Enhanced electricity generation and effective water filtration using graphene-based membrane air-cathodes in microbial fuel cells

Xiangru Song[a], Jia Liu[a,*], Qing Jiang[a], Youpeng Qu[b], Weihua He[a], Bruce E. Logan[c], Yujie Feng[a,*]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No 73 Huanghe Road, Nangang District, Harbin 150090, China
[b] School of Life Science and Technology, Harbin Institute of Technology, No. 2 Yikuang Street, Nangang District, Harbin 150080, China
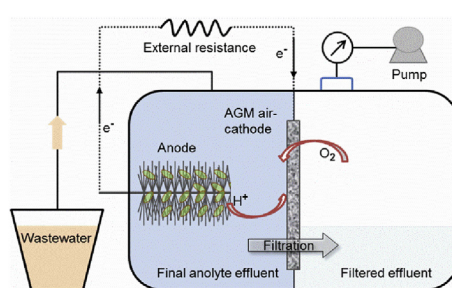[c] Department of Civil and Environmental Engineering, Penn State University, 212 Sackett Building, University Park, PA, 16802, USA

HIGHLIGHTS

- Graphene was added to the activated carbon catalyst of an air cathode (AGM).
- The AGM air-cathode was made using a simple phase inversion method.
- Power and COD removal were improved in the MFC with AGM air-cathode.
- Anti-fouling properties of the AGM air-cathode were improved.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Air-cathodes in microbial fuel cells that can also filter wastewater provide the dual benefits of electricity production and reduction of the effluent chemical oxygen demand. Air-cathodes prepared using a novel activated carbon/graphene membrane (2, 5 or 10% graphene by weight) prepared by phase inversion have good conductivities (5.6 ± 0.5 to $7.3 \pm 0.6\,\mathrm{mS\,cm^{-1}}$) compared to control ($3.0 \pm 0.4\,\mathrm{mS\,cm^{-1}}$, activated carbon, no graphene). The cathode with $5\,\mathrm{wt\%}$ graphene produces the highest maximum power density of $1460 \pm 10\,\mathrm{mW\,m^{-2}}$, which is 58% higher than that the control ($928 \pm 8\,\mathrm{mW\,m^{-2}}$). The increased power is due to an 88% reduction in charge transfer resistance of $6.0 \pm 0.3\,\Omega$ (cathode with $5\,\mathrm{wt\%}$ graphene) compared to the control. Following a cycle of treatment and current generation, $60 \pm 1\%$ of the chemical oxygen demand is removed from the remaining chemical oxygen demand, producing an effluent chemical oxygen demand concentration of $20 \pm 1\,\mathrm{mg\,L^{-1}}$. Biomass ($4.99 \pm 0.02\,\mathrm{mg\text{-}protein\,cm^{-2}}$) is decreased by 33% compared to the control. These results demonstrate that cathodes made with graphene can produce electricity and a high quality effluent with low cathode biofouling.

1. Introduction

Wastewater is a potential source, as it contains more energy than that needed to treat it using conventional wastewater treatment technologies [1,2]. While aerobic wastewater treatment technologies cannot be used to extract this energy, microbial fuel cells (MFCs) are bioelectrical technologies that can be used to harvest this energy and accomplish wastewater treatment [3–5]. For efficient power generation, air cathodes must be used in the MFCs to produce power as this avoids the need to aerate the water [6]. The oxygen reduction reaction (ORR) using an air-cathode MFC does not require water aeration, but the cathode needs to have excellent catalytic activity, a high oxygen

transfer efficiency, and a high proton transfer to the catalyst site, and the cathode materials must be inexpensive and durable over time [7]. The most commonly used catalyst in MFCs is activated carbon, as it is inexpensive and it resists fouling better than platinum over long term operation [8]. However, the cathode can limit power generation in MFCs, and thus it is important to improve the ORR to increase power production.

Graphene is a pure carbon material which can be formed as an atom-thick sheet [9] or used with many layers as a dense honeycomb crystal structure [10–12]. Graphene has several features which are all useful characteristics for the ORR in MFC cathodes, including high electron transfer rates, a large specific surface area, excellent electrical conductivity and electrochemical stability, and good mechanical flexibility [13]. Recent research has shown that graphene can be added to an MFC cathode to improve performance and power densities of MFCs [14]. The three-dimensional structure of the graphene improved the ORR, which increased power production compared to plain activated carbon cathodes [15]. Nitrogen-doped graphene can have even better performance than plain graphene, as it has been shown to compare well to a Pt/C control in terms of polarization data and number of electrons transferred [16]. However, cathodes previously made using activated carbon and graphene have only been made using a traditional multiple-step, and energy-intensive press method.

A phase inversion process was recently used as a novel one-step approach to produce both the catalytic and diffusion layers of an air-cathode [17]. This method was shown to be very simple, and making cathodes using this method significantly reduced the total cost of the MFC [18]. The phase inversion process used hydrophobic polyvinylidene fluoride (PVDF) to bind the activated carbon catalyst to a stainless steel mesh current collector [17,19,20]. It was further demonstrated that water retention could be increases using an additional PVDF membrane on the air-facing side of the cathode [17]. However, for some MFC applications the cathode has been designed to allow water filtration, thus accomplishing both power generation and filtration of the effluent [21]. In this case, the choice of the binder is essential to allow water passage rather than water retention. Polyvinyl chloride (PVC) is a polymer that can be used to produce low-cost porous and ultrafiltration membranes that have a good water fluxes and particle rejection properties [22,23].

