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RESEARCH

Impact of modified electrodes on boosting power density of microbial fuel cell for effective domestic wastewater treatment: A case study of Tehran

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Abstract: Utilizing microbial fuel cells (MFCs) is a promising technology for energy-efficient domestic wastewater treatment, but it still faces practical barriers such as low power generation. In this study, the $LaMnO_3$ perovskite-type oxide nanoparticles and nickel oxide/carbon nanotube/polyaniline (NCP) nanocomposite (the cathode and anode catalysts, respectively) have been prepared and used to enhance power density of MFC. The prepared La-based perovskite oxide catalysts were characterized by X-ray diffraction (XRD) and scanning electron microscopies (SEM). The electrocatalytic properties of the prepared catalysts were investigated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and Tafel plot at ambient temperature. Results show the exchange current densities of $LaMnO_3$/carbon cloth cathode and NCP nanocomposite/carbon cloth anode were 1.68 and 7 times more compared to carbon cloth cathode, respectively. In comparison to the bare carbon cloth anode, the MFC with the modified electrodes shows 11 times more enhancement in power density output which according to electrochemical results, it can be due to the enhancement of the electron transfer capability. These cathodic and anodic catalysts were examined in batch and semi-continuous modes to provide conditions close to industrial conditions. This study suggests that utilizing these low cost catalysts has promising potential for wastewater treatment in MFC with high power generation and good COD removal efficiency.

Key words: carbon nanotube; nickle oxide**;** La-based perovskite oxide; semi-continuous mode

Nowadays, the world is facing depletion of fossil fuels and also their significant negative drawbacks, such as air pollution and global warming which have stimulated the high demand for large renewable energy[1]. Proper treatment of wastewater is a beneficial part of using wastewater as a source of renewable energy[2]. On the other hand, wastewater treatment protects the environment and the water bodies that serve as drinking water sources. Still in many cases, wastewater treatment processes such as anaerobic digestion only can be applied to treat high strength substrate (with more than 1 g COD per liter) and cannot be used at low temperature[3], whereas microbial fuel cells (MFCs) are being developed as a sustainable energy technology, as they can directly produce electricity from wastewater in treating low concentration COD substrates at low temperatures (10–20°C)[4]. In addition, MFCs significantly reduce the sludge production and save 100% of aeration energy with extra electricity output which can reduce the treatment costs and the challenges associated with sludge treatment and disposal[5]. MFCs utilize microorganisms to release electrical energy by breaking the chemical bonds of organic compounds in wastewater[6]. A customary laboratory MFC is consisted of anodic and cathodic chambers in which microorganisms oxidize the substrate and produce electrons and protons in the anode chamber. Electrons are transferred to cathode by external circuit and protons are transported through the cation exchange membrane internally. The MFC is influenced by several critical factors[7,8]. Low power density in microbial fuel cell is still a big issue even for a conventional MFC system. Electrodes as components that have the greatest impact on the power generation of practical MFCs have been highly regarded and discussed in the past decade[9]. Electron transfer from exoelectrogenic bacteria to the anode and the oxygen reduction and electron acceptance in the cathode chamber of MFCs are still challenging factors of this field[10,11]. In this study, the $LaMnO_3$ perovskite-type oxide nanoparticles and nickel oxide/carbon

