. (2019). Characterization of PM2.5-bound PAHs and carbonaceous aerosols during three-month severe haze episode in Shanghai, China: Chemical composition, source apportionment and long-range transportation. Atmospheric Environment, 203, 1–3. https://doi.org/10.1016/j.atmosenv.2019.01.046

[8] Pandit, S., Sengupta, A., Kale, S., & Das, D. (2011). Performance of electron acceptors in catholyte of a two-chambered microbial fuel cell using anion exchange membrane.

Bioresour Technolgy, 102(3), 2736-2744. https://doi.org/10.1016/j.biortech.2010.11.038

[9] Lu, M., & Li, S. F.Y. (2012). Cathode reactions and applications in microbial fuel cells: A review. Critical Reviews in Environmental Science Technolog, 42(23), 2504-2525. https://doi.org/10.1080/10643389.2011.592744

[10] Noori, M.T., Ghangrekar, M. M., & Mukherjee, C. K. (2016). V2O5 microflower decorated cathode for enhancing power generation in air-cathode microbial fuel cell treating fish market wastewater. International Journal of Hydrogen Energy, 41(5), 3638-3645. https://doi.org/10.1016/j.ijhydene.2015.12.163

[11] Kodali, M., Santoro, C., Herrera, S., Serov, A., & Atanassov, P. (2017). Bimetallic platinum group metal-free catalysts for high power generating microbial fuel cells. Journal of Power Sources, 366, 18-26. https://doi.org/10.1016/j.jpowsour.2017.08.110

[12] Kim, S., Kato, S., Ishizaki, T., Li, O.L., & Kang, J. (2019). Transition Metal (Fe, Co, Ni) Nanoparticles on Selective Amino-N-Doped Carbon as High-Performance Oxygen Reduction Reaction Electrocatalyst. Nanomaterials, 9(5), 742. https://doi.org/10.3390/nano9050742

[13] Deng, L., Yuan, Y., Zhang, Y., Wang, Y., Chen, Y., Yuan, H., & Chen, Y. (2017). Alfalfa leafderived porous heteroatom-doped carbon materials as efficient cathodic catalysts in microbial fuel cells. ACS Sustainable Chemistry & Engineering, 5(11), 9766-9773. https://doi.org/10.1021/acssuschemeng.7b01585

[14] Zhang, L., Lu, Z., Li, D., Ma, J., Song, P., Huang, G., Liu, Y., &Cai, L. (2016). Chemically activated graphite enhanced oxygen reduction and power output in catalyst-free microbial fuel cells. Journal of Cleaner Production, 115, 332-336. https://doi.org/10.1016/j.jclepro.2015.12.067

[15] Wang, Z., Cao, C., Zheng, Y., Chen, S., & Zhao, F. (2014). Abiotic oxygen reduction reaction catalysts used in microbial fuel cells. ChemElectroChem, 1(11),1813–1821. https://doi.org/10.1002/celc.201402093

[16] Santoro, C., Arbizzani C., Erable B., & Ieropoulos, I. (2017). Microbial fuel cells: From fundamentals to applications. A review. Journal of Power Sources, 356, 225-244. https://doi.org/10.1016/j.jpowsour.2017.03.109

[17] Yuan, H., & He, Z. (2015). Graphene-modified electrodes for enhancing the performance of microbial fuel cells. Nanoscale, 7, 7022–7029. https://doi.org/10.1039/C4NR05637J

[18] Ren, P., Ci, S., Ding, Y., & Wen, Z. (2019). Molten-salt-mediated synthesis of porous Fe-containing N-doped carbon as efficient cathode catalysts for microbial fuel cells. Applied Surface Science, 481, 1206–1212. https://doi.org/10.1016/j.apsusc.2019.03.279

[19] Pan , Y., Mo, X., Li, K., Pu, L., Liu, D., & Yang, T. (2016). Iron-nitrogen-activated carbon as cathode catalyst to improve the power generation of single-chamber air-cathode microbial fuel cells. Bioresour Technology, 206, 285-289. https://doi.org/10.1016/j.biortech.2016.01.112

[20] Pu, L., & Li, K. (2016). Inverse Spinel NiCo2S4 Nanoparticles Coated on Activated Carbon as an Electrocatalyst Applied in Air Cathode Microbial Fuel Cells. The Electrochemical Society, 01,1832. https://doi.org/10.1149/MA2016-01/36/1832

