Supplementary Materials: Bioelectrochemical Changes during the Early Stages of Chalcopyrite Interaction with *Acidithiobacillus Thiooxidans* and *Leptospirillum* sp.

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1. Potentiostatic modification of massive chalcopyrite electrodes (MCE)

Mineral coupons of 1.0 cm^2 were coated with Cu via electrolytic deposit using a $CuSO_4$ solution, to improve the current distribution; a Cu wire was added with a silver solder to enhance the electrical contact of the MCE. Finally, the electrode was imbibed in epoxy resin and the exposed MCE surface was polished with a water sandpaper until it reached a mirror-like surface condition. The MCE were maintained in desiccators under anaerobic conditions until their use.

The potentiostatic modification was conducted with an EPSILON BASi 2.10.73 potentiostat (Indiana, USA), at 25°C, in a typical electrochemical, three-electrodes device; the MCE was used as working electrode, the reference electrode was a saturated sulfate electrode, Hg/Hg_2SO_4 (0.615 V vs. SHE, the standard hydrogen electrode), and a graphite rod (Alfa Aesar, Massachusetts, USA, 99.9995% purity) was used as counter-electrode. These MCE* were then achieved by application of anodic pulse (Ean, 3600 s); ATCC-125 culture at pH 2.0 was the electrolyte, hence emerging S^0 and S_n^{2-} compounds (reduced sulfur species, RSS), as a function of the applied Ean, from 0.36 to 1.015 V vs. SHE. The Raman spectra were recorded with a triple subtractive monochromator (T64000 Jobin Yvon spectrometer, Kyoto, Japan) equipped with a confocal microscope, Olympus BH2-UMA (λ= 514 nm). At least 10 spectra were recorded for each MCE* surface. Calibration was done using a Si wafer, which showed a single peak at 521 cm^{-1}. The noise/signal ratio was better than 100.

After the CV and Raman analysis of the MCE, anodic Ean of 695 mV and 915 mV were chosen to electrogenerated two different RSS, since at these Ean was observed minor electrooxidation and low activation current (anodic peak a1 at the open circuit potential, OCP; Figure. S1a and b). Raman peaks for these MCE* indicate the predominance of S_n^{2-} and heptagonal sulfur S_7 for Ean < 695 mV; such electrode was referred as MCE*-S_n^{2-}. Octagonal sulfur S_8 was detected at Ean > 915 mV, for MCE*-S^0. The reactivity j_{act} and of the MCE*–S_n^{2-} was significantly lower than of the MCE*-S^0 (Fig. S1 c and d); thus, more energy is necessary to (bio)oxidize the MCE*-S^0 than for MCE*-S_n^{2-} surface.

