Journal of Power Sources 372 (2017) 38–45

Contents lists available at ScienceDirect

Journal of Power Sources

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

Using sewage sludge pyrolytic gas to modify titanium alloy to obtain high-performance anodes in bio-electrochemical systems

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HIGHLIGHTS

- Sludge pyrolysis gas modification used to improve titanium alloy hydrophilicity.
- Modified titanium electrodes accelerated biofilm formation.
- Modified electrode current density was 316-fold higher than that of bare electrode.
- New method proposed to dispose of sewage sludge.

ARTICLE INFO

Keywords:
Bio-electrochemical system
Surface modification
Titanium alloy
Pyrolytic gas
Current generation

ABSTRACT

Titanium is under consideration as a potential stable bio-anode because of its high conductivity, suitable mechanical properties, and electrochemical inertness in the operating potential window of bio-electrochemical systems; however, its application is limited by its poor electron-transfer capacity with electroactive bacteria and weak ability to form biofilms on its hydrophobic surface. This study reports an effective and low-cost way to convert a hydrophobic titanium alloy surface into a hydrophilic surface that can be used as a bio-electrode with higher electron-transfer rates. Pyrolytic gas of sewage sludge is used to modify the titanium alloy. The current generation, anodic biofilm formation surface, and hydrophobicity are systematically investigated by comparing bare electrodes with three modified electrodes. Maximum current density (15.80 A/m^2), achieved using a modified electrode, is 316-fold higher than that of the bare titanium alloy electrode (0.05 A/m^2) and that achieved by titanium alloy electrodes modified by other methods (12.70 A/m^2). The pyrolytic gas-modified titanium alloy electrode can be used as a high-performance and scalable bio-anode for bio-electrochemical systems because of its high electron-transfer rates, hydrophilic nature, and ability to achieve high current density.

1. Introduction

Bio-electrochemical systems (BES) are promising technology that uses electrochemically active microorganisms (EAM) as catalysts to convert organic waste into electrical energy [1,2]. At present, however, the technology is constrained by low power-generating ability [3]. Bio-electrodes are the core engine of BES, not only being the carrier for the EAMs, but also acting as the electron acceptor or donor. It is thus important to create bio-electrodes with high current density.

Carbon-based electrodes (carbon cloth, carbon felt, carbon brush and graphite plates) were seen as the most versatile electrode materials for use in BES, but their low conductivity severely hindered their practical application on a larger scale [4]. Although many metallic materials can effectively solve the above-mentioned problems and give satisfactory power generation [5], the low corrosion resistance of copper and stainless steel and the high prices of gold, platinum, and silver do not allow their commercialization. Fortunately, titanium (Ti) may be preferred for use as a stable anode in BES, mainly because of its high conductivity, suitable mechanical properties, and electrochemical inertness in the operating potential window of BES [6,7]. Despite these positive properties, Ti also possesses a major disadvantage: it exhibits poor power generation in BES, which primarily results from its weak

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http://dx.doi.org/10.1016/j.jpowsour.2017.10.073
Received 30 April 2017; Received in revised form 24 September 2017; Accepted 22 October 2017
Available online 05 November 2017
0378-7753/

ability to form biofilms on its surface [5]. Surface modification of Ti with biocompatible materials could be an effective way to convert it into a high-performance bio-electrode for BES. Feng [8] reported that in situ growth of titanium dioxide nanotubes on the surface of Ti was conducive to anodic biofilm formation; however, this method required large amounts of NaF and ethylene glycol as etching agents. An effective, simple and low-cost modification method for Ti electrodes is therefore still required.

Wastewater treatment plants are associated with the production of sewage sludge (SS), the treatment and disposal of which is a complex environmental problem. Annual production of SS exceeds 25 million tons in China [9]; hence, it is available almost free of charge to be used in other forms for various applications. Methods of SS disposal generally include landfills, composting, and incineration [10], all of which may result in waste of land area and heavy metal pollution. In contrast to these processes, pyrolysis presents a potentially economic prospect because it can convert SS into biochar. Yuan et al. [11] used *S*S-derived biochar as an electrode material that had good biocompatibility; however, its performance was unsatisfactory due to poor electrical conductivity and weak mechanical strength. Sludge pyrolysis gas is a product of the pyrolysis process and has potential biocompatibility because it is enriched in carbon disulfide, acetic acid, pentane, benzene, toluene, and ethylene, among other components [12,13]. The objective of this study was therefore to investigate whether modification of a Ti electrode with sludge pyrolysis gas could provide a hydrophilic and larger specific surface area for EAM biofilm formation and further enhance the current generation of BES.

2. Material and methods

2.1. Electrode preparation and modification

The Ti alloy plates (Oudifu, Guangzhou, China; thickness of 0.5 mm; Content:Ti ~ 25%, C: ~ 30%, O: ~ 45%) were cut into 1.0 cm × 2.0 cm pieces. Before being modified, the plates were sequentially cleaned in acetone, ethanol, and deionized (DI) water by ultrasonication for 15 min. SS with a moisture content of approximately 98% was collected from Tianchuang Sewage Treatment Plant, Hangzhou, China. It was filtered and screened using a 40-mesh sieve to remove large particles, dried at 50 °C, then further broken down by a grinder (ZM200, Retsch Co. Ltd. Germany). A 1:1 mass ratio of Ti alloy plates and SS were heat-treated together in a tube furnace by increasing the temperature at a rate of 15 °C/min under N_2 atmosphere (100 ml/min) to 700 °C, 900 °C, or 1100 °C. The as-prepared Ti alloy electrodes were defined as Ti-700, Ti-900, and Ti-1100, respectively. In addition, a control group heated under the same conditions without SS was set up. These electrodes were respectively defined as Ti-700CK, Ti-900CK, and Ti-1100CK. The untreated electrode was defined as Ti-CK.

