Biomass Electrochemistry : from cellulose to sorbitol

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1.1 Biomass

Fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. Unfortunately, the growing demand for fossil fuel resources comes at a time of diminishing reserves of these nonrenewable resources, such that the worldwide reserves of oil are sufficient to supply energy and chemicals for only about another 40 years, causing widening concerns about rising oil prices.[1]

Biomass, biological material from living, or recently living organisms, most often referring to plants or plant-derived materials, can serve as a renewable source for both energy and carbon. Plant remains the largest biomass energy and chemical source today including forest residues. Biomass energy is derived mainly from several distinct sources i.e. wood, plants, waste, landfill gases, and alcohol fuels.

Biomass-derived energy products have been utilized since the time when people began burning wood to make fire either to generate electricity via steam turbines (or gasifiers) or to produce heat via direct combustion. There are a number of technological options available to make use of a wide variety of biomass types as a renewable energy source. First, thermal conversion processes (i.e. combustion, pyrolysis, and gasification) use heat as the dominant force to convert biomass into another chemical form i.e. syngas. Second, chemical processes (i.e. Fisher-Tropsch synthesis, methanol production) are used to produce a fuel that is more conveniently used, transported or stored. Third, biochemical processes have been developed in nature by using enzymes of bacteria, micro-organisms to break down the molecules of biomass.

There are many important advantages of producing hydrocarbon fuels and chemicals from biomass. First of all, biomass-derived energy reduces green house gas emissions since biomass does not release “new carbon” into the atmosphere compared to fossil fuels. Second, “green” hydrocarbons are the same as those currently derived from petroleum. Therefore, it will not be necessary to modify existing infrastructure. Third, biomass-based hydrocarbon fuels are produced at high temperatures, which allows for faster conversion reactions in smaller reactors. Thus, processing units can be placed close to the biomass source.[2] Current advances in agriculture and biotechnology have made it possible to produce inexpensive biomass. In this respect, the “Roadmap for Biomass Technologies”, a report authored by 26 leading experts, has predicted that 20% of transportation fuel and 25% of chemicals will be produced from biomass by 2030.[3]

As the most important skeletal component in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties formed by the repeated connection of d-glucose building blocks, the highly functionalized, linear stiff-chain homopolymer.[4] Since cellulose cannot be digested by human beings, its use, unlike corn and starch, will not impose a negative impact on food supplies.[5] The most attractive routes for cellulose utilization are its conversion into energy and useful organic compounds by catalysis. The key bottleneck for cellulosic-derived fuels and chemicals is the lack of technology for the efficient conversion of biomass into desired products. Therefore, there’s no doubt that chemistry, chemical catalysis, thermal processing, and engineering have to play an essential role in the conversion of cellulosic biomass into green fuels and chemicals.

1.2 Catalysis

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst, which is not consumed by the chemical reaction. Catalysis is one of the most important and widely-spread concepts of chemistry and it has been estimated that 85-90% of all chemicals and materials are produced in catalytic processes.[6] Nature is also full of catalysts in the form of enzymes, which are vital to all chemical reactions taking place in organisms.

Catalysts work by providing an (alternative) mechanism involving different transition states and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed down by a kinetic barrier. The catalyst may increase both reaction rate and the selectivity.

Catalysis can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate or not. Biocatalysis (such as enzymes) are often seen as a separate group.

- Heterogeneous catalysis: catalysis where the phase of the catalyst differs from that of the reactants. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries.

- Homogeneous catalysis: the catalyst exists in the same phase as the reactants. Most commonly, a homogeneous catalyst is a molecule co-dissolved in a solvent with the reactants.

- Biocatalysis: the use of natural catalysts, such as proteins and enzymes, to perform chemical transformations on organic compounds.

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects.[7] Electrocatalysis is the variation of rate of an electrochemical reaction with change in electrode material. An electrocatalyst is thus a heterogeneous catalyst at which charge transfer occurs between electrode and solution, the region where the charge distribution differs from that of the bulk phases.[8]

1.3 Biomass electrocatalysis

Biomass has the potential to be a valuable energy and chemical resource, but the complexity of biomass limits the access of electrocatalysis to produce feedstock (i.e. from cellulose to glucose). However, biomass derived alcohols have low volatility and high reactivity due to the high level of functionality (i.e. –OH, -C=O, -COOH groups), thus these feeds can be processed in liquid-phase catalysis. Therefore, recent application of electrocatalysis in biomass conversion is to generate hydrogen in direct alcohol fuel cell or electrolyzer from potential fuels (i.e. ethanol, ethylene glycol, and glycerol).[9-13] However, there are challenges of these approaches to develop a suitable catalyst for complete oxidation of biomass-derived alcohols to CO_2 and a resistant system for reactions up to 200°C.[14] Recently, co-generation of hydrogen and valuable chemicals from the partial oxidation of poly-ols has attracted immense research interests.[10,11,14] For instance, the selective oxidation of glycerol can be achievable to glyceraldehyde, glyceric acid, dihydroxyacetone, and formic acid (Chapters 2~4) with careful selection of catalysts, pH, and applied potential.