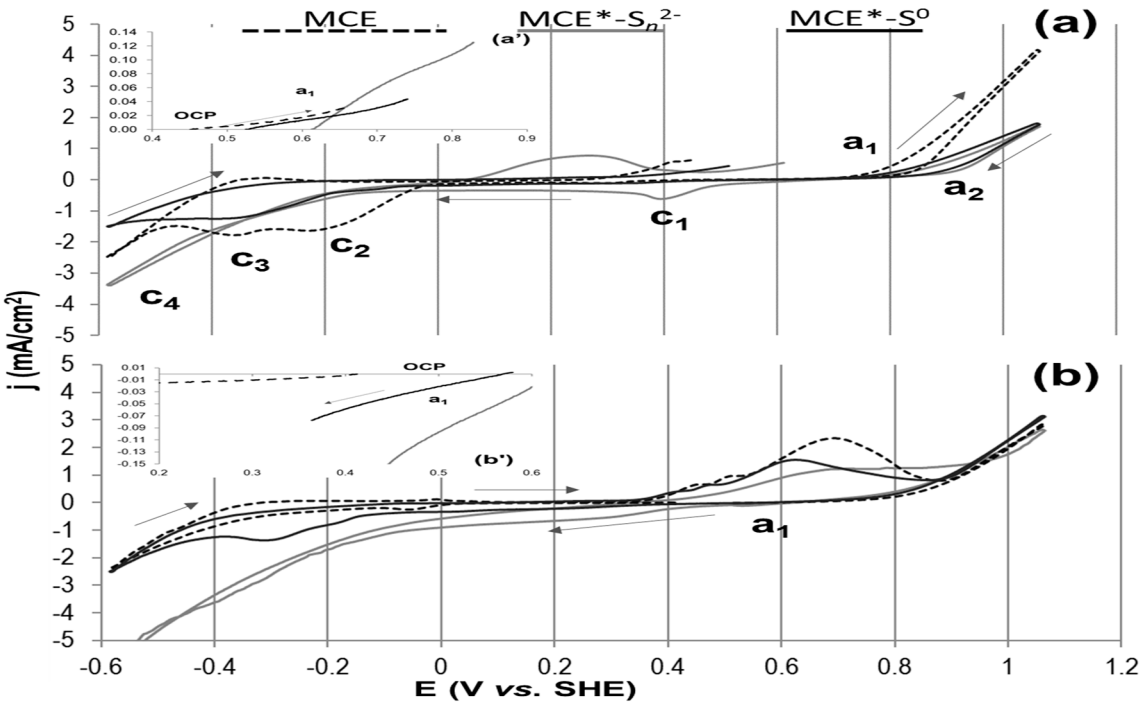

Figure S1. Voltammograms in positive (**a**) and negative (**b**) potential sweep of pristine MCE (dotted line), and electrooxidized EMC at 695 mV, MCE*-S_n^{2-} (gray line), and at 915 mV, MCE*-S^0 (black line), in ATCC-125 medium pH 2. Scan rate: 20 mV/s with stirring; the potential scan was initiated at the OCP.

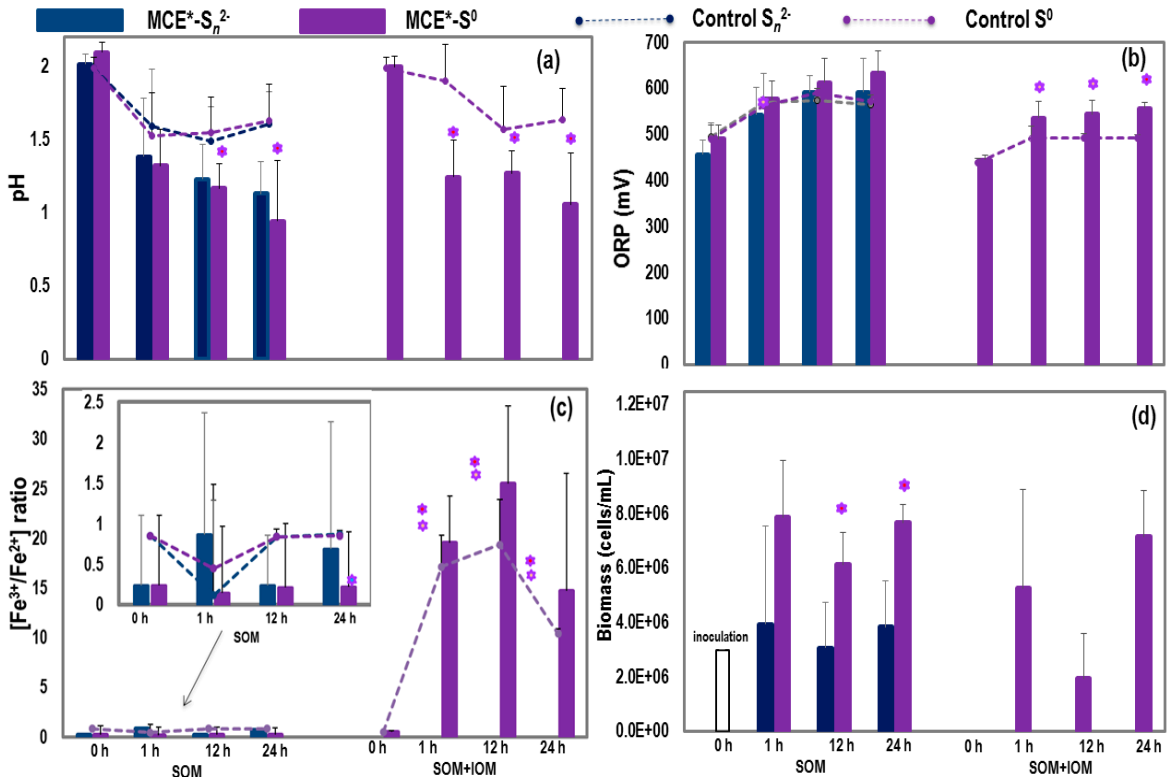

Figure S2. Certain characteristics of the media as electrolyte (after 1, 12 and 24 h of the exposure of MCE*-S_n^{2-} (blue) and MCE*-S^0 (purple) to SOM or SOM + IOM media (abiotic controls; doted lines) and cultures (biotic; columns): pH (**a**); ORP (**b**), soluble Fe^{3+}/Fe^{2+} (**c**), and biomass of non-attached bacteria (**d**). Data: Average values (n = 3) and standard deviation (error bars). *: Values significantly different from both, controls and surficial SRS (−S_n^{2-} or −S^0).