[21] Wang, Z., Cao, C., Zheng, Y., Chen S., & Zhao, F. (2019). Hydrothermal synthesis of fe-mn bimetallic nanocatalysts as high efficiency cathode catalysts for microbial fuel cells. Journal of Power Sources, 414, 444–452. https://doi.org/10.1016/j.jpowsour.2019.01.024

[22] Huang, Q., Zhou, P., Yang, H., Zhu, L., & Wu, H. (2017). In situ generation of inverse spinel CoFe 2 O 4 nanoparticles onto nitrogen-doped activated carbon for an effective cathode electrocatalyst of microbial fuel cells. Chemical Engineering Journal, 325, 466-473. http://dx.doi.org/10.1016/j.cej.2017.05.079

[23] Ayyaru, S., Mahalingam S., & Ahn, Y. H. (2019). A non-noble V2O5 nanorods as an alternative cathode catalyst for microbial fuel cell applications. International Journal of Hydrogen Energy, 44, 4974-4984. https://doi.org/10.1016/j.ijhydene.2019.01.021

[24] Yuan, H., Hou, Y., Abu-Reesh, I. M., Chen, J., & He, Z. (2016). Oxygen reduction reaction catalysts used in microbial fuel cells for energy-efficient wastewater treatment: A review. Materials Horizons, 3, 382—401. https://doi.org/10.1039/C6MH00093B

[25] Tang, H., Zeng, Y., Zeng, Y., Wang, R., Cai, S., Liao, C., Cai, H., Lu, X., & Tsiakaras, P. (2017). Iron-embedded nitrogen doped carbon frameworks as robust catalyst for oxygen reduction reaction in microbial fuel cells. Applied Catalysis B: Environmental, 202, 550-556. https://doi.org/10.1016/j.apcatb.2016.09.062

[26] Hirooka, K., Ichihashi, O., & Takeguchi, T. (2018). Sodium cobalt oxide as a non-platinum cathode catalyst for microbial fuel cells. Sustainable Environment Research, 28(6), 322-325. https://doi.org/10.1016/j.serj.2018.07.002

[27] Wu, Y., Wang, L., Jin, M., Kong, F., Qi, H., & Nan, J. (2019). Reduced graphene oxide and biofilms as cathode catalysts to enhance energy and metal recovery in microbial fuel cell. Bioresource Technology, 283, 129–137. https://doi.org/10.1016/j.biortech.2019.03.080

[28] Majidi, M. R., Farahani, F. S., Hosseini, M., & Ahadzadeh, I. (2019). Low-cost nanowired α-MnO2/C as an ORR catalyst in air-cathode microbial fuel cell. Bioelectrochemistry, 125, 38–45. https://doi.org/10.1016/j.bioelechem.2018.09.004

[29] Chiodoni, A., Salvador, G. P., Massaglia, G., Delmondo, L., Munoz-Tabares, J. A., Sacco, A., Garino, N., Castellino, M., Margaria, V., Ahmed, D., Pirri, C. F., & Quaglio M. (2019). MnxOy- based cathodes for oxygen reduction reaction catalysis in microbial fuel cells. International Journal of Hydrogen Energy, 44(9), 4432-4441. https://doi.org/10.1016/j.ijhydene.2018.11.064

[30] Lv, C., Liang, B., Zhong, M., Li, K., & Qi, Y. (2019). Activated carbon-supported multi-doped graphene as high-efficient catalyst to modify air cathode in microbial fuel cells. Electrochimica Acta, 304, 360-369. https://doi.org/10.1016/j.electacta.2019.02.094

[31] Zheng, S., Yang, F., Chen, S., Liu, L., Xiong, Q., Yu, T., Zhao, F., Schroder, U., & Hou, H. (2015). Binder-free carbon black/stainless steel mesh composite electrode for high-performance anode in microbial fuel cells. Journal of Power Sources, 284, 252-257. https://doi.org/10.1016/j.jpowsour.2015.03.014

[32] Santoro, C., Kodali, M., Shamoon, N., Serov, A., Soavi, F., Merino-Jimenez, I., Gajda, I., Greenman, J., Ieropoulos, I., & Atanassov, P. (2019). Increased power generation in supercapacitive microbial fuel cell stack using Fe—N—C cathode catalyst. Journal of Power Sources, 412, 416–424. https://doi.org/10.1016%2Fj.jpowsour.2018.11.069

