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Hydrogen as electron donor for copper removal in bioelectrochemical systems

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Abstract

Hydrogen gas is an attractive alternative electron donor since it is produced in large quantities as a side product in the metallurgical industry. Aim of this study was to demonstrate that microbial anodic hydrogen oxidation on a non-catalyzed graphite electrode can be coupled with cathodic copper reduction in a BES to simultaneously recover copper and produce power. The strategy was first to grow an anodic biofilm on acetate, then replace the acetate with hydrogen as electron donor, and finally combine hydrogen oxidation with copper reduction in the cathode. The maximum current density was 1.8 A/m^2 at -250 mV anode potential vs Ag/AgCl. When coupled with Cu^{2+} reduction, the maximum power density was 0.25 W/m^2 at a current density of 0.48 A/m^2. Anode overpotentials were higher compared to acetate oxidation, probably a result of limited hydrogen solubility and transfer.

Introduction

Significant volumes of heavy metal containing wastewaters are produced continuously at metal producing or electroplating companies. Heavy metals have been proven highly toxic for human, microbial and plant life[1,2]. Because heavy metals, even at low concentrations have negative effects on the environment, there is a need to remediate metal containing waste streams. Moreover, metal resources are finite, making their recycling crucial, since their production and transportation results in high energy consumption and arises unwanted and highly pollutant gas, solid and liquid emissions[3,4].

Conventional heavy metal removal technologies include electrochemical, chemical precipitation and ion-exchange. Although these technologies are applied in practice and a large scale their economic and environmental impact could still be improved by reduction of the high operational costs due to chemicals and energy consumption and the reduction of excessive production of hazardous wastes. This improvement could possibly also be achieved by the removal of these heavy metals in bioelectrochemical systems (BES).*[3,5].* In order to improve economic revenue and environmental impact of heavy metal treatment, we propose the removal of metals with BES. In BES the costs for chemicals and also for energy are minimized, and even power is produced in some cases; the biological oxidation of organic substrates provides part of required energy input. Three basic components comprises a BES: an anode, where substrate is oxidized and electrons are entering an electrical circuit, a cathode where a reduction reaction takes place and electrons are leaving the electrical circuit and, in most of the cases, an ion-exchange membrane that keeps the anolyte and catholyte separated and prevents substrate/product crossover[6].

Several metals have been demonstrated as electron acceptors in BES cathodes such as silver [7,8], iron [9–11], Nickel [12], zinc [13] and copper [13–19]. A common feature in all these studies is that the electron donor in the anodic compartment is an organic substrate. Electrochemically active bacteria are efficient oxidizers of organic substrates such as glucose, ethanol, glycerol, cellulose feedstocks, sewage sludge and aromatic compounds, but also inorganic such as hydrogen and sulfur compounds[20–22]. The use of organic substrates limits application of BESs to certain locations were organic wastewaters are available, but in reality organic waste streams are not ubiquitous. At the same

time, mining and metal industries, being the ones most interested in metal recovery, produce large amounts of hydrogen as a side product of their electroplating activities [23,24]. Hydrogen is also produced in reduction furnace operations[25] and as a side product of electro-catalytic treatment for acidity in mine waters[26,27].

Hydrogen can be used as electron donor in chemical fuel cells where it reacts with oxygen to produce electric current. The drawbacks of fuel cells is that they utilize noble metal catalysts like platinum, which are expensive and rare materials, and often operate at extreme conditions [28,29]. Microorganisms could serve as an alternative catalyst for the hydrogen oxidation reaction. Production of current by hydrogenotrophic anodophilic bacteria in MECs has already been reported by a number of researchers [30–32]. Rozendal et al. (2008) [33] used hydrogen as electron donor in order to grow a bioanode, which was after start-up changed to a hydrogen producing biocathode by reversing the polarity of the electrode. Moreover, Wang et al. (2014) [34], succeeded in perchlorate reduction in a bioelectrochemical reactor utilizing autotrophic hydrogen oxidizing bacteria. Both studies did not analyze the performance of a hydrogen oxidizing biofilm on the anode.

The main objective of this study was to explore the feasibility to utilize hydrogen as electron donor in combination with electrochemically active microorganisms at the anode for the recovery of copper at the cathode of a bioelectrochemical system. The strategy was to first to grow an anodic biofilm on acetate, then replace the acetate with hydrogen as electron donor and finally couple the hydrogen oxidation to copper reduction in the cathode. The performance of this system was studied by analyzing current as a function of anode potential, and, when coupled to copper reduction, power production.

Materials and methods

Experimental set up**.** Two identical cells (biotic and abiotic control) with a surface area of 22 cm^2 were constructed, as described by ter Heijne et al (2008) [35]. Each of them comprised of two graphite plates (Müller & Rössner GmbH & Co., Troisdorf, Germany) serving as anode current collector and cathode. The anode material was graphite foil (1.0 g/cm^3 density, 99% purity; Coidan Graphite Products Ltd., York, UK), which was pressed on the anode current collector.

Two plexiglass plates with a single flow channel as middle compartments contained anolyte and catholyte and were separated by a Ralex anion exchange membrane (MEGA a.s.,Stráž pod Ralskem, Czech Republic). Two additional plexiglass plates served as temperature control (30 °C) on the outside of the cell.

Temperature and pH were continuously logged (Endress + Hauser, Liquiline data logger) through pH electrodes (Endress + Hauser, CPS41 D) that were placed in the recirculation of anolyte and catholyte. In the headspace of each of the recirculation bottles, a gas sampling point was placed. The outgoing gas flow was measured using a bubble counter (MilliGascounter, Type MGC-1, Ritter, Bochum, Germany).

