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Non-precious metal nanoparticle electrocatalysts for electrochemical modification of lignin for low-energy and cost-effective production of hydrogen

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ABSTRACT

The electrochemical oxidation of lignin waste from pulping mills and biorefineries represents a potentially renewable process for generating hydrogen for energy storage with co-generation of industrial chemicals. Such a process could significantly reduce the cost of generating hydrogen by 1) a low voltage (low energy) anodic oxidation process and 2) generation of value-added chemicals that can be sold. To date, the electrochemical oxidation of large organic molecules like lignin has mainly been investigated on either expensive metals like platinum or on bulk metal electrodes (i.e., large, flat electrodes). Nanoparticle electrocatalysts, though, enhance the surface area available for electrochemical reactions and may lead to improved mass transport of reactants and products through the electrocatalyst layer. In addition, nanoparticle electrocatalysts allow for unique alloying and synergistic effects between different metals. We report here on non-precious metal nanoparticle electrocatalysts for the oxidation of lignin in alkaline media, and show that lignin oxidation occurs at lower voltages than oxygen evolution. Such results are a first step toward demonstrating that lignin oxidation at lower overpotentials than required for oxygen evolution could lead to efficient generation of hydrogen. We present 1) electrochemical evidence of lignin oxidation in alkaline media and 2) spectroscopic evidence of electrochemical modification of the lignin biopolymer.

Introduction

The electrochemical oxidation of large organic molecules is interesting because of its potential in applications ranging from the use of renewable raw materials and renewable energy to control for generating specific value-added products [1–5] with co-generation of hydrogen for energy storage. Lignin is an abundant, underutilized biomaterial with huge potential as a renewable raw material. As the primary waste from biorefineries and the kraft pulping process [6–9], large quantities of lignin are released to the environment or burned to generate heat. However, the chemical structure of lignin makes it a potentially ideal raw material for production of industrial chemicals like aromatic compounds, as shown in Fig. 1 [10,11].

