Complete cobalt recovery from lithium cobalt oxide in self-driven microbial fuel cell − Microbial electrolysis cell systems
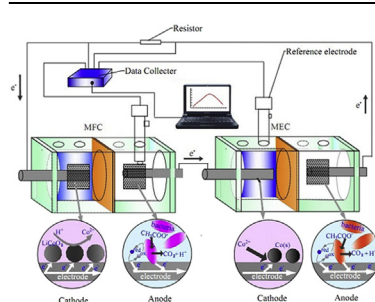
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GRAPHICAL ABSTRACT

ABSTRACT

Complete cobalt recovery from lithium cobalt oxide requires to firstly leach cobalt from particles $LiCoO_2$ and then recover cobalt from aqueous Co(II). A self-driven microbial fuel cell (MFC)−microbial electrolysis cell (MEC) system can completely carry out these two processes, in which Co(II) is firstly released from particles $LiCoO_2$ on the cathodes of MFCs and then reduced on the cathodes of MECs which are powered by the cobalt leaching MFCs. A cobalt leaching rate of 46 ± 2 mg L^{-1} h^{-1} with yield of 1.5 ± 0.1 g Co g^{-1} COD (MFCs) and a Co(II) reduction rate of 7 ± 0 mg L^{-1} h^{-1} with yield of 0.8 ± 0.0 g Co g^{-1} COD (MECs), as well as a overall system cobalt yield of 0.15 ± 0.01 g Co g^{-1} Co can be achieved in this self-driven MFC−MEC system. Coulombic efficiencies reach $41 \pm 1\%$ (anodic MFCs), $75 \pm 0\%$ (anodic MECs), $100 \pm 2\%$ (cathodic MFCs), and $29 \pm 1\%$ (cathodic MECs) whereas overall system efficiency averages $34 \pm 1\%$. These results provide a new process of linking MFCs to MECs for complete recovery of cobalt and recycle of spent lithium ion batteries with no external energy consumption.

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1. Introduction

Recovery of cobalt, an element with excellent ferromagnetic properties, relatively stable against corrosion and easily to handle,

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from lithium cobalt oxide owns both economic and environmental perspectives due to its rich concentration in the spent lithium ion batteries annually increasing in astonishing quantities [1]. Traditional pyrometallurgical process, hydrometallurgical process or the combination of both, as well as electrochemical process are high cost, generation of serious second pollution, and great energy consumption [2–4]. While conventional bioleaching is cost effective and eco-friendly, microorganisms can only endure to a certain cobalt concentration, after which inhibition of the bioleaching
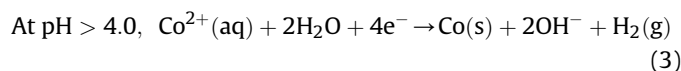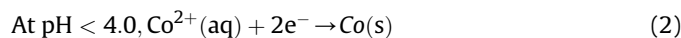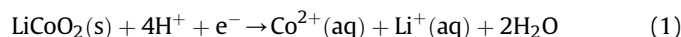
process takes over. In addition, the leaching solution is often contaminated and impure, and excess sludge is also generated, both of which bring about more burdens to the downstream cobalt separation and purification as well as sludge treatment [5,6]. The newly developed microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) can hurdle the above drawbacks and leach the cobalt [7–9]. Electrons provided by the cathode have been previously found to be able to replace conventional chemical reductants and play a synergetic interaction with HCl for cobalt leaching, leading to the decrease of apparent activation energy of cobalt leaching in both MFCs (30.6 kJ mol^{-1}) [7] and MECs (16.6 kJ mol^{-1}) [8], in comparison with the 44.5–98.7 kJ mol^{-1} in MFC controls [7] and 30.8–54.6 kJ mol^{-1} in MEC controls [8]. The presence of Cu(II) catalyst further decreases the apparent activation energy of cobalt leaching in MFCs to 11.8 kJ mol^{-1} [9] whereas multiple factors including initial pH, solution conductivity, solid/liquid ratio, applied voltage, and temperature affect cobalt leaching in either MFCs [7,9] or MECs [8]. While these results illustrate effective for cobalt leaching in the bioelectrochamical systems, parameters including cobalt leaching yield, anodic and cathodic coulombic efficiencies (CEs), overall system cobalt yield, and overall system efficiency have not been previously and systematically assessed [7–9]. More importantly, the resultant solution, which contains cobalt ion, still needs to be separated and recovered. Conventional chemical precipitation, extraction, or electrodeposition can recover cobalt from solution [1], the challenges of these processes include extensive cost, second pollution, and great energy consumption. Exploring environmental friendly and cost-effective strategies to completely recover cobalt from LiCoO$_2$ are still in demand.