Electron donor and electrolyte composition. The anode of both cells was first fed with an acetate containing solution (20 mM) at a rate of 2 mL/min. This solution furthermore contained the following buffer and nutrients: 0.68 g/L KH_2PO_4, 0.87 g/L K_2HPO_4, 0.74 g/L KCl, 0.58 g/L NaCl, 0.28 g/L NH_4Cl, 0.1 g/L $MgSO_4.7H_2O$, 0.1 g/L $CaCl_2{\cdot}2H_2O$ and 0.1 mL/L of a trace element mixture [36].

The anolyte chamber was operated in a continuous mode and the catholyte in a batch mode. The anolyte was recirculated at 200 mL/min via two recirculation bottles of 0.5 L each. The catholyte was recirculated with the same rate in a 1 L bottle, which was shared by both the biotic and abiotic cell.

During stage 1, the bioanode tests on acetate and hydrogen, the catholyte consisted of 10 mM of phospha During stage 1, the bioanode tests on acetate and hydrogen, the catholyte consisted of 10 mM of phosphate buffer solution (pH 7). In stage 2, the bioanode coupled to copper reduction, the catholyte consisted of 1 g/L Cu^{2+} (prepared from $CuCl_2$ and deionized water; pH = 4).

The cathode was kept anaerobic by flushing with nitrogen gas.

In the second stage both cells were fed with hydrogen gas as electron donor. This hydrogen gas inflow was controlled with a mass flow controller (Bronkhorst HICH-TECH BV, Ruurlo, Nederland) at 3, 10 and 30 mL/min. Hydrogen was sparged in the recirculation bottles and continuously recirculated through the headspace of the recirculation bottles with a vacuum pump to achieve saturation of the anolyte with hydrogen. Buffer and nutrients remained the same when the hydrogen gas served as electron donor.

Experimental strategy: The biotic cell was inoculated with a mixed microbial culture from an active MFC utilizing acetate as electron donor. The abiotic cell was not inoculated and served as control. This cell was tested under the same hydrogen flows as for the biotic cell and with the anode potential ranging from -400 to -200 mV.

Table 1 gives an overview of the two experimental stages. First, the cell was started with acetate as electron donor and during the experiment the acetate was first partly and later fully replaced with hydrogen. For both cells the anode potential was controlled with a potentiostat ranging from -400 mV to -200 mV (50 mV steps), in order to see the response of current generation as a function of the anode potential. When a stable current was reached, the acetate concentration was decreased stepwise to 10 and 5 mM acetate. For these last two concentrations of acetate the anolyte was flushed with 3 mL/min H_2 at the same time. Next, only hydrogen was provided to the cells as a sole electron donor with a flow of 3, 10 and 30 mL/min were tested.

In the second experimental stage, hydrogen oxidation at the anode was combined with copper reduction at the cathode. The potentiostat was replaced by an external resistor and the resistance was stepwise reduced when the current reached a stable value; 1000, 500, 250, 100, 75, 50 Ω. The hydrogen flow provided during these experiments was 30 mL/min, while the catholyte was a

Copper solution replaced regularly to keep copper concentration constant during the experiment. The copper concentration was checked twice every day to be sure that concentration was close to 1g/L, and never lower than 0,7 g/L.

. Finally, bicarbonate was added as carbon source in addition to hydrogen as electron donor (30 mL/min H_2). Again, the anode potential was controlled with a potentiostat between -400 and -200 mV in 50 mV steps.

The biotic cell was inoculated again a few times during the experiment when a sharp drop in current was observed. At these points the system was also supplied with additional acetate. The experiment was only resumed when the supplied acetate was completely depleted, as confirmed by IC measurements.

Table 1 Overview of the three experimental stages for the biotic cell.

Stage of experiment	Electron donor	Anode potential vs Ag/AgCl or value of resistor	Duration (days)	Cathode reaction
1: bioanode development on acetate and switch to hydrogen	20 mM Acetate	-400 mV to -200 mV	10	Hydrogen production
	10 mM acetate + 3ml/min H_2	-350 mV to -250 mV	8	
	5 mM acetate + 3ml/min H_2	- 400 mV to -200 mV	8	
	3 ml/min H_2	- 400 mV to -200 mV	11	
	10 ml/min H_2	-350 mV and -200 mV	11	
	30 ml/min H_2	- 400 mV to -200 mV	7	
2. Bioanode on hydrogen coupled to copper reduction and addition carbon source	30 ml/min H_2	1000 Ω to 50 Ω	14	Copper reduction
	30 ml/min H_2+ HCO_3^-	400 mV to -200 mV	15	

Electrochemical control. The anode potential was controlled with a potentiostat (BANK ELEKTRONIK, WENKING POTENTIOSTAT KP 3A5V). Since the anode potential was controlled and the cathode was anaerobic, the cell voltage was negative, such that hydrogen gas was produced in the cathode. The potentials of the cell compartments were controlled and measured versus Ag/AgCl 3M KCl reference electrodes (Qis, QM711X – Reference electrode, Epoxy, Refillable, 4mm) that were placed in the electrolyte, for both the anodic and the cathodic compartment. All potentials are reported versus the Ag/AgCl reference electrode (+0.201 vs SHE).

The cell voltage, anode, cathode and membrane potential (defined as the potential difference between the two reference electrodes), as well as the current produced were recorded every minute on a data logger (Endress + Hauser RSG40). Chronoamperometry tests were conducted in order to check the current production of the abiotic cell with different hydrogen flows and anode potential control, using Autolab equipment (Metrohm Autolab B.V., PGSTAT 302N).

