Supporting Information

Mutual benefits of acetate and mixed Tungsten and Molybdenum for

their efficient removal in 40 L microbial electrolysis cells

Liping Huang<sup>1,\*</sup>, Fuping Tian<sup>2</sup>, Yuzhen Pan<sup>2</sup>, Liyuan Shan<sup>1</sup>, Yong Shi<sup>1</sup>, Bruce E Logan<sup>3</sup>

1. Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of

Education (MOE), School of Environmental Science and Technology, Dalian University of

Technology, Dalian 116024, China

2. College of Chemistry, Dalian University of Technology, Dalian 116024, China

3. Department of Civil and Environmental Engineering, The Pennsylvania State

University, University Park, Pennsylvania, 16802

Corresponding author: (Huang L.) <a href="mailto:lipinghuang@dlut.edu.cn">lipinghuang@dlut.edu.cn</a>

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## **S2** Materials and methods

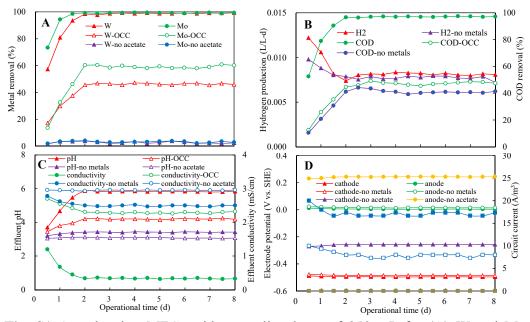
## S2.1 Bacterial community analysis

Electrodes samples were fragmented using sterile scissors, with cells extracted by rinsing three times with sterile water, and concentrated by centrifugation for 10 min at 10,280 × g. DNA extraction and quantitation, and PCR amplification were performed before sequencing using an Illumina Miseq following standard procedures (Huang et al., 2015; Song et al., 2018). The data were optimized through removal of low-quality sequences, unrecognized reverse primers, and any ambiguous base calls, with a length < 200 bp. High quality sequences were aligned, grouped into OTUs (97% similarity) using the uclust algorithm, and a representative sequence from each OUT was classified phylogenetically assigned to a taxonomic identity (phylum, class, and genus level) using the RDP Naíve Bayesian rRNA classifier at a confidence threshold of 90%. Rarefaction curves, Shannon and Simpson diversity indices, and species richness estimates of Chao1 were generated for each sample using QIIME software (v1.3.0). All analyses described were conducted in triplicates, and the means were reported.

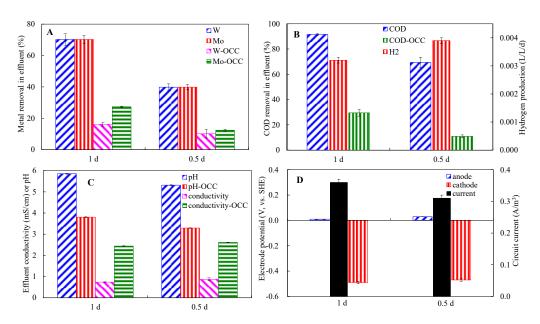
## S2.2 Measurements and analyses

Electrochemical impedance spectroscopy (EIS) was conducted using a potentiostat (VSP, BioLogic) with a three electrode system, with one of the electrodes as the working electrode, a Ag/AgCl reference electrode (195 mV vs. SHE) located 1 cm away from the cathode in the cathodic chamber or the anode in the anodic chamber, and a Pt foil (2 × 4 cm) counter electrode placed in the anodic or cathodic

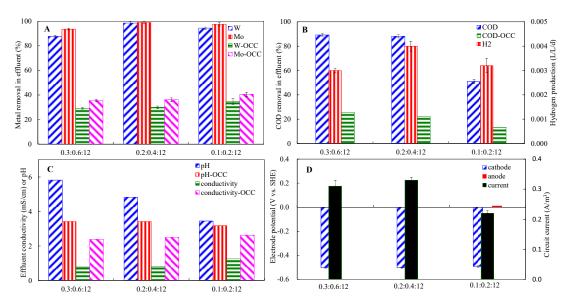
chambers. Impedance analysis was conducted at set cathode (-0.2 V) or anode (0.0 V) potentials under OCCs with either the bare electrodes, or the electrodes deposited with W and Mo (obtained after a 30-day continuous operation) to determine the influential W and Mo deposits. EIS frequency ranged from 100 kHz to 10 mHz, with a sinusoidal perturbation of 10 mV amplitude. The equivalent circuits and detailed values of different resistances were obtained as previously described (Zhang et al., 2015; Wu et al., 2016).



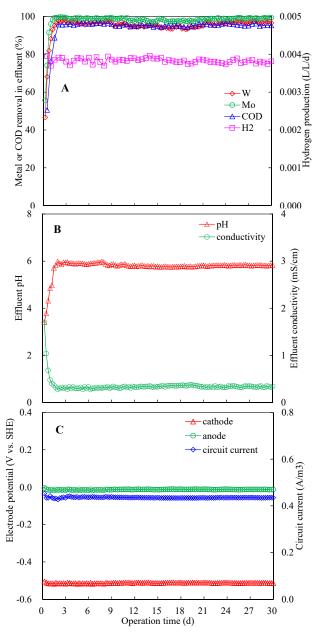
**Fig. S1** One-chamber MECs with a small volume of 250 mL for (A) W and Mo removals, (B) COD removal and hydrogen production, (C) effluent pH and solution conductivity, and (D) electrode potential and circuit current in the presence of circuit current, or in the controls of open circuit conditions (OCC) or in the absence of either metals or organics (W:Mo:acetate = 0.5:1.0:24; HRT: 2 d)



**Fig. S2** Comparison of (A) W and Mo removals, (B) COD removal and hydrogen production, (C) effluent pH and solution conductivity, and (D) electrode potential and circuit current at an HRT of 1 d or 0.5 d (W:Mo:acetate = 0.5:1.0:12).



