Bioresource Technology 138 (2013) 353–358

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Lack of anodic capacitance causes power overshoot in microbial fuel cells

Xinhong Peng, Han Yu, Hongbing Yu **, Xin Wang *

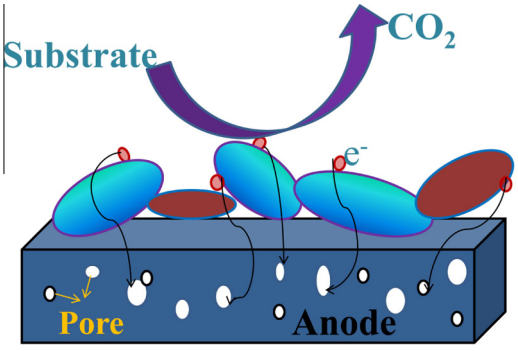
MOE Key Laboratory of Pollution Processes and Environmental Criteria, College of Environmental Science and Engineering, Nankai University, No. 94 Weijin Road, Nankai District, Tianjin 300071, China

Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Research Center for Cleaner Production, College of Environmental Science and Engineering, Nankai University, No. 94 Weijin Road, Nankai District, Tianjin 300071, China

HIGHLIGHTS

- Power overshoot can be eliminated by sufficient anodic abiotic capacitance.
- Abiotic capacitance of the anode is from micropores and mesopores.
- Bacterial capacitance is an effective compensation to eliminate power overshoot.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 February 2013
Received in revised form 26 March 2013
Accepted 28 March 2013
Available online 6 April 2013

Keywords:
Microbial fuel cell
Power overshoot
Capacitance
Exoelectrogenic biofilm

ABSTRACT

Power overshoot commonly makes the performance evaluation of microbial fuel cells (MFCs) inaccurate. Here, three types of carbon with different capacitance (ultracapacitor activated carbon (UAC), plain activated carbon (PAC) and carbon black (CB)) rolled on stainless steel mesh (SSM) as anodes to investigate the relationship between overshoot and anodic capacitance. It was not observed in all cycles of UAC-MFCs (from Cycle 2 to 4) due to the largest abiotic capacitance ($C_m^{abiotic}$) of 2.1 F/cm^2, while this phenomenon was eliminated in PAC-MFCs ($C_m^{abiotic}$ = 1.6 F/cm^2) from Cycle 3 and in CB-MFCs ($C_m^{abiotic}$ = 0.5 F/cm^2) from Cycle 4, indicated that the $C_m^{abiotic}$ of the anode stored charges and functioned as electron shuttle to overcome the power overshoot. With bacterial colonization, the transient charge storage in biofilm resulted in a 0.1–0.4 F/cm^2 increase in total capacitance for anodes, which was the possible reason for the elimination of power overshoot in PAC/CB-MFCs after multi cycle acclimation.

1. Introduction

Microbial fuel cell (MFC) is one of emerging energy technologies that exploits exoelectrogenic bacteria to harvest energy from organic or inorganic matters (Ren et al., 2011; Zhang et al., 2011). In an MFC, current is provided by utilizing the bacteria as the biocatalysts to oxidize biomass. As a promising technology of *in situ* biological oxygen demand (BOD) sensor (Kim et al., 2003) or toxicity biosensors (Wang et al., 2013), and better desalination results under higher current density in microbial desalination cell (MDC) (Kim and Logan, 2013), the precise evaluation of MFC performance (such as current and power density) is vital to ensure a reliable

* Corresponding author at: MOE Key Laboratory of Pollution Processes and Environmental Criteria, College of Environmental Science and Engineering, Nankai University, No. 94 Weijin Road, Nankai District, Tianjin 300071, China. Tel.: +86 22 87030650; fax: +86 22 23501117.

** Co-corresponding author at: MOE Key Laboratory of Pollution Processes and Environmental Criteria, College of Environmental Science and Engineering, Nankai University, No. 94 Weijin Road, Nankai District, Tianjin 300071, China. Tel./fax: +86 22 23502756.

E-mail addresses: hongbingyu1130@sina.com (H. Yu), xinwang1@nankai.edu.cn (X. Wang).

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http://dx.doi.org/10.1016/j.biortech.2013.03.187

result. The performance of MFC is usually estimated by polarization curve (Pinto et al., 2011) or linear sweep voltammetry (LSV) (Jacobson et al., 2011). However, the phenomenon named 'power overshoot' including Type M and Type D, which is commonly observed associated with a sharp decay of anode performance instead of higher current density, makes the evaluation of performance inaccurate (Hong et al., 2011; Mahdi Mardanpour et al., 2012; Watson and Logan, 2011; Winfield et al., 2011).

Type M is attributed to an over fast scan rate of LSV or a lacking of stabilization time at a fixed resistance (Hong et al., 2011). However, up to date, there are a few of studies explaining the possible reasons of Type D overshoot. Mass transport limitations (Aelterman et al., 2006) has been proved not the reason since overshoot is not prevented by stirring in the anode chamber (Nien et al., 2011; Winfield et al., 2011). Electrical and ionic depletion on the anode under low external resistances (Ieropoulos et al., 2010) is unlikely to be a key factor because the overshoot can be avoid without any change in solution composition. Thus, much more attentions have been focused on the anodic biofilm. Insufficient acclimation time for microbes to adapt to a new resistance (Hong et al., 2011), the population of the anode community (Winfield et al., 2011), bacterial substrate utilization (Nien et al., 2011) and the maturity of the biofilm are reported as influence factors. However, the overshoot cannot be eliminated by long-term enrichment until 100 days (Watson and Logan, 2011), indicating that this phenomenon is due to but not limited to the bacterial factors listed above. Although power overshoot is widely encountered in MFCs, the mechanism still needs more interpretations and investigations.