Analytical procedures and calculations: The acetate concentration in the cells was measured using ion chromatography (Metrohm 761 Compact IC equipped with a conductivity detector and a Metrosep Organic Acids 6.1005.200 ion exclusion column) and the bicarbonate concentration was determined using a total carbon analyzer (Shimadzu TOC-VCPH). The gas composition in the headspace of the cells was also examined with a gas chromatographer (Varian Inc. (Part A) - CP-4900 Micro-GC).

When the catholyte was changed to the copper solution, the current and power production were calculated according to

$$I = \frac{V_{cell}}{R_{ext} * A_{an}} \quad (2)$$

$$P = \frac{Vcell^2}{R_{ext} * A_{an}} \quad (3)$$

where V_{cell} is the cell voltage, R_{ext} is the external resistance (Ω), A_{an} is the projected surface area of the anode (0.0022 m^2).

Results and discussion

Hydrogen as electron donor for an electroactive biofilm. The performance of the anodic biofilm with acetate and hydrogen as electron donors is summarized in Figure 1.

Initially an acetate solution (20 mM) was used to achieve fast growth of an electroactive anodic biofilm and a stable current. The performance of this bioanode was analyzed at controlled anode potentials in steps of 50 mV (every 50 hours) ranging from -400 to -200 mV. The bioanode produced a maximum current of 3.98 A/m^2 at -250 mV. After that, the acetate concentration was stepwise decreased while an inflow of hydrogen was introduced to the system. When the acetate concentration decreased to 10 mM and 3 mL/min H_2 was flushed in the anolyte, the maximum current density was 1.80 A/m^2 at -250 mV. When the acetate concentration was decreased further to 5 mM, the maximum current density was 0.92 A/m^2 at an anode potential of -250 mV.

In the next experimental stage, after depletion of acetate, the anolyte was provided only with hydrogen at a flow of 3 mL/min. The maximum current density was 0.67 A/m^2 at an anode potential of -250 mV. This was the highest current obtained during this experimental cycle. Increase of the anode potential to -200 mV led to a slight decrease in current density (0.62 A/m^2). These results show that also in absence of acetate, hydrogen can be used as electron donor for the bioanode.

Nevertheless, the produced current with hydrogen as electron donor was a factor 6 lower than with only acetate. A possible limitation of current production from hydrogen is the availability of hydrogen gas for the microorganisms, due to its low solubility. To test if hydrogen was limiting, after 11 days, the hydrogen inflow into the anolyte was increased from 3 mL/min to 10 mL/min H_2 gas. For -200 mV (the only anode potential measured at this H_2 flow), the bioanode now produced 1.84 A/m^2. A further increase of the H_2 gas flow to 30 mL/min and repeating the experiments at anode potentials in the range of -350 to -200 mV did not lead to a further increase in current density. The maximum current density at this hydrogen flow was 1.57 A/m^2 at an anode potential of -200 mV.

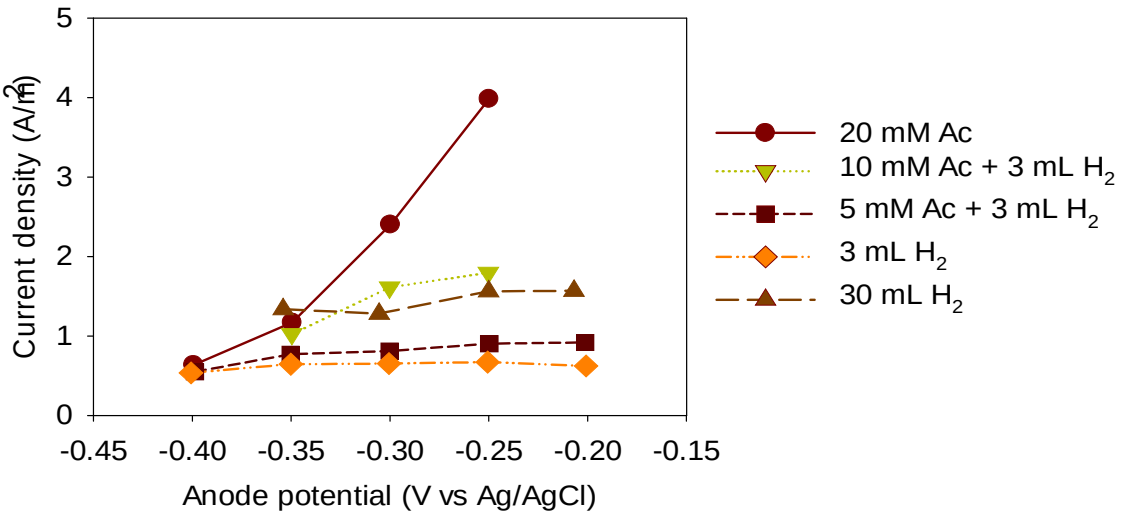

Figure 1- Performance of biotic cell when shifting from acetate to H_2 as electron donor

Abiotic control experiments. Hydrogen can be oxidized in the absence of microorganisms at noble metal based catalysts like Pt. Possibly, it can also be oxidized on a plain graphite electrode. To verify if the biological catalysis, and not the graphite electrode, was responsible for hydrogen oxidation, the current produced in an abiotic cell was compared to the current produced in the biotic cell. In Figure 2 the current density obtained from the biotic cell is compared with the current produced from the abiotic cell, at an anode potential of -200 mV and at different hydrogen inflows. The current density in the abiotic cell was much lower than the current produced in the biotic experiment at all flow rates. Some negative current was measured for the abiotic cell, meaning that a reduction reaction, instead of an oxidation reaction, occurred at -200 mV electrode potential, due to the potentiostatic control of the cell.

