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A novel carbon black graphite hybrid air-cathode for efficient hydrogen peroxide production in bioelectrochemical systems

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HIGHLIGHTS

- A hybrid air-cathode with the optimal carbon black/graphite ratio of 1:5 is made.
- The maximum H_2O_2 yield is 11.9 mg L^{-1} h^{-1} cm^{-2}.
- Continuous flow without H_2O_2 accumulation increases current efficiency.
- Oxygen for H_2O_2 synthesis is mainly contributed by air diffusion (66–94%).
- The use of bioanode increases H_2O_2 yield and current efficiency.

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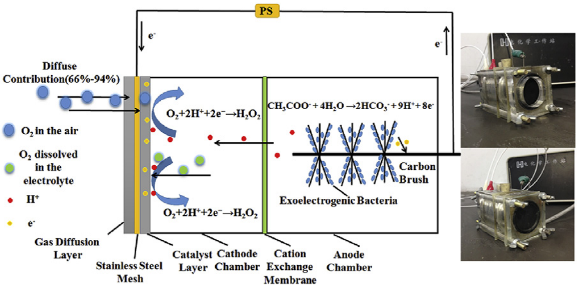
GRAPHICAL ABSTRACT



ABSTRACT

Carbon black and graphite hybrid air-cathode is proved to be effective for H_2O_2 production in bioelectrochemical systems. The optimal mass ratio of carbon black to graphite is 1:5 with the highest H_2O_2 yield of 11.9 mg L^{-1} h^{-1} cm^{-2} (12.3 mA cm^{-2}). Continuous flow is found to improve the current efficiency due to the avoidance of H_2O_2 accumulation. In the biological system, the highest H_2O_2 yield reaches 3.29 mg $L^{-1}h^{-1}$ (0.079 kg $m^{-3}day^{-1}$) with a current efficiency of 72%, which is higher than the abiotic system at the same current density. H_2O_2 produced in this system is mainly from the oxygen diffused through this air-cathode (>66%), especially when a more negative cathode potential is applied (94% at −1.0 V). This hybrid air-cathode has advantages of high H_2O_2 yield, high current density and no need of aeration, which make the synthesis of H_2O_2 more efficient and economical.

1. Introduction

Hydrogen peroxide (H_2O_2) has been widely known as an environmentally friendly chemical which leaves no hazardous residues, since it decomposes only to water and oxygen. As a powerful and versatile chemical, H_2O_2 is effective throughout the pH range from 0 to 14 with high oxidation potential ($E^0 = 1.763$ V at pH = 0 and $E^0 = 0.878$ V at pH = 14) [1]. Hence, H_2O_2 is applied to numerous industrial areas such as chemical synthesis, pulp paper and textile bleaching, medical disinfection, treatment of wastewater and destruction of hazardous organic wastes [2–5]. In general, H_2O_2 is commercially produced on an industrial scale by anthraquinone

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oxidation, which needs multi-step procedure and significant energy input. Considering the transport, handling and storage of H_2O_2 are potentially hazardous, anthraquinone oxidation method is thought to be inefficient and insecure [6,7]. In recent decades, a lot of researches have demonstrated that H_2O_2 can be in situ generated by reduction of oxygen in alkaline [Eq. (1)], neutral or acidic solution [Eq. (2)] in an electrochemical system [8].

$$O_2+H_2O+2e^- \rightarrow HO_2^- + OH^- \tag{1}$$

$$O_2+2H^+ +2e^- \rightarrow H_2O_2 \tag{2}$$

Bioelectrochemical systems (BESs), also known as microbial electrochemical systems or MXCs, demonstrated the possibility of H_2O_2 production using renewable energy from wastewaters in recent years [9]. BES reactor consists of an anode, a cathode and a separator. Electrochemically active bacteria on the anode directly oxidize soluble organic waste to generate electron for the cathode. On the cathode, electrons can be used for four-electron oxygen reduction reaction (ORR) to water or through a two-electron pathway to produce H_2O_2 [10–12].

Due to the advantages of high conductivity, low price, good stability and low catalytic activity of H_2O_2 decomposition, carbon-based cathodes such as carbon clothes [10], graphite granules [11], spectrographically pure graphite (SPG) rods [12] and modified graphite [13] were usually used in the H_2O_2 electrosynthesis process in BESs. Most of these cathodes, such as our three-dimensional electrodes [11], were immersed in the electrolyte to provide the reaction zone for proton/electron and O_2 that diffuses along with the electrolyte to synthesize H_2O_2. This kind of cathode has more potential use in refractory pollutant removal and can be easily scaled-up. However, the low solubility of O_2 in the electrolyte is a key limitation where external power is also needed for cathodic aeration in these systems.

