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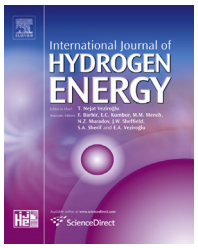

Assessment of five different cathode materials for Co(II) reduction with simultaneous hydrogen evolution in microbial electrolysis cells

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ABSTRACT

Cobalt recovery from aqueous Co(II) is one critical step for recovery of cobalt and recycle of spent lithium ion batteries, but suffers from consumption of large amount of energy and chemicals. Previous tests have primarily examined the performance of graphite felt cathode for Co(II) reduction and hydrogen production in microbial electrolysis cells (MECs). The materials of nickel foam (NF), stainless steel woven mesh (SSM), titanium sheet (TS), carbon cloth (CC), and nickel foam + graphene (NF + G) were compared here as cathodes for Co(II) reduction and hydrogen evolution in MECs. Co(II) reduction on the cathodes of TS, SSM, CC and NF + G was not significantly different from each other and increased with the increase of applied voltage from 31.8 ± 6.0% at 0.2 V to 72.2 ± 4.6% at 0.5 V, which was always higher than 16.5 ± 1.8%–53.4 ± 2.2% on the NF cathodes at the same range of applied voltage. While a low dissolved oxygen (DO) of 1.0 mg/L benefited to both Co(II) reduction and hydrogen evolution for all the materials cathodes with generally appreciable differences from each other, cobalt produced in previous fed-batch operations improved hydrogen evolution in the subsequent batch cycles. These results provide the first assessment of these materials for Co(II) reduction with simultaneous hydrogen evolution, and SSM as the most promising inexpensive alternative to the others.

Introduction

Cobalt is an element with excellent ferromagnetic properties, relatively stable against corrosion and easily to handle, and thus been useful in microelectronic fields such as lithium ion batteries [1–3]. Recovery of cobalt from spent lithium ion batteries is in consequence one of the primary objectives in the recycling of these wastes due to the environmental/ecological and economic benefits [2,3]. Pyrometallurgical, hydrometallurgical, bioleaching or microbial fuel cell processes can leach cobalt after the spent battery dismantling occurs [2,4]. The Co(II) ions in resultant solution need to be further recovered. While solvent extraction and conventional

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electrochemical processes recover cobalt from the solution [5,6], the newly developed microbial electrolysis cells (MECs) with graphite felt cathodes can achieve cobalt recovery with simultaneous hydrogen evolution [7], providing a new approach for aqueous cobalt recovery. Considering the substantial effects of hydrogen production by electrode materials [8] and the dependency of Co(II) reduction on electrode potential [1,5,9–11], alternative electrodes to graphite felt may be more favorable for Co(II) reduction, hydrogen evolution, and the consequent system efficiency in MECs.

Non-precious metals and alternatives including stainless steel wool mesh (SSM) [12–14], nickel foam (NF) [15,16], titanium sheet (TS) [17–21] and carbon cloth (CC) [22,23] have been investigated for either hydrogen evolution reaction in MECs or electricity production from microbial fuel cells because of their low electrical resistivity, good hydrogen evolution reaction catalysis and/or low cost with high efficiency [12–23]. Either graphene-based electrode or nickel foam + graphene (NF + G)/Co + graphene is additionally efficient for electricity production in microbial fuel cells [24–26] and photocatalytic hydrogen production from water [27–29] due to the graphene high electrical conductivity, charge carrier mobility, huge specific surface area, high transparency and great mechanical strength. In the case of cobalt recovery and hydrogen evolution in MECs, however, these materials of NF, TS, SSM, NF + G and CC have not been well explored.