According to these results, it can be concluded that the electroactive biofilm oxidized hydrogen at the graphite electrode.

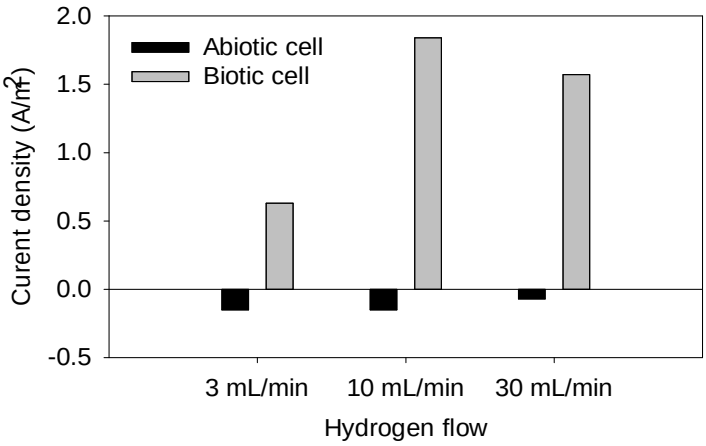

Figure 2 Abiotic cell vs biotic cell performance at an anode potential of -0.200 V at different hydrogen inflow rates.

Cathodic copper reduction coupled with anodic hydrogen oxidation. Finally, experiments were conducted where the electrons from hydrogen oxidation at the bioanode were used to reduce copper at the cathode. The anolyte was continuously flushed with 30 mL/min H_2, in order to operate at high hydrogen concentration, while the catholyte was a copper solution ($[Cu^{2+}]$=1 g/L). Copper concentration was replenished regularly so that copper concentration was always >0.7 g/L.

Figure 3A shows the performance of the system in a polarization and power curve. During the experiment the external resistor was stepwise reduced: 1000, 500, 250, 100, 75 and 50 Ω. The initial cell voltage and current density obtained with 1 kΩ were 0.61 V and 0.28 A/m^2, respectively, giving a power density of 0.17 W/m^2. The maximum power density obtained was 0.25 W/m^2. At that point the cell voltage was 0.53 V and the current density was 0.48 A/m^2. The highest current density was 0.66 A/m^2 in combination with a power density of 0.24 W/m^2.

The following equations show the potentials for acetate and hydrogen oxidation, copper reduction and the overall cell voltages.

Acetate oxidation

$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$ E_{an} = -0.496 V at pH 7 (1)

Hydrogen oxidation

$H_2 \rightarrow 2\ H^+ + 2\ e^-$ E_{an} = -0.554V at pH=7 (2)

Copper reduction

$Cu^{2+} + 2\ e^- \rightarrow Cu\ (s)$ $E_{cat} = 0.082$ V at pH=3 (3)

Overall

$CH_3COO^- + 4H_2O + 4Cu^{2+} \rightarrow 2HCO_3^- + 9H^+ + 8e^- + 4Cu(s)$ $E_{cell} = 0.578$ V (4)

$H_2 + Cu^{2+} \rightarrow 2H^+ + Cu\ (s)$ $E_{cell} = 0.636$ V (5)

Figure 3B shows the anode, cathode and membrane potential and their contribution to the total cell voltage. The maximum cell voltage close to the open circuit voltage was 0.608 V; which is very close to the theoretical open cell voltage of 0.636 V for copper reduction combined with hydrogen oxidation (equation 5). The anode potential close to open circuit was –0.468 V, slightly more positive than the theoretical potential (equation 2). The cathode potential was quite stable throughout the range of measured current densities varying between 0.097-0.141 V, close to the theoretical potential of copper reduction (equation 3). The copper concentration in the catholyte decreased in the course of the experiment, indicating that indeed copper was recovered at the cathode. Copper recovery and its efficiency was not further analyzed in this study, but has been analyzed by others [37].

As can be seen from this figure, both the membrane and cathode potential are stable over the whole current range. The drop in cell voltage at higher current densities is caused by increase in anode potential. This increase in anode potential is most likely caused by limited transport of hydrogen towards the biofilm. Even though the gas flow was increased hydrogen supply to the biofilm might be limited due to its limited solubility in water at atmospheric pressure.

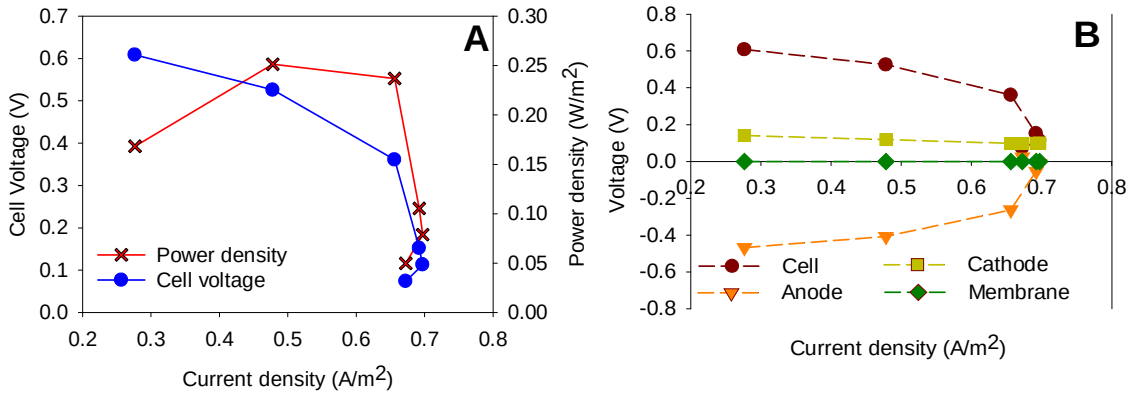

Figure 3 (A) Power and polarization curve for hydrogen oxidation coupled to copper recovery and (B) contribution of the anode, cathode and membrane potential to the cell voltage.