As reported previously, the anodic biofilm of MFCs is electrochemically a capacitor because the oxidative metabolism of the substrate temporarily stores electrons in the reductive extracytoplasmic cytochromes and/or self-produced mediators of exoelectrogenic bacteria when the circuit is disconnected (Peng et al., 2012; Schrott et al., 2011). As soon as the polarization applies again, extracellular cytochromes and mediators discharge to the electrode to produce current. The hypothesis addressed in present study is that the power output at high current can be stabilized by the capacitance of the anode. Thus, three types of carbon with different capacitances including ultracapacitor activated carbon (UAC, SPC-01, Xinsen Carbon Co. Ltd., Fujian, China), plain activated carbon (PAC, Jiangtian Chemical Technology Co. Ltd., Tianjin, China) and carbon black (CB, BP-2000, Horizon LID, Shanghai, China) had been rolled on stainless steel mesh (SSM, Anping County Shengze Screen Co., Ltd., Hebei, China) here as different anodes. Anodic capacitances, resulted from both the temporary charge storage of the biofilm and the electrode material, were compared before and after inoculation to interpret power overshoot in MFCs.

2. Methods

2.1. Fabrication of anodes

SSM (type 304L, 80 × 80 mesh, thickness of 0.2 mm) was utilized as both matrix and current collector. Prior to use, the SSM was ultrasonically degreased in acetone and ethanol successively each for 10 min, followed by rinsing with distilled water. Each kind of carbon was dispersed in ethanol, followed by dripping 33 μL polytetrafluoroethylene (PTFE; 60 wt.%; Horizon LID, Shanghai, China) emulsion per gram carbon to the mixture (carbon mass percentage is 95%) and stirring at 80 °C water bath until a resembled ointment in appearance was obtained (Peng et al., 2013). The mixture was roll-pressed into a flexible film (0.2 mm in thickness). The film was further bonded on the SSM as an anode. Anodes were cut into circles with the diameter of 4 cm and dried at 70 °C for evaporation of ethanol before using.

2.2. MFC construction and operation

Single chambered membrane-less MFCs (4 cm long by 3 cm diameter; net volume of 28 mL; electrode spacing of 4 cm) were operated in batch mode as previously described (Wang et al., 2009). Electrode made of UAC, PAC and CB, respectively, was used as the anode with target project area of 7 cm^2. Air-cathodes were made of carbon mesh (10 wt.% wet proof, Jilin Carbon Plant Co. Ltd., China) with four PTFE diffusion layers and 0.5 mg/cm^2 platinum loaded as catalyst according to Wang et al. (2012). The electrodes were connected to the external resistance (1 kΩ except as stated otherwise) with titanium wire.

MFCs were inoculated using effluent from MFCs operated under similar conditions. The medium was prepared according to our previous report (Peng et al., 2012) with sodium acetate (1 g/L) as an electron donor in 50 mM phosphate buffer solution (PBS). When cell voltages were ⩾500 mV, polarization curves were performed in consequent three cycles (Cycle 2 to Cycle 4) to catch power overshoots. All the measurements were carried out in a 30 ± 0.5 °C temperature-controlled biochemical incubator in duplicate.

2.3. Analysis and calculation

Polarization and power density curves, calculated based on the project area of the anode, were obtained by varying external resistances (1000, 600, 300, 200, 150, 100, 50 and 10 Ω, expected as noted) with a time interval of 30 min. Anode and cathode potentials were simultaneously recorded with Ag/AgCl as the reference electrode (+197 mV, 3.5 M KCl, vs. SHE).

Cyclic voltammetry (CV) was conducted using a potentiostat (CHI660D, CH Instruments Inc., China) over a potential range of −0.8 to 0 V (vs. Ag/AgCl) at a scan rate of 0.1 mV/s in a single chambered MFC, with the anode as the working electrode, the air-cathode as the counter electrode and an Ag/AgCl close to the anode as the reference electrode. Abiotic anodes were soaked in 50 mM PBS for 48 h before CV tests, while CVs of biotic anodes were performed when acetate was depleted with the cell voltage <20 mV. Biotic CV was performed at the end of each cycle.

The specific capacitance C_m (F/cm^2), described as the integration over the entire set of data per unit area of the anode, is calculated from the CV according to the equation as follow (Jeon et al., 2010; Song et al., 2007):

$$C_m = (Q_a + Q_c)/(2A\Delta E) \quad (1)$$

where Q_a (C) and Q_c (C) are the sums of anodic and cathodic voltammetric charges, A (7 cm^2) is the surface area of anode and ΔE (V) is the range of potential drop during CV.

Porous characteristics of these three carbons were analyzed via nitrogen sorption analysis at 77 K using a conventional volumetric technique by a TriStar 3000 (Micromeritics, ASAP2020, USA). Before measurements, 0.1 g carbon was heated to remove all the adsorbed species. The specific surface area (S_{BET}) and total pore volume were calculated using Brunauer–Emmett–Teller (BET) theory for N_2 adsorption data in the relative pressure (P/P_o) from 0 to 0.99. Pore size distribution was estimated by the Barret–Joyner–Halenda (BJH) method, while *t*-plot method was employed to extract the microporous surface area (S_{micro}) (Pognon et al., 2011). The morphological images were recorded using a Shimadzu SS-550 scanning electron microscope (SEM) at 15.0 kV.

3. Results and discussion

3.1. Power overshoot in polarization tests

Cell voltages up to 500 mV were observed 4 cycles after inoculation. And the cycle where voltages were ⩾500 mV was marked