The real challenge in biomass electrocatalysis is to produce platform chemicals (i.e. glucose, sorbitol) from raw materials (i.e. cellulose) using electrochemistry. Although an extensive number of works has been devoted to the hydrolysis of cellulose using enzymes, mineral acids, supercritical water, and heterogeneous catalysts,[15-20] the application of electrochemical methods for cellulose conversion to generate feedstock has been limited mainly by the low solubility of cellulose in aqueous media.[21] Many years ago, Baizer and Nobe[22] introduced the acid-catalyzed cellulose hydrolysis by electrochemically generated acid (H^+) at the platinum anode in an electrochemical cell. However, in this research, there's no direct interaction between cellulose and electrocatalyst, thus it provides very limited information of electrocatalysis. Recently, Li[23] reported the effect of hydroxyl radical (OH•) generated on a Pb/PbO_2 anode for depolymerization of cotton cellulose. In these cases, the electrode provides the active homogeneous catalysts or promoters (i.e. H^+, OH•) for the reaction. However, more detailed studies of reaction kinetics, intermediate species, and the effect of heterogeneous reactions between reactants and electrode have not been reported.

As a coupled reaction of cellulose hydrolysis to glucose, the hydrogenation of glucose to sorbitol is a very important reaction from synthetic and hydrogen storage points of view. Sorbitol is a promising platform polyol used as additives in foods, drugs, cosmetics, and various chemicals including vitamin C.[24] Using electrochemical approaches, sorbitol has been produced from aqueous glucose solution by applying certain current or potential on large-surface-area catalysts such as Raney-Ni[25,26] or poor (main group) metals at moderate pH (3~11)[25,27-29] and temperature ($<60^oC$)[25-29] in a flow reactor.[25-27,30] In addition to Raney-Ni[19,20], the most applied catalysts for the electrocatalytic hydrogenation of glucose are poor metals such as Pb,[27-30] Hg,[31] Pb(Hg),[27,31] and Zn(Hg)[25,31] since they suppress the hydrogen evolution reaction (HER).

Although electrocatalytic synthesis of sorbitol from glucose was once applied on an industrial scale,[32] unfortunately, a fundamental understanding of the reactions linking catalysts and voltammetry has not been reported mainly due to existing technical limitations regarding the online analysis of products. Since 1950 sorbitol has been produced by catalytic hydrogenation of glucose on Raney-Ni or noble metals such as Ru[33-35] under hydrogen pressure (1~350 atm) at various temperatures (ambient to 400°C).[36]

1.4 Scope of this thesis

The primary aim and objective of this thesis is to study and develop an electrochemical route for the conversion of cellulosic material into sorbitol in aqueous-phase solutions, within the framework of the CatchBio program, titled "Biomass Electrochemistry: from Cellulose to Sorbitol". In order to assess the potential of electrochemistry in biomass conversion, we were in need of an analysis method that is consistent with the time scale of the electrochemist's favorite technique, i.e. voltammetry. However, the combination of voltammetry especially with high-performance liquid chromatography (HPLC) has been limited due to the long analysis times in the column. To overcome the different time scale of voltammetry and chromatographic techniques, especially an HPLC system, we developed an online analysis system by using a fraction collector with a micrometer-sized sampling tip placed close to the working electrode. Figure 1 gives an overview of the electrochemical conversions described in this thesis by a combination of voltammetry and HPLC.

