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Cooperative light irradiation and in-situ produced H₂O₂ for efficient tungsten and molybdenum deposition in microbial electrolysis cells

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ABSTRACT

Tungsten (W) and molybdenum (Mo) deposition from ore dressing wastewater is a promising process for recovery of W and Mo with simultaneous ore dressing wastewater treatment, but suffers from consumption of large amount of extraction agent and energy, and generation of excess secondary polluted sludge. Here we reported light irradiation and in-situ produced H₂O₂ cooperatively enhanced W and Mo deposition in microbial electrolysis cells (MECs), achieving deposition of 81.5 ± 1.7% (W) and 97.2 ± 2.4% (Mo) with a Coulombic efficiency (CE) of 82.5 ± 1.5%. Only 52.0 ± 1.4% (W), 75.7 ± 2.1% (Mo) and 38.6 ± 1.4% (CE) were observed in the controls in the absence of both in-situ produced H₂O₂ and light irradiation, 62.4 ± 2.2% (W), 84.1 ± 1.5% (Mo) and 51.3 ± 1.7% (CE) with light irradiation only, and 57.6 ± 1.6% (W), 81.7 ± 1.7% (Mo) and 71.6 ± 0.8% (CE) with in-situ produced H₂O₂ only. A shift from the in-situ produced H₂O₂ at a period of 2.5 h to the absence of this species for another 2.5 h further improved W (98.1%) and Mo (100%) deposition. These results provide a sustainable and environmentally benign approach for efficient W and Mo recovery. The evidence of influence factors including light irradiation, in-situ produced H₂O₂, shift from in-situ produced H₂O₂ to the absence of this species, and applied voltage can contribute to improving understanding of and optimizing W and Mo deposition in MECs.

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1. Introduction

Tungsten (W) and molybdenum (Mo) are un-abundant transition metals, which impart high-strength, high hardness, good electrical and thermal conductivity, and good corrosion resistance to strong acids [1–3]. The annual global production in 2011–2012 is 73,000 t (W) and 2,64,000 t (Mo) with over 80% of W and nearly 40% of Mo being produced in China with requirement of a significant consumption of energy (11580 kWh/ton) [2]. As a result, large amounts of acidic ore dressing wastewater rich in W and Mo are available, which has to be neutralized at the industrial site before they can be discharged into a sewage system or wastewater treatment plant [4]. Alternatively, recovery of W and Mo from this wastewater has attracted great attention due to the shortage of natural ores and environmental/ecological considerations [5]. Conventional processes including electrochemical deposition, solvent extraction, ion exchange and adsorption have been employed

for recovering W and Mo from wastewater [4–11]. The high chemical costs and high energy consumption, as well as serious second pollution associated with these methods, however, require more environmental friendly and cost-effective strategies for efficient W and Mo recovery.

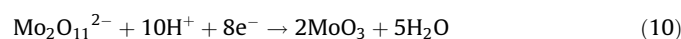
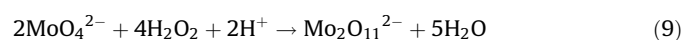
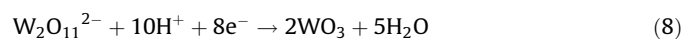
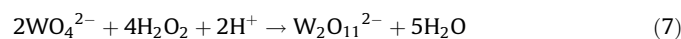
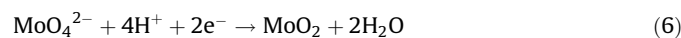
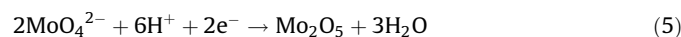
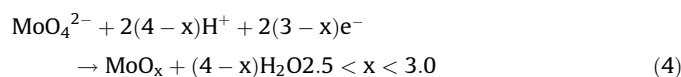
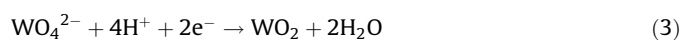
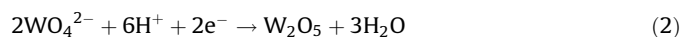
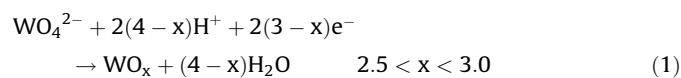
Microbial electrolysis cells (MECs) and microbial fuel cells (MFCs) have recently emerged as promising methods for anodic organic wastewaters treatment with simultaneously producing the reducing equivalents for generation of cathodic products such as heavy metals and H₂O₂, and even in-situ utilization of H₂O₂ for many recalcitrant wastes treatment [12–17]. The acidic W and Mo ore dressing wastewater can be directly used as catholyte in MFCs or MECs for W and Mo deposition, which always requires consumption of H⁺ and electrons according to Eqs. (1)–(10). Although the self-driven MFC-MEC systems have been conceptually explored for W and Mo deposition, the cathodic anaerobic and weak reductive environment led to the occurrence of less W and Mo deposition with lower efficiencies [18]. Due to the fact of aqueous W(VI) and Mo(VI) mostly reduced to dissolved tungsten blues and molybdenum blues (Eqs. (1) and (4)) with a small portion of solid W and Mo oxides (Eqs. (2) and (3), (5) and (6)) on the electrodes, chemical H₂O₂ is externally added to thermodynamically form intermediates of peroxo-tungstate and