Perspectives and long term performance. The results presented here show the proof of principle for the use of hydrogen as electron donor for the recovery of copper in BESs. The current and power densities obtained in this study (0.48 A/m^2 in combination with 0.25 W/m^2) are in the same order as previous investigations of copper removal in BESs. However, all previous studies used an organic electron donor while here for the first time hydrogen was used. Tao et al. produced 0.26 W/m^2 power density at 0.86 A/m^2 current density [18], using glucose as electron donor. Ter Heijne et al obtained a maximum power density for acetate oxidation coupled to copper reduction of 0.43 W/m^2 at a current density of 1.7 A/m^2 in exactly the same cell configuration as used in this study [16].

Second, our analysis of overpotentials shows that the anode overpotential for hydrogen oxidation is higher than for acetate oxidation. A probable reason for this higher overpotential is limited hydrogen availability due to its low solubility, even at higher flow rates. A future configuration should avoid these limitations, for example through more efficient gas transport and elevated gas pressure.

Finally, the long term performance of this system should be investigated Hydrogen acts only as an electron donor, while microorganisms require also a carbon source for growth. In the final stage of our experiment, we observed a slow decrease in current density, with limitations in carbon source as a possible reason. To test the effect of carbon source, we provided the cell with bicarbonate and were able to run it under stable conditions (~1.2 A/m^2) for over two weeks (data not shown). It should be further investigated what the minimum requirement of carbon source is and if an inorganic source is sufficient for these microorganisms to survive for long periods of time. For example, Jeremiasse et al showed that a hydrogen producing biocathode required two times lower startup time with acetate compared to a biocathode starting on bicarbonate [38]. When adding a carbon source, either in the form of acetate or bicarbonate, care should be taken not to produce methane instead of electricity, since both acetate and bicarbonate are suitable substrates for methanogens. In the present research, already small amounts of methane (max 4%) were detected in the headspace.

Conclusions

With a BES, biologically catalyzed hydrogen oxidation at the anode can be coupled with copper reduction Results show a maximum current density of 0.67 A/m^2 combined with a power density of 0.25 W/m^2 when hydrogen is used as single electron donor Further research and optimization of the system could lead to a novel practical application for BESs for metal recovery.

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Highlights:

- Biological hydrogen oxidation was successfully combined with copper reduction.
- Open circuit voltage was close to theoretical voltage of the cell.
- Power density of 0.25 W/m^2 was achieved at 0.48 A/m^2.
- Hydrogen solubility was limiting the rate of the process.

Reviewer 1:

Overall I think the paper is clearly written. However, the following information should be added:

-Give information about the chemical composition of the catholyte. This info could be provided in the paragraph on lines 92-95.

The composition of the catholyte has been added to lines 92 to 95:

During stage 1, the bioanode tests on acetate and hydrogen, the catholyte consisted of 10 mM of phosphate buffer solution (pH 7). In stage 2, the bioanode coupled to copper reduction, the catholyte consisted of 1 g/L Cu^{2+} (prepared from $CuCl_2$ and deionized water; pH = 4).

-Show Cu concentration data. On line 223, it is stated the the Cu concentration in the catholyte decreased. Although the focus of the paper is on the H2-utilizing anode, there is no reason not to show the Cu data as well (for example in a supplementary material). Also, use the Cu concentration measurements to estimate a coulombic efficiency for the cathode.

The copper solution was replaced regularly to keep copper concentration constant during the experiment. The copper concentration was checked twice every day to be sure that concentration was close to 1g/L and never lower than 0,7 g/L.

-Discuss the possible reactions taking place at the anode. On line 256 it is stated that small amounts of CH4 was produced during H2-feed. It is also possible that acetate is produced from H2 and bicarbonate. That acetate could then potentially be used by the bioanode or by methanogens. Was any acetate detected during feed with only H2?

Indeed, alternative electron donors besides H2 could play a role. We did analyze the anolyte for Acetate concentration, and it was below detection limit, on the other hand, methane was detected in the headspace of the cell, likely originating from H2 and CO2 We have added this to the text.

-I think the sentence on lines 252-253 should have the word acetate in it somewhere. Please check.

The word acetate has been added to line ...:

Jeremiasse et al showed that a hydrogen producing biocathode required two times less time for startup with acetate compared to a biocathode starting on bicarbonate

-Clarify what led you to add bicarbonate in the last phase of the study. Was there any evidence that the bioanode was not stable with only H2 feed? Or was it just to check if the current could be increased with a higher concentration of the carbon source?

When H2 was used as energy source for a longer period, current density decreased gradually (data not shown in manuscript). It is well known that microorganisms need a carbon source, besides an energy source to survive a longer period of time. Therefore, we decided to demonstrate that a combination of bicarbonate as carbon source combined with hydrogen allowed to maintain the cell performance for a longer period of time or even improve it.

Reviewer 2:

- The focus of the article is clear and experiments are well described.

- In the introduction all the treatments look very bad and only BES are the only good. Comments should be soften.

