## Local Investigations of Electrochemical Reactions for Biotechnological Applications

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The interface of redox proteins with electrode materials allows us to address fundamental biological questions and make use of such biological elements in the fabrication of electrode architectures for different biotechnological applications. Redox enzymes are highly active and selective biological catalysts, performing catalytic conversions with high yields under mild conditions, such as aqueous solutions, near-neutral pH, and ambient temperature and pressure. Therefore, they are widely studied in combination with electrodes targeting different applications. Among others, relevant examples include the implementation of biofuel cells for clean energy generation and sensing applications, and the development of novel catalytic materials used in bioelectrosynthesis aiming at the conversion of surplus residues into valuable products. In addition, the photosynthetic reactions enabled by light-activated protein complexes show an exceptionally high quantum yield, close to 100%, for the photon-to-electron conversion. As a result, there is a great interest in the study and coupling of photosynthetic elements with electrode materials for the fabrication of semi-artificial biodevices that will enable the conversion of solar light energy into electrical power and the synthesis of valuable products.

As it will be shown, we can fabricate various functional bioelectrodes consisting of electrically conductive materials and integrate isolated enzymes or photosynthetic elements for diverse applications. Taking advantage of relatively simple but powerful electrochemical characterization tools, the biohybrid materials are investigated to assess performance and electrochemical reactions at the biotic/abiotic interface, aiming at appropriate immobilization strategies and a productive interaction between the biological entities and the electrode surface. The possibility of performing electrochemical characterizations at the microscale allows direct local analysis with higher spatial and temporal resolution. Therefore, the use of miniaturized electrochemical probes offers important advantages for analytical purposes. Since the probe has a substantially smaller size compared to the investigated sample, the analysis is carried out with a rather low substrate consumption, which ensures minimal invasiveness and avoids possible interferences during the measurement. In addition, the small size of the sensor helps to increase mass transport rates and allows sample characterization and the measurement of catalytic reactions under operando conditions. Examples will be shown highlighting the possibility of performing electrochemical characterizations at the microscale when using micro(bio)sensors for direct local analysis.

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