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Cobalt recovery with simultaneous methane and acetate production in biocathode microbial electrolysis cells



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HIGHLIGHTS

• Biocathode microbial electrolysis cells as a new tool for cobalt recovery.

- Cobalt recovery with simultaneous methane and acetate generation.
- An applied voltage of 0.2 V was
- optimal for system performance. • The apparent *E*_a obtained was 26.7 kJ/ mol.

G R A P H I C A L A B S T R A C T



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ABSTRACT

Cobalt was successfully recovered with simultaneous methane and acetate production in biocathode microbial electrolysis cells (MECs). At an applied voltage of 0.2 V, 88.1% of Co(II) was reduced with concomitantly achieving yields of 0.266 ± 0.001 mol Co/mol COD, 0.113 ± 0.000 mol CH₄/mol COD, and 0.103 ± 0.003 mol acetate/mol COD. Energy efficiencies relative to the electrical input were $21.2 \pm 0.05\%$ (Co), $100.9 \pm 3.2\%$ (CH₄), and $1.0 \pm 0.01\%$ (acetate), and overall energy efficiencies relative to both electrical input and energy of anodic substrate averaged $3.7 \pm 0.05\%$ (Co), $17.5 \pm 1.4\%$ (CH₄) and $0.5 \pm 0.001\%$ (acetate). Applied voltage, initial Co(II) concentration, and temperature affected system performance. The apparent activation energy (E_a) obtained in MECs was 26.7 kJ/mol compared to 40.5 kJ/mol in the abiotic controls, highlighting the importance of cathodic microbial catalysis to Co(II) reduction. Dominant microorganisms most similar to *Geobacter psychrophilus*, *Acidovorax ebreus*, *Diaphorobacter oryzae*, *Pedobacter duraquae*, and *Prolixibacter bellariivorans* were observed on the biocathodes. This study provides a new process for cobalt recovery and recycle of spent lithium ion batteries with simultaneous methane and acetate production in the biocathode MECs.

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1. Introduction

Cobalt is one major component of the extensively applied lithium-ion batteries. Recovery of cobalt from spent lithium-ion batteries is considered to be a beneficial way to prevent environmental pollution and as alternative resource of cobalt [1]. While conventional pyrometallurgical, hydrometallurgical and bioleaching, and even newly developed microbial fuel cell can release cobalt in the spent lithium-ion batteries after battery dismantling occurs [1–3], the resultant solution of aqueous Co(II)



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needs to be further recovered. Multiple technologies such as chemical precipitation, adsorption, solvent extraction and ion exchange are effective to recover Co(II). However, there are practical limitations arising from operational costs associated with continuous chemical addition, high volume sludge generation, low selectivity and inefficiency at low concentrations, as well as the presence of organic pollutants in using most of the methods [1]. Alternatively, Co(II) can be reduced in electrochemical processes. The main disadvantage of this process is the extensive energy consumption for producing the potential needed for Co(II) reduction and the lack of suitable catalysts able to efficiently decrease the overpotential [4]. Energy efficiency and cobalt yield in this process have not additionally well explored.

One new promising method for more efficient recovery of aqueous Co(II) is the use of microbial electrolysis cells (MECs). Multiple aqueous recalcitrant substances are proved to be reduced on the cathodes of MECs [5] and even Co(II) can be released from particles LiCoO₂ on the surface of MEC cathodes [6]. The production of hydrogen, hydrogen peroxide, caustic solution and struvite as a part of wastes treatment, also brings about a considerable environmental benefit to the overall treatment process and appears to be a promising application of MECs [7–11]. One disadvantage of these MECs, however, is that a precious metal catalyst (e.g. Pt) is usually used on the cathodes. Biocathodes, which use bacteria as biocatalysts to accept electrons from the cathode substratum, provide a different path that both avoids the use of noble catalysts and enables the use of alternative electron acceptors, and thus expands the scope of applicable MECs [12–14]. The electrotrophic capabilities of both lowing overpotentials and removing recalcitrant substrates enable the biocathodes more advantages over chemical cathodes, particularly at a neutral pH environment. At present, some microorganisms have been shown to be able to extract electrons from a cathode, use them in their metabolic reactions and finally transfer them to CO₂ [12,15–20], nitrobenzene [21], chloramphenicol [22] and glycerol [23], which are reduced to various compounds. While mix culture is able to electrosynthesize CO_2 to unidentified organics [15], various acetogenic bacteria colonizing a graphite electrode can reduce CO_2 to acetate [16–17]. In terms of microbial electrosynthesis of methane, a culture of Methanobac*terium palustre* on a carbon electrode can reduce CO₂ to methane [18–19]. In linkage with cobalt recovery from aqueous wastes, no essential attention has been paid to the biocathode MECs as a promising technology for efficient Co(II) reduction with simultaneous methane and acetate production.