Air-cathode is an advanced design where oxygen is passively supplied without aeration. It is usually composed of a catalyst layer (CL) facing to the electrolyte and a gas diffusion layer (GDL) facing to the air [14]. It had been demonstrated that H_2O_2 can be efficiently generated using air-cathodes [10] with a production rate 2 kg $m^{-3}day^{-1}$. However, in previous reports, most air-cathodes that utilized for H_2O_2 production didn't have a GDL [11,15], which may have a problem of electrolyte leakage and catalyst flooding when the system is scaled up. Apart from oxygen diffusion, the oxygen dissolved in electrolyte should be a considerable amendment for cathodic H_2O_2 produce [15,16]. However, to the best of our knowledge, the contribution of dissolved oxygen to H_2O_2 in air-cathode BES has not been investigated yet. In the present work, BESs equipped with novel carbon black and graphite hybrid air-cathodes made by rolling-press method were utilized to produce H_2O_2. The performances of cathodes with different carbon black/graphite mass ratio were analyzed. The contributions of dissolved and diffused oxygen on H_2O_2 production were also evaluated.

2. Experimental

2.1. Carbon black and graphite (CB&G) hybrid air-cathode

The CB&G air-cathode consisted of a CL and a GDL with the stainless steel mesh as the current collector and matrix. CL was prepared according to the following procedures. Carbon black (CB, 30 nm, Vulcan XC-72R, Cabot Corporation, US) and graphite (40 μm, HTF0325, >99.9%, Huatai Chemical Reagent Co. Ltd., Qingdao, China) were cleaned by ultrasonic in deionized water for 20 min at room temperature. After drying, a mixture of 6 g CB and graphite powders at different mass ratios (4.8 g CB and 1.2 g graphite as CB&G4:1; 4 g CB and 2 g graphite as CB&G2:1; 3 g CB and 3 g graphite as CB&G1:1; 1.5 g CB and 4.5 g graphite as CB&G1:3; 1 g CB and 5 g graphite as CB&G1:5 and 0.75 g CB and 5.25 g graphite as CB&G1:7) was individually dispersed into 45 mL ethanol in a beaker in an ultrasonic bath at room temperature for 10 min. Polytetrafluoroethylene (PTFE) emulsion (60%, Horizon, Shanghai, China) as binder was slowly added to the mixture to fabricate the catalyst layer as previously described [17]. The mixture was then stirred at about 80 °C to get a dough-like paste. The paste was firstly rolled to a 0.5 mm CL film and then roll-pressed on one side of the stainless steel mesh (4 cm × 4 cm, Type 304N, 60 meshes, Detiannuo Commercial Trade Co. Ltd., Tianjin, China) to be a flat sheet (0.5 mm in thickness). CLs made of pure CB and graphite were also fabricated and marked as PCB and PG. The GDLs of each cathode were made in parallel by rolling a mixture of carbon black and PTFE emulsion with a mass ratio of 4:9 according to the procedure described previously [18]. After heating at 340 °C for 25 min, GDLs were rolled onto the opposite side of different CLs to form a final air-cathode with a total thickness of 1 mm [18].

2.2. Material characterization

The specific surface area and pore parameters of carbon black and graphite powders were determined by the multipoint Brunauer–Emmett–Teller (BET) measurement at 77 K using Autosorb-1 (Quantachrome, USA). Porous properties and the pore size distribution were analyzed based on the BJH model. The porous structure of the CLs were characterized based on capillary law with a mercury porosimeter (Autopore IV, Micromeritics) which can analyze porous media with a pore size ranging from 6 nm to 300 μm. Samples were firstly dried in an oven at 105 °C for 3 h in a stream of nitrogen, and then intruded volume analysis was carried out over the pressure ranging from 5 kPa to 414 MPa. After each change in pressure, the system equilibrated for 15 s to minimize overlap of the intra- (0.002–1 μm pore radius) and inter- (1–100 μm pore radius) porosity regions as determined by the porosimeter. Images of the surface morphology of CLs were taken with a scanning electron microscope (SEM, Nanosem 430, USA).

2.3. BES configuration and operation

The experiments were performed on dual-chamber reactors shown in Fig. 1 equipped with different CB&G air-cathodes. The anode chamber was 3 cm in diameter and 4 cm in length (net volume of 28 mL) while the cathode chamber was 3 cm in diameter and 2 cm in length (net volume of 14 mL) [19]. Both chambers were assembled tightly on two sides of a cation exchange membrane (Ultrex CMI-7000, Membranes International Inc., Glen Rock, NJ, USA) by four clamping bolts. Anodes were made of carbon fiber brushes (3 cm in diameter and 2 cm in length). Different CB&G air-cathodes were assembled to the other side of cathode chambers.

Two 4 mm diameter holes were drilled on the top and at the bottom of the cathode chamber connecting to the effluent beaker and the influent aeration tank as showed in Fig. 1. N_2 gas or air was continuously aerated into the aeration tank to obtain an oxygen free or oxygen saturated influent. Peristaltic pump (BT100L, 8 channels, Longer Precision Pump Co. Ltd, Baoding, China) was used to feed the cathode with electrolyte from aeration tank at the rate of 10 mL min^{-1}.

All anode chambers of BESs were inoculated with the effluent from MFCs and pre-acclimated under 1 kΩ of external resistance with activated carbon air-cathode for 2 months before coupling with cathode chambers [19]. The medium contained acetate (1.0 g L^{-1}), a phosphate buffer solution (50 mM PBS; NH_4Cl 0.31 g L^{-1}, KCl 0.13 g L^{-1}, NaH_2PO_4 $2H_2O$ 2.772 g L^{-1},Na_2HPO_4