2.2. Construction and operation of bio-electrochemical systems

The BES reactors consisted of an anode and cathode chamber, each with working volume of 45 mL. The chambers were separated by a Nafion 117 proton-exchange membrane (DuPont, USA), which was immersed in 5% NaCl solution for 24 h prior to use. The cathodes were made of graphite plate and had an effective area of 8 cm^2. A Geobacter-dominated mixed culture was pre-enriched in our laboratory [14] and added as the anodic inoculum. The anode chambers were loaded with substrate containing 1 g/L sodium acetate in M9 solution (NH_4Cl, 0.1 g/L; NaCl, 0.5 g/L; KH_2PO_4, 4.4 g/L; K_2HPO_4, 3.4 g/L; $MgSO_4$, 0.1 g/L; $NaHCO_3$, 2 g/L; $FeSO_4{\cdot}7H_2O$, 1.0 mg/L; $CuSO_4{\cdot}5H_2O$, 0.02 mg/L; H_3BO_3, 0.014 mg/L; $MnSO_4{\cdot}4H_2O$, 0.10 mg/L; $ZnSO_4{\cdot}7H_2O$, 0.10 mg/L; $Na_2MoO_4{\cdot}2H_2O$, 0.02 mg/L; $CoCl_2{\cdot}6H_2O$, 0.02 mg/L) in sequencing batch mode and cathode chambers loaded with exactly M9 solution in sequencing batch mode. All BES reactors were placed in an incubator (DHP303-4A, Jingmai, China) and the temperature maintained at 30 ± 1 °C. The data were recorded using an electrochemical workstation (Biologic VSP, Claix, France) at an anode potential of −0.2 V (vs. Ag/AgCl).

2.3. Characterization of electrode surface and pyrolytic gases

The morphologies of the different electrodes were observed using scanning electron microscopy (SEM; JEOL, JSM-6330F, Japan). X-ray photoelectron spectra (XPS) were recorded using an XSAM800 instrument (Kratos, Britain) equipped with a Mg *K*α achromatic X-ray source (1235.6 eV) and analyzed using *XPSPEAK41* software. Samples taken from the organic layers on the electrodes were measured by Fourier Transform infrared spectroscopy (FTIR; Bruker, VERTEX 70, Germany). To confirm the hydrophobicity, water-absorption experiments were conducted in test tubes using Milli-Q water. The pyrolytic gases were sampled in gas-collecting tubes (2.5 L) that had been purged in triplicate with high-purity nitrogen. Sample gases were analyzed by gas chromatography–mass spectrometry (GCMS; JEOL, JMS-700D, Japan).

It was previously reported that an increase in capacitance is consistent with an increase of the surface area [8,15], so the measurement of electrochemical impedance spectra (EIS) was carried out at the open-circuit potential in the frequency range from 100 kHz to 0.05 Hz and using an amplitude of 10 mV. The Nyquist plots were fitted using a suitable equivalent electrical circuit (by fitting of the equation ($R1 + R2/C2 + R3/Q3$, where $R1$ is the internal resistance, $R2$ is charge-transfer resistance, $R3$ is diffusion resistance, and $C2$ is the surface capacitance).

2.4. Electrochemical and biofilm measurements

The surface electrochemical properties were characterized by cyclic voltammetry (CV), which was performed using a three-electrode electrochemical workstation. The three-electrode setup was carried out with the anode as the working electrode, the cathode (graphite plate, effective area of 8 cm^2) as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The potential window was −0.7 V to 0.2 V (vs. Ag/AgCl) and the scan rate was 1 mV/s. The output power and corrosion potential of the different electrodes were measured by linear-sweep voltammetry (LSV) using the same workstation.

The biofilm samples were subjected to the LIVE/DEAD BacLight bacterial viability test (LIVE/DEAD® BacLight™ Bacterial Viability Kit, Molecular Probes, America) as per the manufacturer's instructions. Labeled cells were visualized and *z*-stacks were captured using a confocal laser scanning microscope (CLSM; LSM 780, Zeiss, Germany). The three-dimensional biofilm images were processed using *ZEN 2010* software. Duplicate biofilm samples were subjected to cell disruption and were then used to measure their protein concentration using the Coomassie brilliant blue method [16]. Biofilm formation ability was measured using a crystal violet staining method. After 24 h of biofilm formation, the non-adherent cells were removed by washing the electrodes with 1 ml of PBS (0.1 M, pH 7). For fixation of the biofilms, 1 ml of 99% methanol (Hannuo, China) was added to each electrode, after 15 min the methanol was removed and the electrodes were allowed to dry at room temperature. Then, 1 ml of crystal violet stain (1%, v/v) (Qiangshun, China) were added to all electrodes. After 5 min, the excess of crystal violet stain was removed and the electrodes were gently washed in water. Finally, 1 ml of ethyl alcohol (33%, v/v) (Hannuo, China) were added to all electrodes to dissolve the crystal violet stain and the absorbance was standardized according to the area of electrodes areas (Abs/cm^2:for each sample, the optical densities were obtained in 1 ml of ethyl alcohol dissolving crystal violet stain). The assays were performed in triplicate and on three separate occasions.