To investigate cobalt reduction with simultaneous methane and acetate production in biocathode MECs, the effect of a number of factors needs to be understood, among which are applied voltage, initial Co(II) concentration, and temperature. Based on thermody-namic calculations, aqueous Co(II) could be reduced electrochemically to cobalt at a voltage of -0.233 V (vs. SHE) whereas CO₂ is respectively reduced to methane at 0.169 V and (CH₂O) (CH₂O represents the approximate formula of organics) at 0.098 V under standard conditions by the reactions of (1)–(3):

$$\mathrm{Co}^{2+} + 2\mathrm{e}^{-} \to \mathrm{Co} \tag{1}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$
 (2)

$$HCO_{3}^{-} + 5H^{+} + 4e^{-} \rightarrow (CH_{2}O) + 2H_{2}O$$
 (3)

Under more biologically relevant conditions and pH 7.0, CO_2 is reduced to methane at a voltage of -0.244 V [12] whereas the voltages required for Co(II) and CO_2 reduction are supposed to be lower than -0.233 V and -0.420 V, respectively taking into account the experimental conditions [15]. Considering that different biocathode conditions away from the standard conditions result in significantly different methane and acetate production in MECs [12,15], and Co(II) reduction in conventional electrochemical processes [4], an applied voltage may substantially change the operational conditions and the consequent Co(II) reduction with simultaneous methane and acetate production in the biocathode MECs. In view of microbial communities, an optimal voltage which can control bacterial community composition and benefit to metabolic activities inside [23], is expected to efficiently activate Co(II) and CO₂ reduction reactions as well as methane evolution. A high Co(II) concentration pushes thermodynamically the reaction of Eq.(1) forward whereas a much high Co(II) concentration is inhibitory to the electrotrophs and thus the consequent system performance [24]. Temperature affects all aspects of the MECs, including system kinetics, mass transfer and thermodynamics [6-8]. An optimal temperature may not only accelerate chemical reaction rates in the anode and cathode, but also keep high biocatalyst activities. both of which are expected to improve cobalt reduction with simultaneous methane and acetate production.

In this study, the feasibility of using the cathode as an electron donor for biological Co(II) reduction with simultaneous methane and acetate production by mixed culture was explored. Kinetic parameters including applied voltage, initial Co(II) concentration, and temperature were examined. Co(II) reduction (%), yields of cobalt (Y_{Co}), methane (Y_{CH_4}), acetate ($Y_{acetate}$) and hydrogen (Y_{H_2}), anodic coulombic efficiency (CE_{an}), cathodic charge distribution, energy efficiencies relative to only electrical input and based on cobalt recovery ($\eta_{E,Co}$), methane production (η_{E,CH_4}), acetate generation ($\eta_{E,acetate}$) or hydrogen evolution (η_{E,H_2}), overall energy recoveries based on both the electricity and anodic substrates, and cobalt recovery ($\eta_{E+S,Co}$), methane production (η_{E+S,CH_4}), acetate generation ($\eta_{\text{E+S,acetate}}$) or hydrogen evolution ($\eta_{\text{E+S,H}_2}$), and energy contributed by the power source (e_E) and anodic substrate (e_S) , were extensively used to evaluate system performance. The composition of bacterial community on the cathodes was analyzed. Deeper insight into these aspects will enhance the performance of biocathode MECs for efficient cobalt recovery with simultaneous methane and acetate production from wastes as discussed subsequently.

2. Materials and methods

2.1. Reactor assembly

A tubular two-chamber reactor similar to previously reported [25] was used in all experiments. Graphite fiber (PANEX33 160 K, ZOLTEK) and porous graphite felt (Sanye Co., Beijing, China) were used as the anodes and the cathodes. Before installation, these electrode materials were washed firstly in 32% HCl and then in 35% NaOH to remove metals from the surface. The net working volume in the anode and the cathode chambers were 25 mL and 40 mL, respectively. A cation exchange membrane (CEM) (CMI-7000 Membranes International, Glen Rock, NJ) was employed to separate the anode and cathode of the tubular reactor.

2.2. Inoculation and operation

Seed sludge was obtained from an anaerobic digester at Lingshui Wastewater Treatment Plant in Dalian, China which received a combination of domestic and metalworking wastewaters. This seed sludge was initially combined with a nutrient solution at a ratio of 10% (w/v), containing (mM) NH₄HCO₃, 4.9; KHCO₃, 1.5; NaH₂PO₄·2H₂O, 21.2; Na₂HPO₄·12H₂O, 28.8; MgSO₄·7H₂O, 0.15; vitamins 12.5 mL/L and minerals 12.5 mL/L [25]. This mixed solution was used to fill the cathode. Prior to add this mixed solution into the cathodes, the catholyte was sparged with N₂ gas for 15 min. The anode was inoculated from the anode of operating Download English Version:

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