The key performance data for the MFC were power generation and effluent quality [24]. In order to produce an MFC with good performance and a cathode with effective water filtration, an activated carbon/graphene membrane air-cathode (AGM air-cathode) was developed here. It was manufactured by a phase inversion process. The charge transfer, filtration, and antifouling properties were the key parameters in evaluating the performance of the membrane cathodes [25]. The AGM air-cathode possessed improved electrochemical performance and antifouling properties compared to a plain activated carbon membrane, and it was easily produced by the phase inversion process.

2. Material and methods

2.1. Materials

PVC (80,000 g mol^{-1}) was provided by Shenyang Chemical Co., LTD. N,N-dimethylacetamide (DMAc, anhydrous, 99.8%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd (Tianjin, China) and 1-methyl-2-pyrrolidinone (NMP, AR) was obtained by Tianjin Zhiyuan Chemical Reagent Co., Ltd (Tianjin, China). Polyvinylpyrrolidone (PVP, k30, AR) was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) and used as a pore-forming agent. Polyaniline (PANI, 300 kDa, Hubei Yuanchengsaichuang Co., Ltd, Wuhan, China) was used to promote oxygen adsorption and electrode conductivity [26]. Activated carbon powder (AC, Carbosino Material Co., Ltd, Shanghai, China) as the electrode substrate, and graphene (G, Suzhou

Hengqiu Co., Ltd, Suzhou, China) as a modifier, were used in the preparation of an electrically conductive membrane.

2.2. Membrane air-cathode preparation

The PVC binder and PVP pore-forming agent (PVC-co-PVP; 12 wt% PVC and 6 wt% PVP) were dissolved in DMAc at ambient temperature in the dark, and mixed using a stir bar for over 24 h to allow them to completely dissolve. The polymer was then placed in the dark for an additional 24 h to allow removal of gas bubbles. PVC-co-PVP (0.81 g), activated carbon (0.58 g), and PANI (0.15 g) were mixed with NMP (3 mL). Graphene (G, Suzhou Hengqiu Co., Ltd, Suzhou, China) was then added into the carbon powder at four different mass ratios (G:AC) of 0 (denoted as control), 0.02 (G2), 0.05 (G5) and 0.10 (G10). After sonicating of the mixture for 30 min at ambient temperature, the homogenized solution was coated onto both two sides of a stainless steel mesh, and then immersed into a coagulation bath (deionized water at ambient temperature) for 20 min to complete coagulation.

2.3. Structure and membrane properties

The morphologies of the membrane air-cathode were observed using a scanning electron microscope (SEM, Hitachi Ltd. S-4700) [27]. Atomic force microscopy (AFM, Veeco Instruments Inc, USA) was used to characterize the roughness of the membrane air-cathode, with the images analyzed using the Nanoscope III software [28]. Contact angles were measured using a sessile drop technique and a surface contact angle measurement instrument (the type JYSP-360, USA, needlepoint 1.5 mm) [29]. The contact angle was tested after water droplets stabilized for 20 s. The surface energies (γ_{SV}, mN m^{-1}) were calculated as: $\gamma_{SV} = \gamma_{SV}^P + \gamma_{SV}^D$ and $\gamma_{LV}(1 + cos\theta) = 2\sqrt{\gamma_{SV}^D \gamma_{LV}^D} + 2\sqrt{\gamma_{SV}^P \gamma_{LV}^P}$ using the experimentally determined intrinsic contact angles of water (γ_{LV} = 72.8 mN m^{-1}, γ_{LV}^D = 21.8 mN m^{-1}, γ_{LV}^P = 51.0 mN m^{-1}) and methylene iodide (γ_{LV} = 58.2 mN m^{-1}, γ_{LV}^D = 39.5 mN m^{-1}, γ_{LV}^P = 18.7 mN m^{-1}) [30]. The membrane conductivities were tested using a digital four – probe tester (ST2263, Suzhou Jingge Electronic Co., Ltd, China). Porosity was measured by a gravimetric method as $\varepsilon = (W_w-W_d)/AH\rho_w$, where W_w is the wet weight (g), W_d is the dry weight (g), L is the membrane thickness (cm), A is the exposed membrane area (cm^2), and ρ_w is the density of water (g cm^{-3}) [31]. The cathode wet weight, W_w, was measured after wiping excessive water on the cathode surfaces with filter paper. The dry weight, W_d, was measured after drying the cathodes in oven at 50 °C for 48 h. The pure water flux ($L_P = V/\Delta PAt$) (L_P, L m^{-2} s^{-1} MPa^{-1}) was calculated as previously described, where V (L) is the volume, ΔP (MPa) is the pressure, and t (s) is the time [32]. The flux attenuation (J_w, %) was characterized the antifouling performance of the membrane cathode, which was calculated by $J_w = (J_0–J_t)/J_0 \times 100\%$, where J_0 (L m^{-2} s^{-1} MPa^{-1}) is the initial flux, and J_t (L m^{-2} s^{-1} MPa^{-1}) is the stable operating flux [33].

2.4. Electrochemical characterization

All electrochemical measurements of the membrane air-cathode were performed with an electrochemical workstation (Auto Lab PGSTAT128 N, Metrohm, Swiss) in a single cell with a three-electrode system, consisting of a membrane air-cathode as the working electrode, a saturated calomel electrode as the reference electrode (+242 mV vs. SHE, Spsic-Rex Instrument Factory, China), and a Pt sheet (1 cm^2) as the counter electrode. The electrolyte for all tests was a 50 mmol L^{-1} phosphate buffer solution (conductivity of 6.9 mS cm^{-1}) at ambient temperature (25 °C). Linear sweep voltammetry (LSV) was conducted over a potential range of −0.3 V to 0.3 V, at a scan rate 1 mV s^{-1} [34]. Electrochemical impedance spectroscopy (EIS) tests were performed at a frequency range of 10 mHz–100 kHz with amplitude of 5 mV [35].