The four copper enzyme laccase catalyzes the four-electron reduction of oxygen to water. The high electrode potential of this enzyme makes it interesting for its use in the development of biological fuel cells.[1] Laccase immobilization on the substrate is a determining step in the construction of the oxygen cathodes. In addition, the efficiency of the electronic transfer between the substrate and the enzyme is highly depending on the orientation of the biomolecule on the substrate.[2]

Laccase has been extensively studied as a catalyst in O$_2$ cathodes both for direct electron transfer (DET)[3] and mediated electron transfer (MET)[4-7] using a redox shuttle to the active site of the enzyme. In most previous studies it has been assumed that O$_2$ is reduced to 2 H$_2$O molecules from the mechanistic studies of Solomon.[8] However, in 2010 Scodeller[9] showed for the first time that osmium mediated laccase O$_2$ cathodes produced hydrogen peroxide which also inhibits the enzyme. This was further confirmed by the group of Minteer.[10]

We will present new experimental evidences on the inhibition of H$_2$O$_2$ both in DET and MET. Laccase electrodes were prepared using two different strategies. The first one uses a Layer-by-Layer Os$^{2+}$ polymer mediator with Trametes Trogii highly purified laccase and the second strategy takes advantages of highly porous carbon surfaces to optimize the direct electron transfer to the active site of the enzyme.