We have changed line to :

Conventional heavy metal removal technologies including electrochemical, chemical precipitation and ion-exchange. Although these technologies are applied in practice and a large scale their economic and environmental impact could still be improved by reduction of the high operational costs due to chemicals and energy consumption and the reduction of excessive production of hazardous wastes. This improvement could possibly also be achieved by the removal of these heavy metals in bioelectrochemical systems (BES).[1,2]

- It is not clear excess H2 in the metallurgical industry for use in the anode. In fact it is ususal produce H2 at the cathode in many BES, as evidenced by numerous articles in this journal

We agree with the reviewer that both processes have been studied before. However, they have not been combined in a single study before; and in addition, the performance of a hydrogen oxidizing bioanode (e.g. as function of anode potential) has not been studied before. This study looks for a combined solution of use the hydrogen oxidation process by bacteria and the copper reduction process, as explained in the introduction: There have been a number of reports of heavy metal removal in BESs. These reports all make use of an organic electron donor. These electron donors are generally not available at sites where heavy metals are produced and their transport to these facilities would be expensive. On the other side, an excess of H2 is produced in smelting companies in the reduction furnace or by electrochemical production as secondary reaction when nickel, cobalt or zinc are plated.

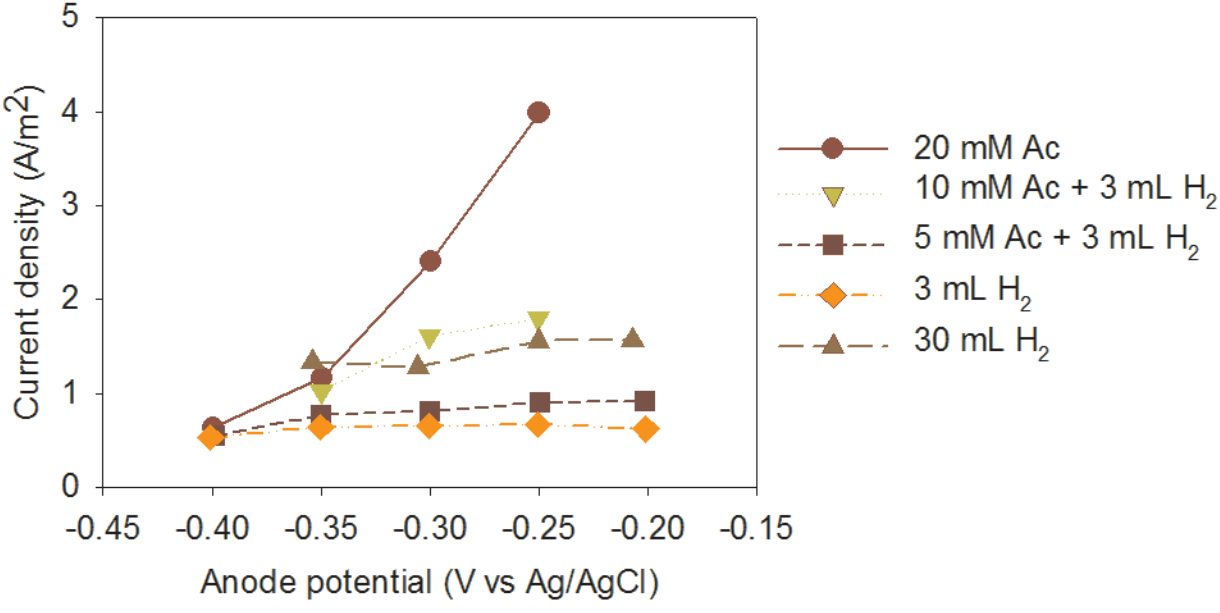
- The main objective of this study is to explore the feasibility to utilize hydrogen as electron donor in combination with electrochemically active microorganisms at the anode for the recovery of copper at the cathode. This approach is not very new.

- Oxidation of H2 at the anode is known. The reduction of copper is also known.

Oxidation of H2 at the bioanode is a novel process that has been reported, but its performance has not been studied before. The reduction of copper is not new, but the combination of both processes in a single device is a novel application of this technology, as discussed in the comment above.

- Discussion of results should increase and use less comments in conclusions.

