

Electrochemical sulfide removal on carbon electrode in sulfate reducing bacteria microbiological fuel cell

Bijuan Zheng, Hongfang Liu\*

School of Chemistry and Chemical Engineering,  
Huazhong University of Science and Technology,  
Wuhan, 430074, P. R. China

The conversion of sulfur-compounds in microbial fuel cell (MFC) has been extensively studied<sup>[1-7]</sup>. The main problem related to the biological sulfate reduction process is the generation of sulfide inhibits bacterial growth, decreases the rate of sulfate reduction, and causes physical or biological constraints that may lead to process failure. In the present study, an air-cathode MFC was successfully started up with *Desulfotomaculum* as electro-active bacteria. Electrochemical sulfide removal on carbon paper was studied. The sulfide oxidizing process was analyzed using the electrochemical methods. Cyclic voltammetry and X-ray photoelectron spectroscopy indicated that the sulfide oxidizing behavior on carbon electrode was an irreversible two-step electrochemical reaction: the metabolic sulfides were firstly oxidized to sulfur and/or polysulfides; and then the intermediates could be oxidized to sulfite if the redox potential was sufficiently positive, as shown in Fig.1. This result provided a tangible proof for the popular hypothesis that the electron generation object was the metabolic sulfide.

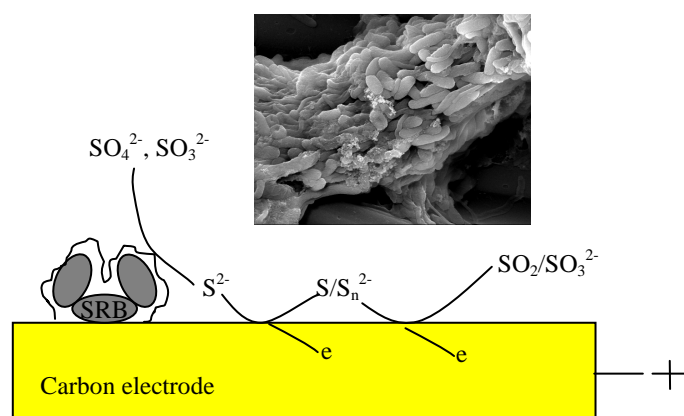


Fig. 1. Conversion of sulfur-compounds in SRB-MFCs

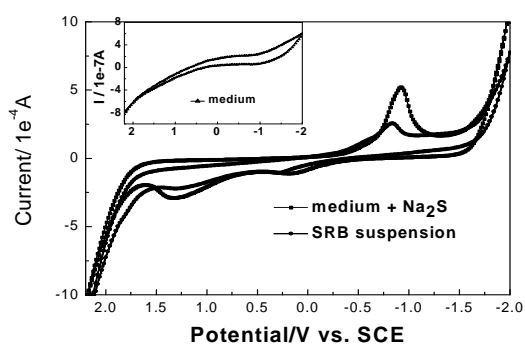


Fig. 2. Cyclic voltammety curves of SRB suspension and abiotic sulfide on glassy carbon electrode (10 mV/s).

The electrochemical activity of SRB solution was measured using cyclic voltammetry (CV) in Fig. 2. The glassy carbon electrodes immersed medium inoculated with SRB and in fresh medium containing  $\text{Na}_2\text{S}$  exhibited the similar CV curves figured with two characteristic oxidation peaks and one reduction peak, and even the position of peaks in biotic and abiotic sulfide were close. In addition, CV performed on a GC electrode immersed in control medium free of  $\text{S}^{2-}$  showed no oxidation/reduction

peak. It could be concluded that the biotic sulfide reduced from sulfate by SRB contributed to the anodic reaction in SRB solution.

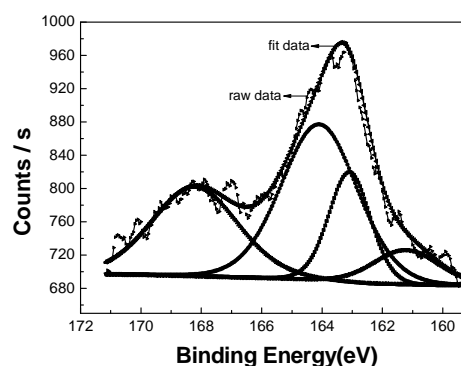


Fig. 3. XPS S2p spectra of biofilms on carbon cloth anode.

Table 1. The electronic binding energy corresponding to S-containing substances

Substance	FeS	FeS <sub>2</sub>	S	SO <sub>3</sub> <sup>2-</sup>	SO <sub>2</sub>
Binding Energy (eV)	161.6	162.9	164.0	167.5	168.1

As shown in Fig.3, the sulfur of the biofilms presented not only as FeS and FeS<sub>2</sub>, but also as S, SO<sub>2</sub> and SO<sub>3</sub><sup>2-</sup>. The formation of FeS and FeS<sub>2</sub> were attributed to the presence of iron in the medium. In addition, the contents of the element O and Fe in EDXA were very small. Considering the equilibrium potentials for these electrochemical processes are close in neutral solution, the sulfur containing compounds in the biofilms probably exist in the form of elemental sulfur and/or polysulfides. Therefore, the intermediates of sulfur re-oxidation were probably sulfur and/or polysulfide, which could be oxidized to SO<sub>3</sub><sup>2-</sup> if the redox potential was sufficiently positive. In addition, a large portion of sulfur survived on this electrode, and it's easy to remove the deposited sulfur. Therefore, it provided a potential for sulfur-based pollutants removal. On the other hand, the decrease of sulfide concentration alleviated the pressure to bacterial growth and sulfate reduction. It's important for the sustained development of the wastewater treatment system.

#### References

- Habermann, W.; Pommer, E. Applied microbiology and biotechnology 1991, 35 (1), 128-133.
- Ieropoulos, I. A.; Greenman, J.; Melhuish, C.; Hart, J. Enzyme and microbial technology 2005, 37 (2), 238-245.
- Zhao, F.; Rahunen, N.; Varcoe, J. R.; Roberts, A. J.; Avignone-Rossa, C.; Thumser, A. E.; Slade, R. C. Biosensors & bioelectronics 2009, 24 (7), 1931-6.
- Garcia-de-Lomas, J.; Corzo, A.; Carmen Portillo, M.; Gonzalez, J. M.; Andrades, J. A.; Saiz-Jimenez, C.; Garcia-Robledo, E. Water research 2007, 41 (14), 3121-3131.
- Zhang, L.; De Schryver, P.; De Gussem, B.; De Mynck, W.; Boon, N.; Verstraete, W. Water research 2008, 42 (1), 1-12.
- Sun, M.; Mu, Z. X.; Chen, Y. P.; Sheng, G. P.; Liu, X. W.; Chen, Y. Z.; Zhao, Y.; Wang, H. L.; Yu, H. Q.; Wei, L.; Ma, F. Environ Sci Technol 2009, 43 (9), 3372-7.
- Xu, X. J.; Chen, C.; Wang, A. J.; Fang, N.; Yuan, Y.; Ren, N. Q.; Lee, D. J. Bioresource technology 2012, 116, 517-21.