[33] Tang C. and Zhang Q.,(2016) Can Metal–Nitrogen–Carbon Catalysts Satisfy Oxygen Electrochemistry?. J. Mater. Chem. A,, 4, 4998–5001. https://doi.org/10.1039/C6TA01062H

[34] Su Y., Jiang H., Zhu Y., Zou W., Yang X., Chen J. and Li C (2014). Hierarchical Porous Iron and Nitrogen Co-Doped Carbons As Efficient Oxygen Reduction Electrocatalysts In Neutral Media. J. Power Sources, 2014, 265, 246–253. https://doi.org/10.1016/j.jpowsour.2014.04.140

[35] Wenmu L., Aiping Y., Higgins DC., Llanos BG., and Zhongwei C.* (2010). Biologically Inspired Highly Durable Iron Phthalocyanine Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells. Journal of the American Chemical Society, 132, 48, 17056–17058. https://doi.org/10.1021/ja106217u

[36] Santoro, C., Serov, A., Gokhale, R., Rojas-Carbonell, S., Stariha, L., Gordon, J., Artyushkova, K., & Atanassov, P. (2017). A family of Fe-N-C oxygen reduction electrocatalysts for microbial fuel cell (MFC) application: Relationships between surface chemistry and performances. Applied Catalysis B: Environmental, 205, 24–33. https://doi.org/10.1016/j.apcatb.2016.12.013

[37] Jiang, C., Yang, Q., Wang, D., Zhong, Y., Chen, F., & Li, X. (2017). Simultaneous perchlorate and nitrate removal coupled with electricity generation in autotrophic denitrifying biocathode microbial fuel cell. Chemical Engineering Journal, 308, 783–790. https://doi.org/10.1016/j.cej.2016.09.121

[38] Sotres, A., Cerrillo, M., Viñas, M., & Bonmatí, A. (2016). Nitrogen removal in a two-chambered microbial fuel cell: Establishment of a nitrifying–denitrifying

microbial community on an intermittent aerated cathode. Chemical Engineering Journal, 284, 905–916. https://doi.org/10.1016/j.cej.2015.08.100

[39] Park, Y., Park, S., Nguyen, V., Yu, J., Torres, C., & Rittmann, B. (2017). Complete nitrogen removal by simultaneous nitrification and denitrification in flat-panel air-cathode microbial fuel cells treating domestic wastewater. Chemical Engineering Journal, 316, 673–679. https://doi.org/10.1016/j.cej.2017.02.005

[40] Santoro, C., Babanova, S., Erable, B., Schuler, A., Atanassov, P. (2016). Bilirubin oxidase based enzymatic air-breathing cathode: Operation under pristine and contaminated conditions, Bioelectrochemistry, 108, 1–7. https://doi.org/10.1016/j.bioelechem.2015.10.005

[41] Breheny, M., Bowman, K., Farahmand, N., Gomaa, O., Keshavarz, T., & Kyazze, G. (2019). Biocatalytic electrode ımprovement strategies in microbial fuel cell systems. Journal of Chemical Technology and Biotechnology, 94(7), 2081-2091. https://doi.org/10.1002/jctb.5916

[42] Christwardana, M., Kim, K. J. & Kwon, Y. (2016). Fabrication of mediatorless/ membraneless glucose/ oxygen based biofuel cell using biocatalysts ıncluding glucose oxidase and laccase enzymes. Scientific Reports,6, 1-10. https://doi.org/10.1038/srep30128

[43] Lai, C., Wu, C., Meng, C., & Lin, C. (2017). Decolorization of azo dye and generation of electricity by microbial fuel cell with laccase-producing white-rot fungus on cathode. Applied Energy, 188, 392–398. https://doi.org/10.1016/j.apenergy.2016.12.044

[44] Bi, L., Ci, S., Cai, P., Li, H., & Wen, Z. (2018). One-step pyrolysis route to three dimensional nitrogen-doped porous carbon as anode materials for microbial fuel cells. Applied Surface Science, 427, 10-16. https://doi.org/10.1016/j.apsusc.2017.08.030

[45] Tao, Y., Liu, Q., Chen, J., Wang, B., Wang, Y., Liu, K., Li, M., Jiang, H., Lu, Z., & Wang, D. (2016). Hierarchically three-dimensional nanofiber based textile with high conductivity and biocompatibility as a microbial fuel cell anode. Environmental Science & Technology, 50(14), 7889-7895. https://doi.org/10.1021/acs.est.6b00648