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peroxo-molybdate (Eqs. (7) and (9)) for enhanced W and Mo deposition in conventional electrochemical processes (Eqs. (8) and (10)) as schematically shown in Fig. 1 [6,19–21]. Based on this principle, MFCs under an aerobic cathodic atmosphere can achieve W and Mo deposition via the formation of either peroxo-tungstate or peroxo-molybdate with in-situ produced H_2O_2 [22]. However, the W and Mo deposition is still not appreciable. Much effort is still needed to employ this bioelectrochemical technology for more efficient W and Mo deposition in order to broaden the applicable field of this technology. Considering the facts of lower cathode potentials and the more in-situ H_2O_2 production in MECs than in MFCs [6,14,15,21], MECs is expected to enhance W and Mo deposition via thermodynamic favor for not only W(VI) and Mo(VI) direct reduction, but also more in-situ H_2O_2 production and subsequent formation of more peroxo-tungstate and peroxo-molybdate (Fig. 1).

Light irradiation reportedly enables to either lower the potentials of W and Mo oxides-coated carbonaceous cathodes for hydrogen evolution in conventional electrochemical processes [23,24] or decrease the electron transfer resistance of CuO nanowire cathodes of MFCs using oxygen as an electron acceptor [25]. This allows the in-situ electrogeneration of H_2O_2 from two-electron reduction of injected O_2 [24]. In the presence of W(VI) and Mo(VI) in catholyte of MECs, this in-situ produced H_2O_2 under light irradiation could be utilized to form peroxo-tungstate/peroxo-molybdate and thus enhance W and Mo deposition (Fig. 1). Alternatively, this H_2O_2 could be utilized for generation of radical $\cdot OH$ as accepted for authors working in photocatalysis and photoelectrocatalysis [24] and thus might disfavor for W and Mo deposition. Whether or not light irradiation could enhance W and Mo deposition through the in-situ produced H_2O_2 for more peroxo-tungstate/peroxo-molybdate rather than direct the H_2O_2 for $\cdot OH$ generation, needs to be clarified. In addition, the lower cathode potentials created by light irradiation were also expected to favor for direct W(VI) and Mo(VI) reduction and thus improve W and Mo deposition (Fig. 1). Despite that light irradiation changes cathode potentials for hydrogen evolution, reduction of oxidative heavy metals and azo dye, as well as tetracycline degradation in bioelectrochemical systems or conventional photocatalytic processes [23–35], light irradiation as a strategy for enhanced W and Mo deposition in MECs is scarcely reported.



An acidic initial pH favors for not only W and Mo deposition in conventional electrochemical processes (Eqs. (1)–(6), (8) and (10)) [36] but also more in-situ produced H_2O_2 in MECs with air sparging [14]. As a consequence, with the prolonged operational time, catholyte pH would unavoidably increase and thus disfavor for W and Mo deposition, compared to the absence of in-situ produced H_2O_2 with N_2 sparging. A shift from an initial air sparging to a N_2 sparging thereafter during one fed-batch operation period would not only delay the pH increase and thus create an appropriate acidic pH for efficient W and Mo deposition, but also eliminate mass transfer loss in catholyte, both of which may favor for efficient W and Mo deposition.

In this study, W and Mo deposition in the presence of both light irradiation and in-situ produced H_2O_2 in MECs was systematically investigated. A shift from an initial air sparging to a N_2 sparging was intentionally used to further achieve more efficient W and Mo deposition. Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were employed to evaluate system performance. The morphologies and valences of products on the cathodes were analyzed by scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). This study provides an innovative and efficient approach for satisfactory W and Mo deposition, and the evidence of influence factors including shift from air to N_2 sparging, and applied voltage can contribute to improving understanding of and optimizing W and Mo deposition in MECs.

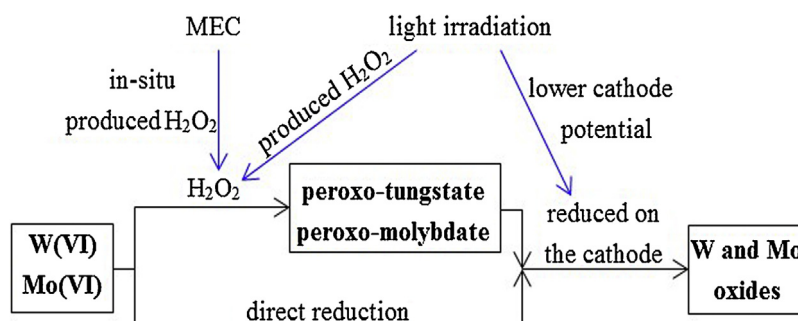


Fig. 1. Schematic diagram of W and Mo deposition in the presence of both in-situ produced H_2O_2 and light irradiation in MECs.

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