Changes already done in the manuscript.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4
3
2
1
0
-0.45
-0.40
-0.35
-0.30
-0.25
-0.20
-0.15
Anode potential (V vs Ag/AgCl)
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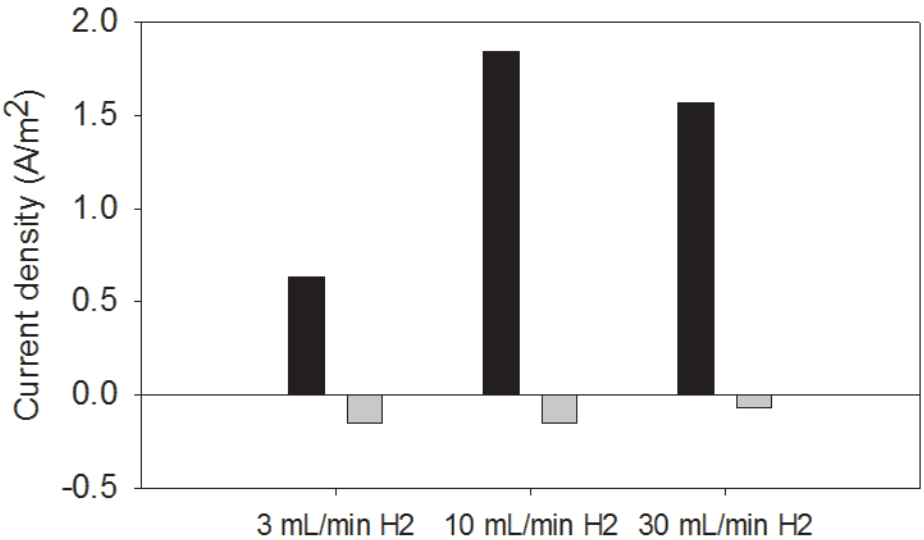
10 mM Ac + 3 mL H2
5 mM Ac + 3 mL H2
3 mL H2
30 mL H2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1.5
1.0
0.5
0.0
-0.5
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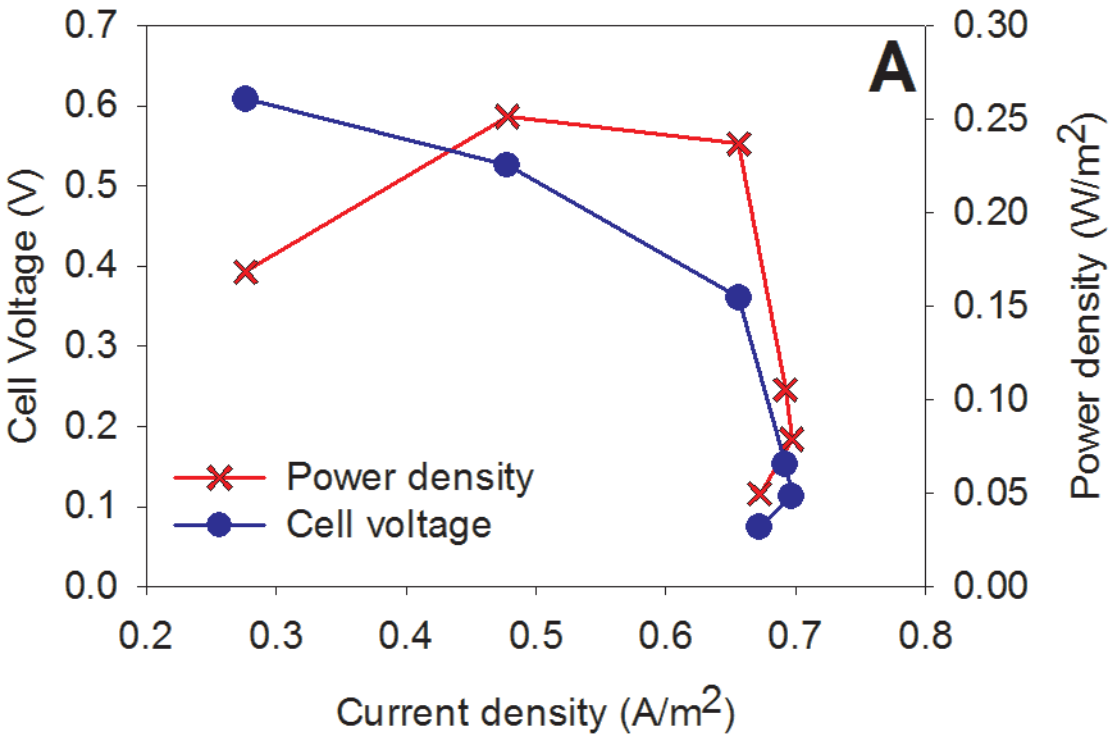
10 mL/min H2
30 mL/min H2


A
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Power density (W/m2)
Current density (A/m2)
Power density
Cell voltage
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0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.00
0.05
0.10
0.15
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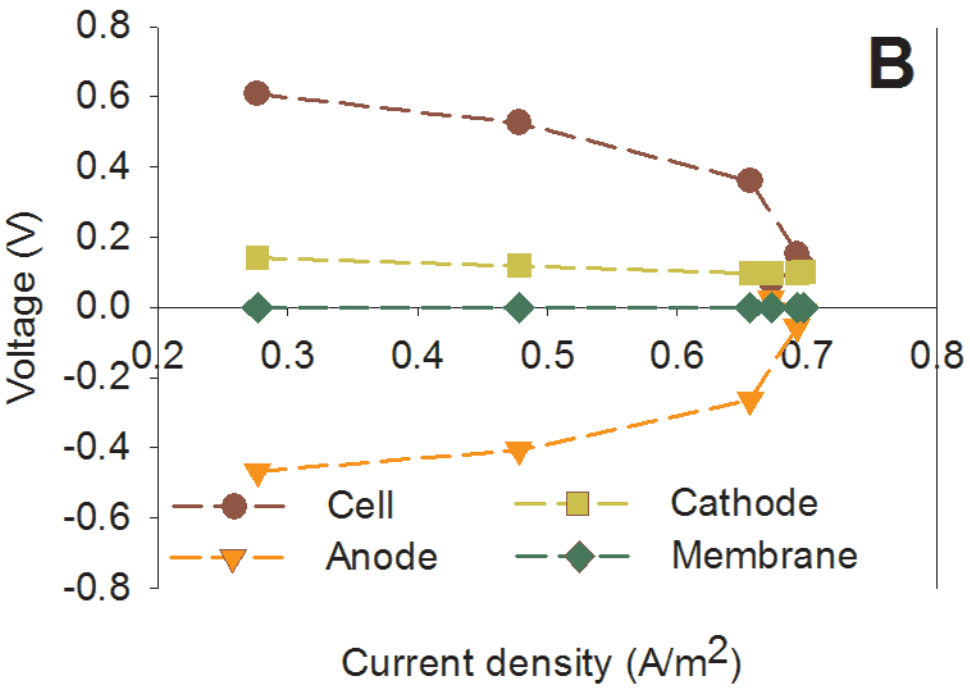
0.8