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nanotube/polyaniline (NCP) nanocomposite (the cathode and anode catalysts, respectively) for the first time have been introduced and used to enhance power density of MFC for effective wastewater treatment. To date, versatile porous carbon-based materials such as graphite[12], carbon cloth[13], carbon paper[14], carbon foam[15] and reticulated vitrified carbon[16] have been frequently applied as electrode in construction of MFCs. Porous carbon-based materials suffer from limited electrocatalytic activity and clogging pores by the entering bacteria. Thus, modification of carbon-based materials has been investigated through different methods for improving MFCs performance[17]. The oxygen reduction and electron acceptance in the cathode chamber of MFCs are mainly limited by the slow reaction kinetics of the oxygen reduction. The oxygen reduction reaction (ORR) requires an efficient catalyst to improve the electrocatalytic reduction of oxygen[18]. Although the Pt group metals are the most efficient electrocatalysts for the ORR, their high cost and sensitivity to poisoning makes them impossible to be utilized in MFCs as substitute technology of wastewater treatment in the future[19]. Therefore, most efforts have been focused on cost effective and durable non-Pt catalysts for the ORR. Transition metal oxides from the perovskite-type oxide family were proposed as low cost catalysts for the ORR[20]. The ORR activity of perovskite type catalysts may be influenced by the ability of B-site cation to adopt different valence states which leads to formation of redox couples at the oxygen reduction potential[21]. Furthermore, for the A-site cation, lanthanum (La) was demonstrated the best performance on the ORR activity[22]. Some recent investigations on perovskite-carbon nanocomposites have revealed that they are appropriate for the ORR in MFCs[18,23]. In the present study, the synthesized La-based perovskite oxide, $LaMnO_3$, is used for this purpose. On the other hand, composite electrodes such as CNT/conductive polymer nanocomposites and metal oxide/conductive polymer nanocomposites are also interesting in anode MFC application due to their effectiveness at the bacterial attachment on anode and the process of electron transfer from bacteria to anode[24]. Among the all conductive polymers, polyaniline (PANI) is more popular due to its simple synthesis process, excellent electrochemical activity and electrical conductivity, biocompatibility, environmental stability and low cost[25]. Furthermore, in recent years, CNTs have shown promising properties as electrode materials in MFCs due to their unique physical/chemical characteristics including extremely high surface-area, good electrical conductivity, superior mechanical properties, acceptable biocompatibility, and high chemical stability[26]. Considering the unique mechanical and electrical properties of CNTs and PANI and their excellent efficiency in transferring electrons from bacteria to anode, the new nanocomposites based on CNTs and PANI with metal oxide could possess properties of the individual components with multiple desirable effects. The metal oxides have been found to exhibit good electrocatalytic activity towards the bacteria metabolites[27,28]. In the past decades, nickel oxide (NiO) has been studied as a low cost, environmentally-friendly and favorable alternative electro-catalyst in batteries, super-capacitors and MFCs due to its high theoretical capacitance[29–31]. In this study, the NiO was used as electron mediators to accelerate the electron transfer between the bacterial cells and the carbon cloth electrode combined with CNT and PANI for synergetic effects on electrochemical characteristics and developing the prospective MFC anode materials. In this study domestic wastewater treatment was examined using two MFC systems, containing MFC with bare carbon cloth (BCC) electrodes and MFC with modified carbon cloth (MCC) electrodes by synthesized catalysts. Transferring of electrons from bacteria to anode was enhanced through the synthesized the NCP nanocomposite as an anode catalyst to improve the electrocatalytic properties of carbon cloth anode in fabricating dual-chamber MFC, and $LaMnO_3$ perovskite-type oxide nanoparticles was used as the MFC cathode catalyst due to their low-cost and high electrocatalytic efficiency. It is a new approach to obtain high power density in MFCs with low cost. The anode and cathode electrocatalysts were prepared and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrocatalytic properties of anode and cathode catalysts in MFC in presence of domestic wastewater were investigated through linear sweep voltammetry (LSV) and Tafel plot at ambient temperature (28 ± 2)°C. The electrochemical impedance spectroscopy (EIS) has been used as a valuable tool to estimate the alteration of internal resistances. The performance of the electrocatalysts in MFC was evaluated in terms of maximum power densities (MPD), maximum current densities (mA/cm^2), and open-circuit voltages (OCVs).

1 Experimental

1.1 Preparation of nano catalysts and characterization

The NCP nanocomposite sample has been prepared by using in situ polymerization and precipitation approach which includes two-steps process with composition of 50% NiO and 20% CNT[32–34]. $LaMnO_3$ catalysts were synthesized using the sol-gel method with La and Mn nitrates in stoichiometric amount[35]. The crystal structure of nano-catalysts was evaluated by XRD using Philips diffractometer PW 3710 equipped with Cu $K\alpha_1$ radiation (λ = 0.154 nm). The diffraction patterns were collected at room temperature by step scanning in the range of $10° \le 2\theta \le 90°$, with the scan rate