



The effect of anode potential on bioelectrochemical and electrochemical tetrathionate degradation



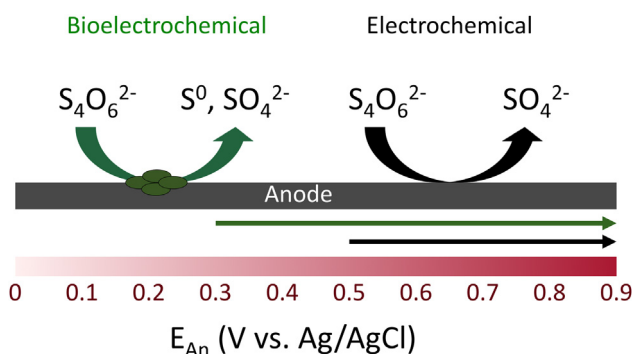
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HIGHLIGHTS

- Electrochemical $S_4O_6^{2-}$ degradation was studied with biological and abiotic anodes.
- Bioelectrochemical current production from $S_4O_6^{2-}$ started at 0.3 V vs. Ag/AgCl.
- Electrochemical current production from $S_4O_6^{2-}$ started at 0.5 V vs. Ag/AgCl.
- $S_4O_6^{2-}$ degradation rate was over three times higher in bioelectrochemical system.
- Reaction products from $S_4O_6^{2-}$ differed between biological and abiotic anodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of poised anode potential on electricity production and tetrathionate degradation was studied in two-chamber flow-through electrochemical (ES) and bioelectrochemical systems (BES). The minimum anode potential (vs. Ag/AgCl) for positive current generation was 0.3 V in BES and 0.5 V in the abiotic ES. The anode potential required to obtain average current density above 70 mA m^{-2} was 0.4 V in BES and above 0.7 V in ES. ES provided higher coulombic efficiency, but the average tetrathionate degradation rate remained significantly higher in BES (above $110 \text{ mg L}^{-1} \text{ d}^{-1}$) than in the abiotic ES (below $35 \text{ mg L}^{-1} \text{ d}^{-1}$). This study shows that at anode potentials below 0.7 V, the electrochemical tetrathionate degradation is only efficient with microbial catalyst and that significantly higher tetrathionate degradation rates can be obtained with bioelectrochemical systems than with electrochemical systems at the tested anode potentials.

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1. Introduction

Uncontrolled biological degradation of reduced inorganic sulfur compounds (RISCs) often found in mining and mineral processing process and waste waters contribute to formation of acidic metal-rich waters in the environment. Bioelectrochemical treatment enables the integration of controlled removal of RISCs to production of electrical energy. Bioelectricity production via

RISCs degradation in acidic conditions was first demonstrated by Sulonen et al. (2015). Recently, Ni et al. (2016) showed that also sulfide mineral flotation process water can be used as the substrate for bioelectricity production and Sulonen et al. (2016) reported stable electricity production from tetrathionate ($S_4O_6^{2-}$) for over 2 years with average current density of 150 mA m^{-2} .

In microbial fuel cells (MFCs), the cell voltage is a result of the potential difference of the anode and cathode electrodes. The minimum anode potential is determined by the reduction potential of the final electron donor, which can be, for example, a cytochrome on the microbial cell surface (direct electron transfer) or an

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electrochemically oxidizable mediator compound (mediated electron transfer). The energy gained for microbial growth is defined by the difference in the reduction potential of the electron donor and the potential of the anode electrode. Therefore, high anode potential leads to high microbial energy gain, but to low cell voltage. To optimize the electrical energy output, the potential of the anode electrode should remain close to the minimum value still supporting the growth and current generation of the electroactive microorganisms.

Besides electricity production, electrochemical systems can be used to run the desired oxidation and reduction reactions, for example for remediation or synthesis purposes (Li et al., 2015, 2016; Qin et al., 2012; Villano et al., 2011). By applying external voltage, thermodynamically unfavorable reactions can be realized, i.e. substrate with high reduction potential can be oxidized at the anode and/or electron acceptor at low reduction potential can be reduced at the cathode. Microbial catalyst on the anode side enables the utilization of biodegradable compounds as a partial source of energy, thus decreasing the total external energy need. Applied external voltage has been used, for example, to recover metals (Colantonio and Kim, 2016) and to synthesize commercially valuable organic compounds such as acetate (Batlle-Vilanova et al., 2016) and butyrate (Ganigué et al., 2015) at the cathode of bioelectrochemical systems.

Anode potential of bioelectrochemical systems can be externally controlled to selectively enrich for electroactive microorganisms (Finkelstein et al., 2006; Kokko et al., 2015) or to enhance the current generation efficiency (Sleutels et al., 2011; Wang et al., 2009), but reports on the optimal potential for enrichment contradict. Some studies report faster start-up and higher current, coulombic efficiency (CE) and chemical oxygen demand (COD) removal rate with more positive anode potentials (Ishii et al., 2008; Wang et al., 2009), while in other studies higher power densities and biofilm densities were obtained with lower anode potentials (Aelterman et al., 2006; Sun et al., 2012; Torres et al., 2009; Zhang et al., 2013). The optimum anode potential for enrichment of anodic cultures and electricity production depends on the used substrate, the composition of the used inoculum, operation conditions and the electrochemical cell configuration (Kumar et al., 2012; Wagner et al., 2010).