B
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Voltage (V)
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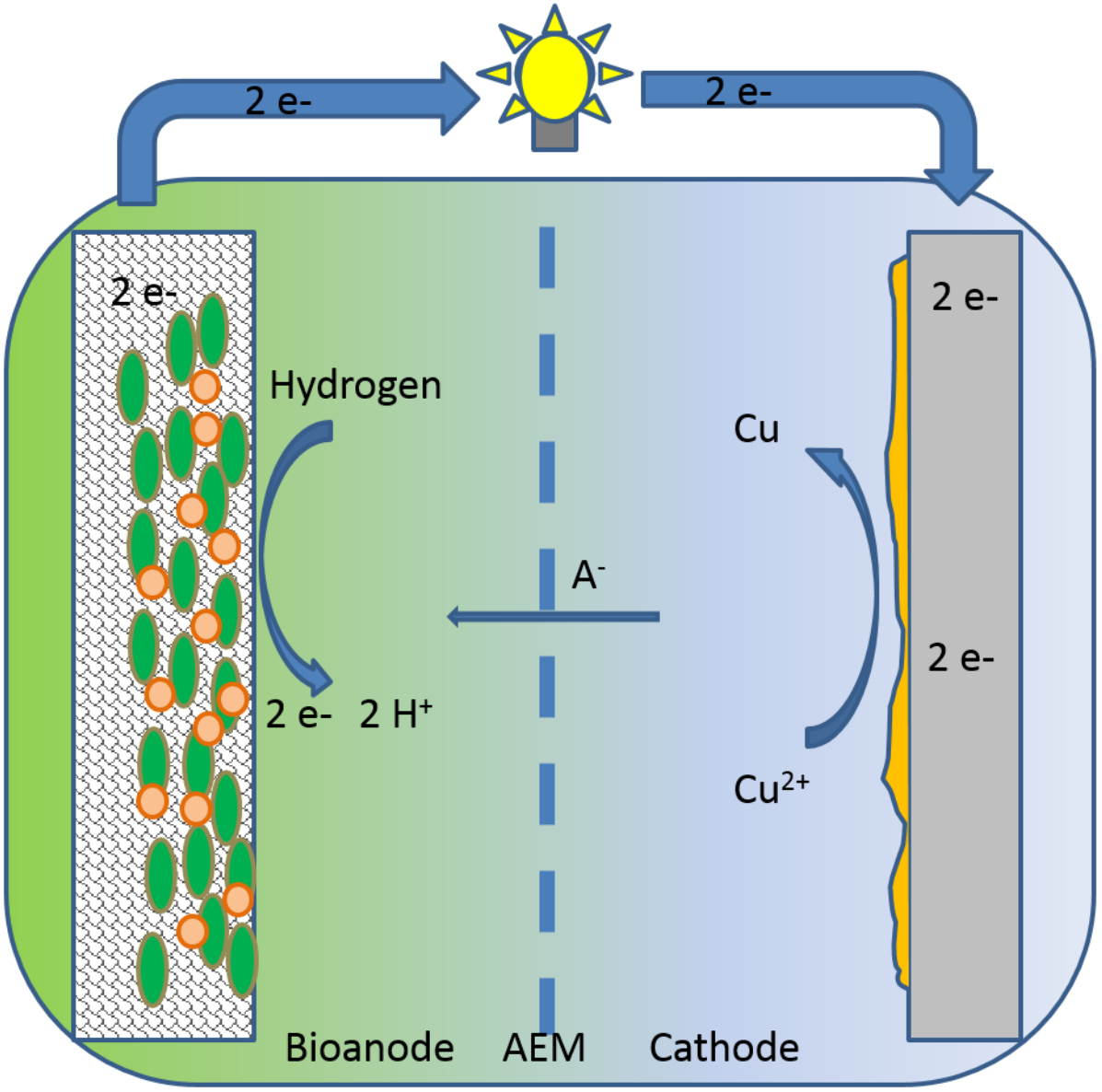
0.3
0.4
0.5
0.6
0.7
0.8
Cell
Cathode
Anode
Membrane
Current density (A/m2)


2 e-
2 e-
2 e-
Hydrogen
2 e- 2 H+
A-
Cu
Cu2+
2 e-
2 e-
Bioanode
AEM
Cathode

Leeuwarden, July 14th 2015

Editorial Office

International Journal of Hydrogen Energy

Dear editor,

Hereby we would like to submit the enclosed manuscript entitled “Hydrogen as electron donor for copper removal in bioelectrochemical systems” as a research paper for *International Journal of Hydrogen Energy.*

The recovery of heavy metals is an important challenge in the hydrometallurgical industry. Recently, the recovery of copper coupled to oxidation of organic matter in a bioelectrochemical system was proposed as a viable option. However, organic electron donors are not always available on-site. Hydrogen gas is an attractive alternative electron donor since it is produced in large quantities as a side product in the metallurgical industry. The aim of this study was to demonstrate that microbial anodic hydrogen oxidation on a non-catalyzed graphite electrode can be coupled with cathodic copper reduction in a BES to simultaneously recover copper and produce power. We show here, for the first time, that it is possible to combine hydrogen oxidation with copper reduction. We believe the results achieved in this study show great promise for the future recovery of heavy metals in bioelectrochemical systems.

We hope you will consider our manuscript for publication in *International Journal of Hydrogen Energy.*

Sincerely,

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