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Bioinspired complex in formate dehydrogenase for formate production from CO₂

Jessica Crivelaro Pacheco^{1,2}, Luana Cristina Italiano Faria¹, Chao Chi Kuo², Ariel Furst², Frank Nelson Crespilho¹

¹São Carlos Institute of Chemistry, University of São Paulo (USP), São Carlos, SP 13566-590, Brazil.

²Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

jessicacrivelaro97@gmail.com

Metal chelation by amino acids plays a crucial role in enzymatic catalysis, providing structural stability and forming catalytic centers in metalloproteins. Protein metal centers found in nature therefore serve as valuable models for the development of biomimetic catalysts¹. In the oxygen-tolerant formate dehydrogenase from *Rhodobacter aestuarii* (RcFDH), a cysteine residue coordinates the Mo center, playing a key role in the catalytic function of the enzyme. Inspired by this natural system, this study aims to synthesize a biomimetic catalyst based on RcFDH for the reduction of CO₂ to formate. The biomimetic was obtained from the electrodeposition of a solution of L-cysteine and sodium molybdate (6:1) on the carbon cloth electrode. The pair of peaks at 0.35/0.03 V observed in the electrodeposition voltammogram was attributed to the Mo(VI)/Mo(V) redox couple, while the peak that appears at 0.07 V in the first cycle and then shifts to -0.03 V in the last electrodeposition cycle is attributed to Mo (IV) species that can be consumed to form Mo(V/VI) species; the current density at this peak decreases, while that at the peak at 0.03 V increases. The peak that starts at 0.9 V and shifts to 0.6 V is attributed to the oxidation of the SH functional group of Cys. The biomimetic was characterized by SEM, EDX, XPS and FTIR, which allowed us to obtain insights into its structure. The SEM images show large globular structures in the carbon fiber, which are characteristic of molybdenum blue compounds. EDX demonstrated the presence of cysteine (derived from sulfur) and molybdenum in the electrodeposited film, which is an indication that cysteine is a complex with Mo and does not act only as a reducing agent. The Mo to S atom ratio of 1:7 obtained by EDX is very close to the ratio of 1:6 predicted for the biomimetic. By FTIR was observed absence of peak at 2550 cm⁻¹ attributed to S–H stretching vibration in both electrodes implied S–H was oxidized, all bands related to NH₃ asymmetric bend had a decrease in intensity, indicating that complexation with Mo occurs in this functional group. A small shift of 2 cm⁻¹ is also observed at 1620 cm⁻¹ and 1580 cm⁻¹. Complexation also occurs in the COO⁻ group, since it is possible to observe a decrease in the intensity of the 1483 cm⁻¹ band, in addition to a small shift of 2 cm⁻¹ in the band related to this functional group. It is also possible to observe a band at strong stretching frequency of S=O from ⁻SO₃H in 965 cm⁻¹, indicating as mentioned in the electrodeposition mechanism formation of cysteic acid by the oxidation of cystine. For complex spectrum is possible to see the appearance of a band at 947 cm⁻¹, a shoulder at 749 cm⁻¹ and a band shift at 609 cm⁻¹ for electrode with complex. The band in the 947 cm⁻¹ region is reported for $\nu(\text{Mo=O})$ and $\nu_s(\text{Mo=O})$, while the band at 749 cm⁻¹ and a band shift at 609 cm⁻¹ may be related to $\nu(\text{Mo-O})$. In the XPS survey spectrum of the polyMocys film, it is possible to see the presence of peaks for sulfur (from cysteine) and Mo, showing that cysteine complexation occurred. The presence of Mo(V) and Mo(VI), confirmed by deconvolution of the high-resolution spectra in the Mo and S region, is a characteristic of the blue molybdenum compound, as previously reported in the literature³. The peak at 163 eV corresponds to the disulfide bond within the cystine molecule. In the N1s region, the peak at 400 eV corresponds to the amino group in cystine. N 1S, O 1S and S 2S undergo changes in the binding energy values for the blue molybdenum complex, indicating that there is coordination with Mo at these points. Finally, the formate obtained from the reduction reaction was quantified by HPLC, 0.33 mM of formate was obtained after application of -1.8V for 60 min.

¹ Graziela C Sedenho and others, 'Secondary Structure in Enzyme-Inspired Polymer Catalysts Impacts Water Oxidation Efficiency', *Advanced Science*, 11.25 (2024), p. 2402234.