A complete recovery of cobalt from LiCoO$_2$ experiences the following two steps:

$$LiCoO_2(s) + 4H^+ + e^- \rightarrow Co^{2+}(aq) + Li^+(aq) + 2H_2O \qquad (1)$$

$$At\ pH < 4.0, Co^{2+}(aq) + 2e^- \rightarrow Co(s) \qquad (2)$$

$$At\ pH > 4.0,\ \ Co^{2+}(aq) + 2H_2O + 4e^- \rightarrow Co(s) + 2OH^- + H_2(g) \qquad (3)$$

At pH 2.0 and 298 K, the potential for the reduction of Co(III) to Co(II) (Eq. (1)) is 1.61 V (vs standard hydrogen electrode, SHE), which is higher than that of the reduction of oxygen to water (1.23 V vs SHE) typically used in aerated cathodes. This indicates that Co(III) reduction on the cathodes of MFCs has the potential to generate higher electricity compared to an aerated cathode with a similar anode. On the other hand, reduction of the released aqueous Co(II) to Co (Eqs. (2) and (3)) exhibits a potential of −0.232 V (vs SHE), comparative to the potential of −0.28 V (vs SHE) using acetate as a fuel at the anode and a voltage is thus required for the Co(II) reduction. Considering the energy generation from MFCs in which Co(III) is reductively released to Co(II), and energy input in MECs, during which aqueous Co(II) is further reduced to pure cobalt (Eqs. (2) and (3)), a complete self-driven cobalt recovery process in the MFC–MEC systems may be achieved, in which cobalt is entirely harvested and the external power supply is saved. Despite of the extensive exploration of MFCs integrated with either conventional processes including a sequencing batch process, an up-flow anaerobic sludge blanket reactor, a rotating biological contactor and a membrane bioreactor for wastewater treatment, or newly developed MECs for hydrogen production and carbon dioxide reduction [10–20], to date, no essential attention has been paid to the self-driven MFC–MEC systems as a promising technology for complete recovery of cobalt from wastes.

To investigate complete cobalt recovery in self-driven MFC–MEC systems, the effect of a number of factors needs to be understood, among which are solution conductivity, catholyte pH, cathode volume, solid/liquid ratio, and serial and parallel connections. Both higher solution conductivities and miniaturization reactors in MFCs substantially reduce internal resistance of itself [7,21–24], and may thus improve cobalt leaching in MFCs and Co(II) reduction in the connected MECs. Similarly, a change in solution conductivity or reactor working volume in MECs can alter the internal resistance of itself and thus affect hydrogen production [8,17,18,21–24]. A change in solution conductivity in MECs may affect not only Co(II) reduction in MECs but also cobalt leaching in the connected MFCs. While cobalt leaching from LiCoO$_2$ and electrodeposition of Co(II) from an aqueous electrolyte are heavily pH-dependent [1,3], solid/liquid ratio greatly affects cobalt leaching in conventional chemical processes due to its controlling by surface chemical reaction [1,25]. Optimizing both solid/liquid ratios in MFCs, and pHs in MFCs and MECs can reveal the complex mutual interactions between MFCs and the connected MECs and is thus essential for bilateral performances for efficient cobalt leaching in MFCs and Co(II) reduction in the connected MECs. Stacking MFCs either in series or in parallel can increase voltage output or circuit current [26–28]. A better understanding of stacking MFCs will enable better design of MFCs to power MECs and allow more efficient cobalt leaching in MFCs and Co(II) reduction in MECs.

In this study a truly integrated and effective self-driven MFC–MEC system was designed, which not only recovered energy from wastewaters through MFCs and in-situ utilized this energy to power MECs, and thus avoided the need for external energy input in MECs, but also achieved simultaneous and complete cobalt recovery from particles LiCoO$_2$. Kinetic parameters including solution conductivity, pH, solid/liquid ratio, cathode volume, and serial and parallel MFC connections were examined. Multiple parameters including cobalt leaching, Co(II) reduction, yields of cobalt in MFCs and MECs as well as overall system, anodic coulombic efficiencies (CEs) in MFCs and MECs, cathodic CEs in MFCs and MECs, and overall system efficiency were extensively used to evaluate system performances. Due to more electrons required for Co(II) reduction in MECs (Eqs. (2) and (3)) than cobalt leaching in MFCs (Eq. (1)), imbalance of electrons based on the same amount of cobalt was unavoidable and the parameter of overall system cobalt yield was thus an effective indicator for this assessment. Deeper insight into these aspects will enhance the performance of MFC–MEC system for efficient and complete cobalt recovery with simultaneous spent lithium ion battery treatment as discussed subsequently.

2. Materials and methods

2.1. MFC–MEC system setup

The MFC–MEC system consisted of a two-chamber tubular MFC and a two-chamber tubular MEC with the electrodes separated by a cation exchange membrane (CEM) (CMI-7000 Membranes International, Glen Rock, NJ) (3.0 cm in diameters) (Fig. 1). The net working volume of each chamber was 25 mL. Graphite felt (Sanye Co., Beijing, China) was used as the anodes of MFCs and MECs, as well as the cathodes of MFCs whereas carbon rod was served as the cathodes of MECs. A carbon rod was immersed into the graphite felt to collect current. Before the installation, the electrode materials were repeatedly and alternatively treated four times using 32% HCl and 35% NaOH in order to remove metals from the surface. A reference electrode (Ag/AgCl electrode, 195 mV versus standard hydrogen electrode, SHE) was used to obtain cathode and anode potentials, with all voltages reported here versus SHE. All of the reactors were wrapped with aluminum foil to exclude light.