# ELECTROCHEMICAL STUDIES OF LYTIC POLYSACCHARIDE MONOOOXYGENASES ON HEMICELLULOSIC SUBSTRATES: DESCRIBING A NOVEL ENZYMATIC ACTIVITY

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## ABSTRACT

Lytic polysaccharide monooxygenases (LPMOs) are mono-copper biocatalysts that oxidatively degrade various polysaccharides and act in synergy with hydrolytic enzymes. These enzymes are classified into six auxiliary activity (AA) families of CAZy database (http://www.cazy.org/), based on the similarity of their primary amino acid sequences, the organism of origin and the substrate specificity. Genes encoding LPMOs in the AA9 family are abundant in filamentous fungi while their multiplicity remains puzzling. The latter has been suggested to relate to variation in the co-polymeric polysaccharide structures present in plant cell walls, thus corroborating the idea that different LPMOs act on various substrates, including cellulose and xylans, such as arabinoxylan, glucuronoxylan etc. In the present study, the activity of a C1-acting AA9 LPMO from the thermophilic filamentous fungi *Thermothelomyces thermophilus* (*Tt*LPMO9G) on oxidative cleavage of different hemicellulosic substrates, more specifically xylans of different biomass origin (hardwoods, softwoods, grasses) in presence and absence of an external reductant was studied. The results indicate a previously unreported xylan-degrading activity of an AA9 LPMO using such type of substrates alone. The ability of the substrate itself to provide electrons was evaluated electrochemically by cyclic voltammetry. The reversible ferrocyanide/ferricyanide reaction was employed as a mediator in the presence of xylan. The experiments, in combination with digital simulation, suggest the occurrence of a homogeneous catalytic reaction scheme where xylan acts as an electron donor. There results support the evidence obtained from the biochemical assays that LPMO can utilize electrons directly from the substrate in order to cleave the β-1.4 glycosidic bonds of the xylan backbone.

**ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ:** cyclic voltammetry, LPMOs, xylan, bioelectrochemistry

## ΑΝΑΦΟΡΕΣ

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