**Fig. S3** (A) W and Mo removal, (B) COD removal and hydrogen production, (C) effluent pH and solution conductivity, and (D) electrode potential and circuit current at influent strengths of W:Mo:acetate of 0.3:0.6:12, 0.2:0.4:12 or 0.1:0.2:12 (HRT: 1 d).



**Fig. S4** (A) W and Mo removal, COD removal and hydrogen production, (B) effluent pH and solution conductivity, and (C) electrode potential and circuit current at influent strengths of W:Mo:acetate of 0.5:1.0:24 and an HRT of 2 d.

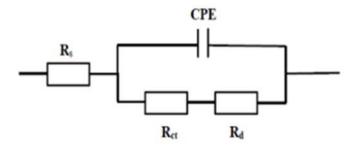
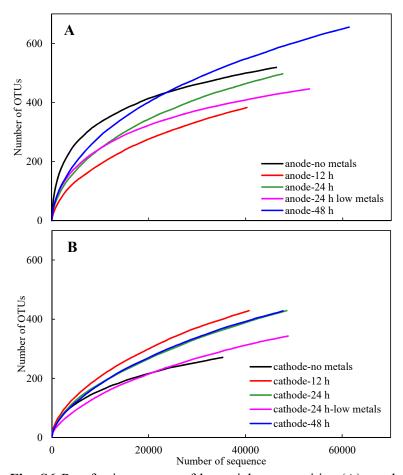
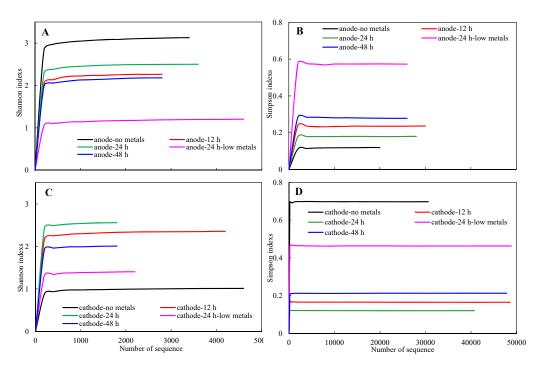


Fig. S5 EIS equivalent circuits.



**Fig. S6** Rarefaction curves of bacterial communities (A) on the anodes and (B) the cathodes well-developed under different HRTs or influent strengths. The OTUs were defined by a distance limit of 0.03.



**Fig. S7** (A and C) Shannon and (B and D) Simpson indexes for bacterial communities on (A and B) the anodes and (C and D) the cathodes.

**Table S1** Component analysis of internal resistances of the cathodes and the anodes at the end of a-30 day operation, and the bare electrodes.

	R <sub>s</sub> (ohm)	R <sub>ct</sub> (ohm)	R <sub>d</sub> (ohm)
bare cathode	23	56	83
cathode-30th d	28	105	73
bare anode	24	77	52
anode-30th d	36	142	66

Table S2 Elemental composites on the cathodes and the anodes analyzed by EDS

Element	Weight (	%) Atom (%)	Weight (%	(%) Atom (%)	
		cathode	anode		
С	40.1	80.7	70.0	90.2	
О	2.1	2.9	4.4	4.2	
Na	1.1	1.3	3.1	2.2	
W	20.8	4.8	6.7	1.0	
Mo	35.1	10.3	14.7	2.4	
others	0.8	0.0	1.2	0.1	
Total	100	100	100	100	

Table S3 Similarity-based OTUs and species richness and diversity estimates

Samples	Reads	OTU	ACE	Chao1	Shannon	Coverage	Simpson
Anode-no metals	46317	519	643	630	3.18	0.997	0.121
Anode-12 h	40233	383	744	569	2.33	0.996	0.240
Anode-24 h	47614	497	873	686	2.55	0.996	0.183
Anode-24 h-low metals	53128	446	576	559	1.23	0.998	0.578
Anode-48 h	61307	655	968	919	2.23	0.996	0.282
Cathode-no metals	35304	271	461	386	1.03	0.997	0.705
Cathode-12 h	40746	429	909	673	2.39	0.995	0.167
Cathode-24 h	48556	429	1038	767	2.63	0.996	0.122
Cathode-24 h-low metals	48818	343	726	513	1.44	0.997	0.469
Cathode-48 h	47803	428	1014	702	2.05	0.996	0.215
Total	469826	4400		•			

## References

Huang, L., Wang, Q., Jiang, L., Zhou, P., Quan, X., Logan, B.E., 2015. Adaptively evolving bacterial communities for complete and selective reduction of Cr(VI), Cu(II) and Cd(II) in biocathode bioelectrochemical systems. Environ. Sci. Technol. 49, 9914-9924.

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