To investigate performances of MECs with these five materials cathodes for cobalt reduction and hydrogen evolution, the effect of a number of factors needs to be understood, among which are applied voltage, dissolved oxygen (DO), and effect of previously recovered cobalt on hydrogen evolution in subsequent operation cycles. An applied voltage not only controls the potentials of cathodes and circuit currents with different materials for hydrogen production [8,13,30,31], but also affects Co(II) reduction and the subsequence morphologies of cobalt crystals in conventional electrochemical processes [1,5,9–11]. Exploration of different material cathode performances under various applied voltages is expected to reveal relationships of Co(II) reduction and hydrogen evolution on the various material cathodes with the changes of cathode potential and circuit currents, and thus benefit to Co(II) reduction with simultaneous hydrogen evolution. Oxygen is one preferred electron acceptor in bioelectrochemical systems because of its availability and high redox potential. While the presence of oxygen in the graphite foil cathode of microbial fuel cell was detrimental to Cu(II) reduction [32], oxygen can also compete with diatrizoate for electrons from graphite felt cathode and thus decreased diatrizoate reduction in MECs [33]. In the case of Co(II) reduction, DO at the cathodes with different materials may thus compete with aqueous Co(II) and protons for cathodic electrons, and affect system performance. Clarifying Co(II) reduction and hydrogen evolution on these different material cathodes at various DO levels will be favorable for efficient Co(II) reduction with simultaneous hydrogen production. In addition, considering the cobalt-based catalysis on hydrogen evolution in MECs [28,34], cobalt recovered in previous batch cycle may affect hydrogen evolution and the consequent Co(II) reduction in the subsequent operation cycles. Assessing the role of previously recovered cobalt in the subsequent system performance is expected to explain the observed improved system performance with prolonged operation time.

In this study, five materials of NF, TS, SSM, NF + G and CC were assessed for Co(II) reduction and hydrogen evolution on the cathodes of MECs. Kinetic parameters including applied voltage and DO were examined whereas cobalt previously recovered on the cathodes was additionally assessed for improvement of hydrogen evolution in the subsequent operation cycles. Multiple parameters including Co(II) reduction, anode potential (E_{an}), cathode potential (E_{ca}), apparent overpotentials for hydrogen evolution (E_{op}), yields of cobalt (Y_{Co}) and hydrogen (Y_{H_2}), anodic coulombic efficiencies (CE_{an}) in terms of cobalt ($CE_{an,Co}$) and hydrogen ($CE_{an,\,H_2}$), cathodic CEs in terms of cobalt ($CE_{ca,Co}$) and hydrogen ($CE_{ca,\,H_2}$), energy efficiency in terms of either energy consumed for Co(II) reduction ($\eta_{E,Co}$) or energy content of hydrogen produced ($\eta_{E,\,H_2}$) to the electrical energy added, and as overall recoveries of cobalt ($\eta_{E+S,Co}$) and hydrogen ($\eta_{E+S,\,H_2}$) were extensively used to evaluate system performances. Deeper insight into these aspects will provide alternative and cost-effective cathodes in MECs for efficient cobalt recovery with simultaneous hydrogen production from aqueous Co(II) as discussed subsequently.

Materials and methods

Reactor setup

Two-chamber MECs (duplicates) were used in all experiments, with the chambers separated by a cation exchange membrane (CEM) (CMI-7000 Membranes International, Glen Rock, NJ). Graphite felt (Sanye Co., Beijing, China) was served as the anode. Nickel foams (NF, 99.9%, Qingyuan Co. China), TA1 titanium sheet (TS, 99.9%, Qingyuan Co. China), SS 304 woven mesh (SSM) [35], and carbon cloth (CC) (type A, E-TEK) [36] with a same projected surface area of 14 cm^2, were evaluated for their suitability as the cathodes. These metal materials were cleaned before tests using 0.5 M H_2SO_4. The preparation of NF + G was carried out as similarly described [29]. Briefly, the NF samples were placed in the central isothermal zone of a 100 mm quartz tube (1400 mm in length) surrounded by a three zones furnace (760 mm in length). They were heated between 700 and 1000 °C in a H_2 and Ar flow and annealed for 5–40 min. Then 25 mL/min of methane under standard conditions were introduced into the reactor during 5–40 min with the same H_2 and Ar flow rate. The samples were then cooled to room temperature under the same H_2 and Ar flow rate without carbon precursor. All experiments were performed at 93.3 kPa. The working volume was 25 mL in the cathode and 20 mL in the anode. Borate (0.1 M) commonly employed in conventional electrochemical processes [5,9] was used as a buffer in the catholyte.

Inoculation and operation

The anode was inoculated from the anode of operating microbial fuel cells running on acetate. The anolyte was composed of (g/L) sodium acetate, 1.0; KH_2PO_4, 4.4; K_2HPO_4, 3.4; NH_4Cl, 1.3; KCl, 0.78; $MgCl_2$, 0.2; $CaCl_2$, 0.0146; NaCl, 0.5; trace vitamins and minerals [37]. The catholyte was 50 mg/L Co(II) in boric buffer solution with a solution conductivity of