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Long-term stability of bioelectricity generation coupled with tetrathionate disproportionation

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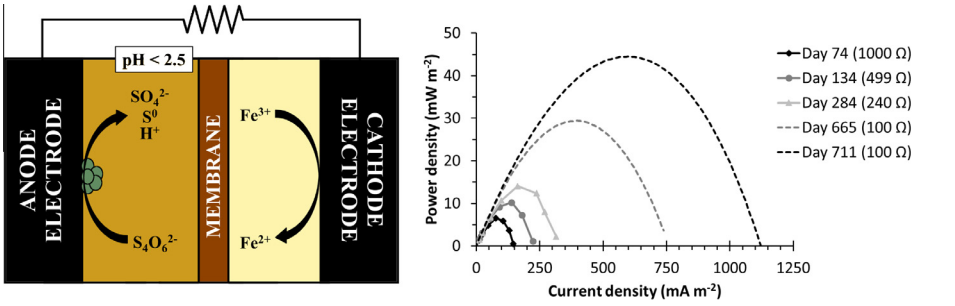
HIGHLIGHTS

- Long-term bioelectricity production was obtained with tetrathionate-fed MFCs.
- Current density was improved by optimizing the external resistance.
- No visible biofouling was observed even after over 700 days of operation.
- Current density and power density increased over time.

GRAPHICAL ABSTRACT



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ABSTRACT

To prevent uncontrolled acidification of the environment, reduced inorganic sulfur compounds (RISCs) can be bioelectrochemically removed from water streams. The long-term stability of bioelectricity production from tetrathionate ($S_4O_6^{2-}$) was studied in highly acidic conditions (pH < 2.5) in two-chamber fed-batch microbial fuel cells (MFCs). The maximum current density was improved from previously reported 80 mA m^{-2} to 225 mA m^{-2} by optimizing the external resistance. The observed reaction products of tetrathionate disproportionation were sulfate and elemental sulfur. In long-term run, stable electricity production was obtained for over 700 days with the average current density of 150 mA m^{-2}. The internal resistance of the MFC decreased over time and no biofouling was observed. This study shows that tetrathionate is an efficient substrate also for long-term bioelectricity production.

1. Introduction

Reduced inorganic sulfur compounds (RISCs) can be found from the mining waters of sulfide mineral processing facilities (Liljeqvist et al., 2011). The biocatalyzed degradation of such compounds is an acid-producing reaction. If it occurs uncontrolled in the environment, the increasing acidity will enhance the dissolution of metals leading to formation of highly acidic metal-rich waters (Johnson, 2008). While selected extremophilic species tolerate such conditions (Dopson et al., 2015), high acidity and metal concentrations are toxic to most organisms.

To prevent the uncontrolled acidification, RISC containing water streams require treatment before they can be released to the environment. Microbial fuel cells (MFCs) are bioelectrochemical systems in which microorganisms convert the chemical energy of biodegradable compounds to electrical energy (Butti et al., 2016; Logan et al., 2006). RISC removal can be obtained by simultaneously utilizing them as a substrate for bioelectricity production, as shown recently by Sulonen et al. (2015) and Ni et al. (2016).

The long-term operation of MFCs without significant maintenance is desirable in respect of reliable wastewater treatment, constant electricity production and cost-efficient operation. One major problem in long-term operated MFCs fed with organic substrates has been the formation of biofilm on the membrane separating the anode and cathode chambers or on the surface of

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the cathode electrode (Choi et al., 2011; Miskan et al., 2016; Xu et al., 2012). Membrane biofouling has been shown to limit the transfer of ions through the membrane, thus increasing the internal resistance of the system (Xu et al., 2012), whereas biofilm on the cathode electrode can decrease power production by blocking the cathodic electron transfer (Yang et al., 2009). Another factor observed to limit the efficiency of bioelectrochemical systems is formation of precipitates that limit ion transfer on the membrane or on the electrodes (Jeremiasse et al., 2010).

Operational conditions, such as pH, temperature as well as the anolyte and catholyte compositions, influence the extent of biofilm and precipitate formation. The long-term stability of electricity production has been previously studied in neutral conditions with several synthetic wastewater streams containing organic compounds (Ge et al., 2013; Moon et al., 2006; Yang et al., 2015), but not under acidic conditions and/or with inorganic sulfur compounds. Therefore, the objective of this study was to investigate the optimization and the long-term performance of acidophilic MFC fed with reduced inorganic sulfur compound, tetrathionate ($S_4O_6^{2-}$). First, the possibility to enhance the electricity production by gradually lowering the external resistance was studied in two parallel fed-batch MFCs. The long-term stability was then studied in similarly optimized tetrathionate-fed MFC, which was monitored for 744 days. The experiments were conducted at highly acidic conditions (pH < 2.5) typical to mining waste waters.