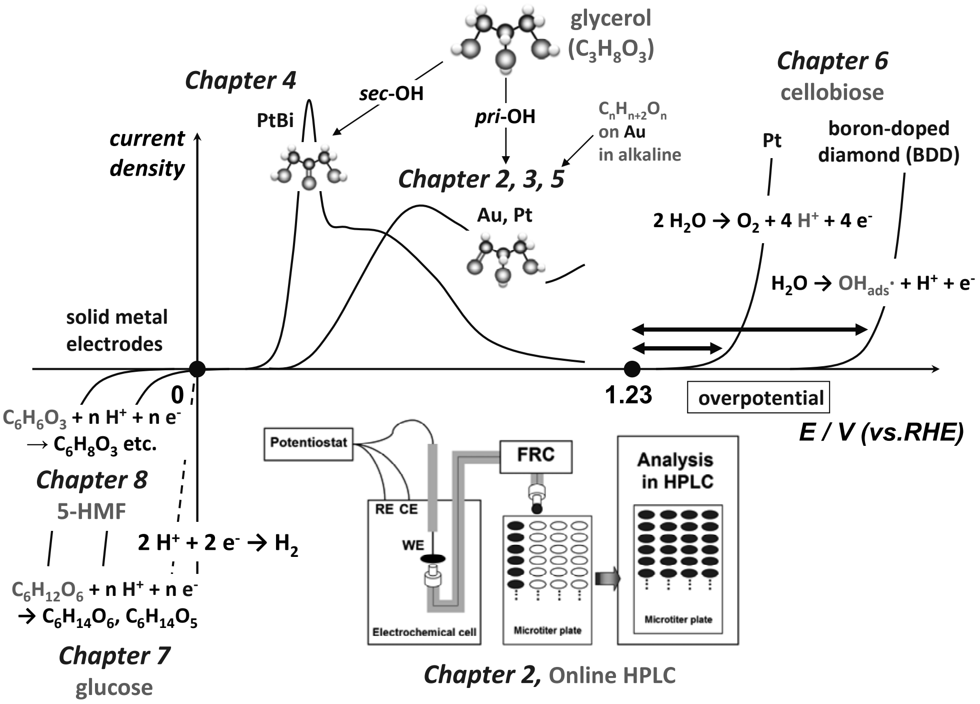

Figure 1. Current-potential representation of the reactions described in the thesis.

The motivation, details of operating conditions, and applications of an online HPLC system are discussed in Chapter 2. In this chapter, glycerol ($C_3H_8O_3$) is used as a model molecule to study its oxidation activity and reaction products on Au and Pt electrodes in alkaline conditions.

Building on Chapter 2, the effect of pH on glycerol oxidation has been investigated on Au and Pt electrodes in Chapter 3 to study the detailed mechanism. Especially, glyceraldehyde and dihydroxyacetone, which are not stable in alkaline condition, are shown in product spectra by continuous injection of ‘stabilizing agent’ through a modified sample collecting tip during sample collection. From this study, we conclude that gold only catalyzes glycerol oxidation under alkaline conditions, in contrast to platinum, which catalyzes glycerol oxidation over the entire pH range.

In order to alter the reaction pathway towards secondary alcohol oxidation, we study glycerol oxidation on Pt electrode in the presence of bismuth in Chapter 4. In a Bi-saturated acidic solution, Pt/C catalyst lowers the onset potential and enhances the turn-over frequency of glycerol oxidation with almost 100% selectivity to dihydroxyacetone (sec-OH oxidation product).

In Chapter 5, we describe why Au shows such as a high activity towards alcohol oxidation in alkaline solution. Based on a comparison of the oxidation activity of a series of similar alcohols with varying pK_a on gold electrodes in alkaline solution, we find that the first deprotonation is base catalyzed, and the second deprotonation is fast but gold catalyzed.

In Chapters 6 and 7, we extend our interest to cellobiose conversion to sorbitol based on the successful combination of voltammetry with online HPLC. Electrochemistry-assisted cellobiose hydrolysis to glucose is investigated in Chapter 6. Platinum and boron-doped diamond (BDD) electrodes were employed to generate acid (H^+) and hydroxyl radicals ($OH\cdot$), respectively, in order to induce the hydrolysis of cellobiose. The results were compared with the hydrolysis promoted by conventional acid (H_2SO_4) and $OH\cdot$ from Fenton's reaction.

In Chapter 7, glucose hydrogenation to sorbitol in neutral solution is described on solid metal cathodes. Three groups of catalysts in the Periodic Table with regard to reaction products are investigated i.e. hydrogen (early transition metals, platinum group metals), sorbitol (late transition metals), and sorbitol and 2-deoxysorbitol (post-transition metals).

In Chapter 8, the hydrogenation of 5-hydroxymethylfurfural (HMF), a derivative of glucose during acid-hydrolysis of cellulose, is described on solid metals in the presence and absence of glucose. The hydrogenation of 5-HMF is a non-catalytic reaction with lower overpotential than that of glucose, although the reaction pathway is determined by the catalyst. Therefore, the glucose hydrogenation is mostly suppressed by the presence of 5-HMF.

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