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Comprehending the Electrochemical Oxidation of Lignins Using Model Molecules

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Highlights

Electrochemical oxidation of lignin model molecules is dependent on the starting chemical. Electronic structure of these chemicals could be investigated by in situ spectroelectrochemistry.

Resumo/Abstract

For the expected transition from fossil fuels and resources, the use of biomass is highly desirable. This is meanly because it can be a source of closed carbon consumption, depending on the processing. However, after producing ethanol, e.g., tons of lignocellulosic biomass waste are generated. This mass is normally burned for thermoelectricity generation, and by so, the important chemical structures, such as all the aromatic rings presented in the lignin structure, are lost. The use of catalysts is interesting for the lignin depolymerization. This macromolecule is the largest aromatic renewable source known, but its complex connectivity between the monomers makes the process of breaking it on high value chemical difficult and expensive. Electrocatalysis is a cheap, selective and easily scalable method that can be used, but to do so, the kinetics and mechanisms need to be understood. Once again, the macromolecule complexity takes place. To overcome this problem, in this work we used model molecules, which are simpler and easier to study. All the molecules have the structures based on a phenolic backbone and substitutions on meta position (metoxyl) and on para (alkyl). The working electrode was a mechanic-, chemical- and electrochemically polished Ni plate, the reference and auxiliary ones a reversible hydrogen electrode and a Pt wire. The electrochemical cell was a quartz cuvette. The experiments were controlled by a spectroelectrochemical set up in the UV-Vis region, and the potentiostat a 302N Autolab. The j-E profile was observed to be dependent on the meta substitution and on the size of the alkyl chain. The spectra have shown a large band around 200 nm, related to the benzenoid transition (A \rightarrow B), which was followed with potential changes. This band presented not just changing in intensity, but also a small shifting depending on the electrode polarization and model molecules, suggesting different mechanisms, or intermediate accumulation, for different molecules.

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