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Área: ELE

Bioelectrooxidation of Water Using Aporeconstituted-copper Proteins

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Highlights

Water is recognized as a plentiful source for water-splitting reactions aimed at generating molecular hydrogen (H_2) and oxygen (O_2). However, when seawater is used, its practical use is hindered by competing chlorine-related reactions occurring at the anode. To address this challenge, we developed a bioelectrooxidation approach utilizing apo-reconstituted proteins embedded with non-native copper(II) metal centers, dispersed within a heteropolysaccharide polymer shell. This strategy demonstrated notable improvements in water bioelectrooxidation under both alkaline conditions (pH 9) and seawater (pH 7.6). Notably, apo-reconstituted with Cu(II) centers exhibited an *onset* potential for the oxygen evolution reaction (OER) approximately 10 mV lower than Cu(II)P alone. Additionally, differential electrochemical mass spectrometry (DEMS) was employed to track reaction products. The findings were further substantiated by *in situ* X-ray absorption near-edge structure (XANES) spectroscopy and electrochemical analysis, which provided insights into the redox transitions between Cu^{2+} and Cu^{+} states.

Abstract

Biological molecules can be a source of inspiration to design new materials with unique properties, such as redox proteins. Artificial or semi-artificial redox proteins are hybrids of proteins with non-biological catalytic groups that has been explored to overcome the natural limits of biocatalysis in nature. Lessons from nature have been reported by several researchers in the field of the design of artificial hemeproteins or even hydrogenases, and many others with tunned catalytic properties in a combinatorial fashion. To create these redox proteins able to overcome the conversion of H_2O into desirable products, it is necessary to design the cofactor meticulously, as shown in Figure 1.

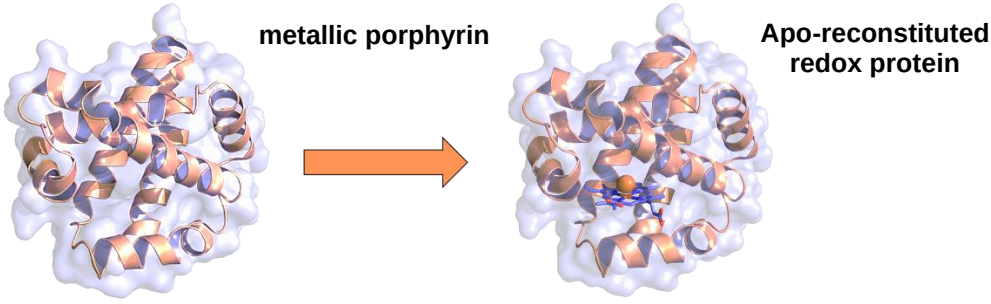

Figure 1. The protein “cage” (apoprotein shell) with a metallic porphyrin to obtain apo-reconstituted proteins.

Acknowledgments

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