2. Materials and methods

2.1. Experiments

The biological electricity production from tetrathionate was enhanced by optimizing the external resistance of two parallel MFCs designated as A and B. In both MFCs, the external resistance was gradually lowered from 1000 Ω to 240 Ω. In MFC B, the cathode side was observed to be regenerative (biological oxidation of Fe^{2+} to Fe^{3+}) enabling relatively constant electricity production. Therefore, in this MFC the external resistance was further lowered to 100 Ω. The long-term stability of electricity production from tetrathionate was studied with an MFC (designated as LT), which was started up by lowering the external resistance as found optimal for current enhancement in MFCs A and B. The MFC LT was monitored up to total run time of 744 days.

2.2. Microbial fuel cell construction

The configuration of the two-chamber MFCs has been previously described by ter Heijne et al. (2008). The working volume of each chamber was 33 mL, and the anolyte and catholyte solutions were continuously recirculated (166–170 mL min^{-1}) over a recirculation bottle, the total volume of each solution being 625 mL. In the MFCs A and B, the anode and cathode chambers were separated with an anion exchange membrane (AMI-7001, Membrane International, USA), whereas in the MFC LT monovalent cation exchange membrane (CIMS Neosepta, Astom, Japan) was used. The anode and cathode electrodes were graphite plates (MR Graphite, Germany) covered with carbon paper (Graphite foil, Coidan graphite products, USA) and had an effective surface area of 22 cm^2. The anode and cathode potentials were measured against silver/silver chloride (Ag/AgCl) reference electrodes (Sentek, UK) connected to the anolyte/catholyte with a glass capillary (QiS, the Netherlands). The standard potential of these electrodes was estimated to be 205 mV vs. Normal Hydrogen Electrode (NHE). The fed-batch reactors were operated at room temperature (22 °C ± 2 °C), which is in the range of typical ambient temperatures for inorganic sulfur containing water streams.

2.3. Microbial culture and solutions

The anolyte contained 10% (v/v) mineral salts medium (MSM) and 1% (v/v) trace element solution (TES) in 20 mM K_2HPO_4 (Sulonen et al., 2015). Oxygen was removed from the anolyte and catholyte solutions by purging with nitrogen (15 min) before inoculation. MFCs A and B were inoculated with hydrometallurgical mining process water (En3) that had shown the best performance in a previous study (Sulonen et al., 2015), the total amount of inoculum being 10% (v/v) of the anolyte volume. In addition, the original process water sample was added twice (5% (v/v)) to MFC A (on days 26 and 59) and MFC B (on days 36 and 72) after removing equal amount of the anolyte to increase microbial cell densities at the anode. According to the microbial community analysis, the dominant microorganisms in the MFC-enrichment culture were *Acidithiobacillus* sp. and *Ferroplasma* sp. (Sulonen et al., 2015). The MFC LT was inoculated (10% v/v) with the anolyte of the MFC B (taken on day 139). Sodium bicarbonate ($NaHCO_3$, 1 M) was added to each MFC (1% (v/v)) after inoculation and every four weeks to provide a carbon source. The initial pH of the anolyte was 2–2.5 and initial tetrathionate concentration 2 g L^{-1}. The reactors were fed by adding 1.25 g of $S_4O_6^{2-}$ in 10 mL of media solution after the anolytic tetrathionate concentration decreased below 0.5 g L^{-1}. This increased the tetrathionate concentration after feeding to 2–2.5 g L^{-1}. To ensure that the cathodic reaction does not restrict the electricity production and to avoid pH gradient across the membrane, ferric iron as $FeCl_3$ (2 g L^{-1} Fe^{3+}) was used as the catholyte at pH 1.5. Ferric iron has a high reduction potential (E_0 = 0.565 V vs. Ag/AgCl) and it remains as ionic Fe^{3+} at pH below 1.8.

2.4. Electrochemical measurements

The cell voltage and the potentials of the anode and cathode electrodes against the reference electrodes were measured with Agilent 34970A Data Acquisition/Switch Unit (Agilent, Canada) every two minutes, and the data is presented as the average of five consecutive measurements. The power density and current density were calculated against the effective surface area of the anode electrode (22 cm^2). Polarization characteristics of the reactors were analyzed by measuring the voltage while decreasing the external resistance every 30 min gradually from 5000 Ω to 10 Ω or with linear sweep voltammetry (LSV) conducted with PalmSens 3 potentiostat/galvanostat (PalmSens BV, the Netherlands) with a scanning rate of 1 mV s^{-1}. All the potential values are reported against Ag/AgCl reference electrodes, if not otherwise stated.

2.5. Sampling and analyses

Samples were taken from the anolyte with the intervals of two to seven days. The anodic samples were filtered (0.2 μm) before the analysis of tetrathionate (modified cyanolysis), thiosulfate, sulfate (ion chromatography) and pH. Cathodic ferric iron reduction was monitored by measuring the ferrous (Fe^{2+}) iron concentration (1,10-phenantroline method) of the catholyte every seven days. The analyses were performed as previously described (Sulonen et al., 2015). The conductivities of the anolytic medium solutions with different sulfate concentrations were measured using inoLab Multi Level 1 meter (WTW, Germany).

2.6. Microbial community profiling

Microbial community samples were taken from the anolyte solution by separating the microorganisms from the solution by centrifugation (10000*g*, 10 min at 22 °C). The DNA was extracted and the microbial communities were analyzed by polymerase chain