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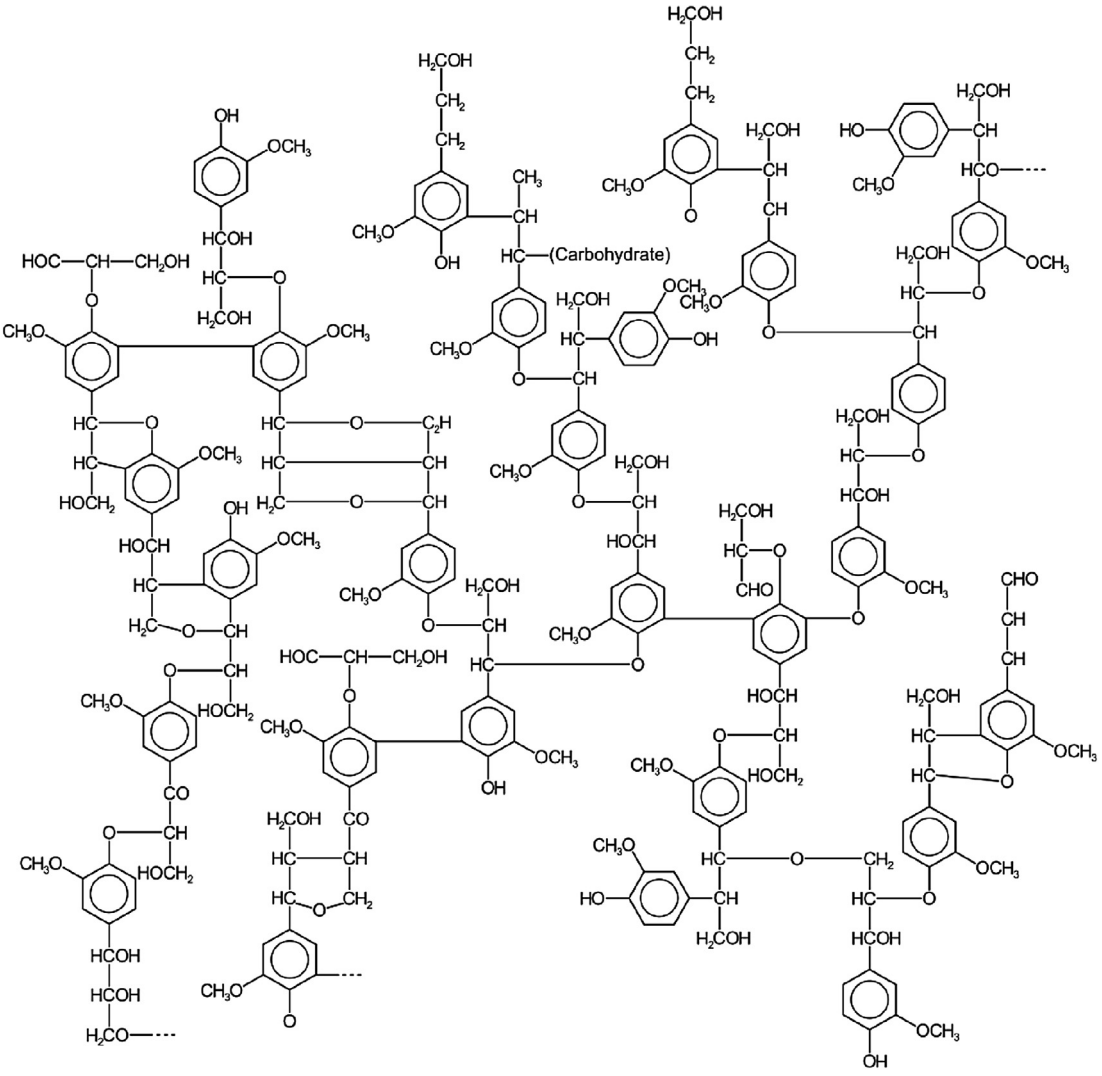

Fig. 1 – Possible structure of lignin (public domain license [10], original source Glazer and Nikaido [11]).

There are several methods to utilize lignin and other large biomass molecules either as a raw material for industrially relevant organic compounds or for hydrogen production, including gasification in supercritical water [12,13] and catalytic steam reforming at high temperatures [14]. Unfortunately, catalytic conversion of the complex lignin biopolymer to industrial chemicals has not been able to overcome limitations. Catalyst development lags behind the required technology readiness level and selective oxidation of lignin to specific compounds is difficult to achieve in practice [7]. In addition, catalytic oxidation of lignin generates an unacceptable amount of solid residue, such as char [15]. Electrochemical pathways, on the other hand, provide a level of control over bond breaking in biopolymers as complex as lignin, and allow for generation of specific products or more tightly controlled molecular weight distributions. Advantages of electrochemical processes over catalytic processes are: 1) electrochemical oxidation provides a low-energy, precise method of generating active intermediates by control of electrode voltage [2]; 2) the current in the electrochemical cell corresponds to the rate of production of intermediates and final products; 3) separation and recycle of toxic solvents and reagents is obviated because electro-oxidation of lignin can be carried out in slightly basic solutions with simple electron transfer processes; 4) the electrochemical oxidation of lignin proceeds with simultaneous generation of H_2, which can be used as an energy storage medium. The last point is particularly salient, as lignin oxidation is expected to occur at lower potential than the oxygen evolution reaction, meaning that lignin-depolarized electrolyzer voltage could potentially be lower than water electrolyzer voltage. Key to such a system is the lignin oxidation mechanism, which, considering the structure of lignin (Fig. 1), is likely quite complex.

Electrochemical oxidation of lignin and other large organic molecules was investigated 20–35 years ago [16–24]. Many of those studies focused on generating H_2 via a lignin-depolarized electrolysis process [16,17,21,22] and were based on preliminary work carried out in the former USSR which focused primarily