Tetrathionate has been shown to be bioelectrochemically degradable (Ni et al., 2016; Sulonen et al., 2015, 2016), but the effect of anode potential on current generation in tetrathionate-degrading bioelectrochemical systems has not been previously studied. In addition, no studies have addressed the abiotic electrochemical degradation of tetrathionate. The objective of this study was to examine the effect of anode potential on current generation in tetrathionate-fed bioelectrochemical and electrochemical systems under highly-acidic conditions (pH < 2.5) typical for mining environments. The adaptation of the acidophilic culture originating from multimetal mining process waters to lower anode potentials than previously reported with tetrathionate-fed MFCs was studied by poisoning the anode electrode. With the abiotic systems, the minimum anode potential required for electrochemical tetrathionate degradation was determined by gradually adjusting the anode potential. The current generation and tetrathionate degradation rates were also studied in electrochemical systems at selected constant anode potentials.

2. Materials and methods

2.1. Electrochemical cell configuration

The electrochemical system used for abiotic and biological experiments has been previously described (ter Heijne et al., 2008). The anode and cathode chambers (33 cm³ each) were sepa-

rated with an anion exchange membrane (AMI-7001, Membrane International, USA). The anolyte and catholyte solutions were recirculated (0.166 L min⁻¹) over a recirculation bottle, the total volume of each solution being 0.625 L. Graphite plates (MR Graphite, Germany) covered with carbon paper (Graphite foil, Coidan graphite products, USA) were used as the anode and cathode electrodes. The effective area of all electrodes was 22 cm². Anode and cathode potentials were measured against Ag/AgCl reference electrodes (Sentek, UK; estimated standard potential 0.205 V vs. Normal Hydrogen Electrode (NHE)) placed in 3 M KCl and connected to the anolyte or catholyte with a glass capillary (QiS, the Netherlands). The potential values reported are against Ag/AgCl-reference electrode, if not otherwise stated.

2.2. Bioelectrochemical system

The solution compositions, the start-up and the operational conditions of the bioelectrochemical system (BES) have been previously reported (MFC A) (Sulonen et al., 2016). BES was inoculated with hydrometallurgical mining process water. With this inoculum, the microbial culture in the anolyte of tetrathionate-fed MFCs has been dominated by *Acidithiobacillus* sp. and *Ferroplasma* sp. (Sulonen et al., 2015). The initial tetrathionate concentration in the anolyte was 2 g L⁻¹ and pH 2.5. The BES was operated at room temperature (20 °C ± 2 °C) in a fed-batch mode. The system was fed by adding medium containing 125 g L⁻¹ S₄O₆²⁻ (final concentration 2–2.5 g L⁻¹ S₄O₆²⁻) after the tetrathionate concentration of the anolyte decreased below 0.5 g L⁻¹. Ferric iron (2 g L⁻¹ Fe³⁺, added as FeCl₃) was used as the terminal electron acceptor at the cathode and the solution pH was adjusted to 1.5 with HCl. The catholyte solution was replaced after the ferrous iron (Fe²⁺) concentration of the solution increased above 1 g L⁻¹ and every time before changing the applied anode potential. Both anolyte and catholyte were purged with nitrogen for 15 min prior the experiment to remove oxygen from the solution.

The external resistance of BES was first gradually decreased from 1000 Ω to 240 Ω (days 0–286) to enhance the current generation and to study the effect of external resistance on anode potential. The effects of the decreasing of the external resistance on current density and tetrathionate degradation rates have been previously reported (Sulonen et al., 2016). After 286 days of operation, the anode potential of the bioelectrochemical cell was gradually lowered from 0.4 V to 0.275 V with a potentiostat to study the effect of lower anode potentials on the current generation and tetrathionate degradation efficiency. The operation time at each anode potential varied from 20 to 60 days, the operation time increasing with decreasing anode potential.

The rate of non-electrochemical degradation of tetrathionate was studied in a control reactor operated in open circuit. The cell was started up as an MFC connected to a resistor of 1000 Ω and inoculated with the anolyte of an MFC that had been operated on tetrathionate for 8 months. After 12 days, the reactor was disconnected and the tetrathionate degradation was followed in open circuit for 14 days.

2.3. Abiotic electrochemical system

The abiotic electrochemical systems (ES) contained tetrathionate (initial concentration 2 g L⁻¹ S₄O₆²⁻) in acidic phosphate buffered MilliQ (20 mM K₂HPO₄, pH 2.5) as the anolyte and ferric iron (2 g L⁻¹ Fe³⁺) as the catholyte. Oxygen was removed from both solutions by purging with nitrogen for 15 min. The operational conditions were otherwise the same as for the bioelectrochemical systems. To study the effect of anode potential on the abiotic electrochemical degradation of tetrathionate, the anode potential was first gradually increased from 0 V to 1.2 V. The cell was let

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