[46] Logan, B., Cheng, S., Watson, V., & Estadt, G. (2007). Graphite fiber brush anodes for ıncreased power production ın air-cathode microbial fuel cells. Environmental Science & Technology, 41, 3341-3346. https://doi.org/10.1021/es062644y

[47] Hou, J., Liu, Z., Yang, S., & Zhou, Y. (2014). Three-dimensional macroporous anodes based on stainless steel fiber felt for high-performance microbial fuel cells. Journal of Power Sources, 258, 204-209. https://doi.org/10.1016/j.jpowsour.2014.02.035

[48] Feng, Y., Yang, Q., Wang, X., Liu, Y., Lee, H., & Ren, N. (2011). Treatment of biodiesel production wastes with simultaneous electricity generation using a singlechamber microbial fuel cell. Bioresource Technology, 102(1), 411-415. https://doi.org/10.1016/j.biortech.2010.05.059

[49] Zhu, N., Che n, X., Zhang, T., Wu, P., Li, P., & Wu, J., (2011). Improved performance of membrane free single-chamber air-cathode microbial fuel cells with nitric acid and ethylenediamine surface modified activated carbon fiber felt anodes. Bioresour Technology, 102(1), 422-426. https://doi.org/10.1016/j.biortech.2010.06.046

[50] Guo, X., Jia, J., Dong, H., Wang, Q., Xu, T., Fu, B., Ran, R., Liang, P., Huang, X., & Zhang, X. (2019). Hydrothermal synthesis of feemn bimetallic nanocatalysts as highefficiency cathode catalysts for microbial fuel cells. Journal of Power Sources, 414, 444–452. https://doi.org/10.1016/j.jpowsour.2019.01.024

[51] Kaewkannetra, P., Chiwes,W., & Chiu, T.Y. (2011). Treatment of cassava mill wastewater and production of electricity through microbial fuel cell technology. Fuel, 90, 2746-2750. https://doi.org/10.1016/j.fuel.2011.03.031

[52] Zhang, Y., Mo, G., Li, X., Zhang,W., Zhang, J., Ye, J., Huang, X., & Yu, C. (2011). A graphene modified anode to improve the performance of microbial fuel cells. Journal of Power Sources, 196(13),5402-5407. https://doi.org/10.1016/j.jpowsour.2011.02.067

[53] Mehdinia, A., Ziaei, E., & Jabbari, A. (2014). Facile microwave-assisted synthesized reduced graphene oxide/tin oxide

nanocomposite and using as anode material of microbial fuel cell to improve power generation. International Journal of Hydrogen Energy, 39(20), 10724-10730. https://doi.org/10.1016/j.ijhydene.2014.05.008

[54] Yang, W., Lu, J. E., Zhang, Y., Peng, Y., Mercado, R., Li, J., Zhu, X., & Chen, S. (2019). Cobalt oxides nanoparticles supported on nitrogen-doped carbon nanotubes as high-efficiency cathode catalysts for microbial fuel cells. Inorganic Chemistry Communications, 105,69–75. https://doi.org/10.1016/j.inoche.2019.04.036

[55] Xu, G., Zheng, X., Lu, Y., Liu, G., Luo, H., Li, X., Zhang, R., & Jin, S. (2019). Development of microbial community within the cathodic biofilm of single-chamber air-cathode microbial fuel cell. Science of the Total Environment, 665, 641–648. https://doi.org/10.1016/j.scitotenv.2019.02.175

[56] Li, M., Zhong, K., Zhang, L., Wang, S., Zhang, H., Huang, Y., Chen, S., Mai, H., & Zhang, N. (2019). Cobalt-based catalysts modified cathode for enhancing bioelectricity generation and wastewater treatment in air-breathing cathode microbial fuel cells. Electroanalysis, 31, 1– 13. https://doi.org/10.1002/elan.201900161

[57] Tatinclaux, M., Gregoire, K., Leininger, A., Biffinger, J. C., Tender, L., Ramirez, M., Torrents, A., & Kjellerup, B. V. (2018). Electricity generation from wastewater using a floating air cathode microbial fuel cell. Water-Energy Nexus, 1(2),97–103. https://doi.org/10.1016/j.wen.2018.09.001