Biomass Electrochemistry : from cellulose to sorbitol

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Summary

The primary goal of this thesis is to study the potential role of electrochemistry in finding new routes for sustainable chemicals from biomass in aqueous-phase solutions. 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 inherent time-scale differences of voltammetry and HPLC, we employed rapid sample collection while sweeping the electrode potential, using a very small micrometer-sized tip inlet system placed close to the electrode surface, with the collected sample fractions subsequently analyzed in an HPLC system. To demonstrate this method, we applied it to the glycerol ($C_3H_8O_3$) electro-oxidation on Au and Pt electrodes in alkaline media in Chapter 2, visualizing the concentration changes of glycerol and its reaction products in correspondence with the current measured in voltammetry.

The electro-oxidation mechanisms of glycerol on Au and Pt electrodes under different pH conditions are further reported in Chapter 3. Especially, glyceraldehyde and dihydroxyacetone, which are not stable in alkaline condition, are shown in product spectra by continuous injection of 'stabilizing agent' through modified sample collecting tip during sample collection. From this study, we found out that glycerol is oxidized dominantly through primary alcohol via glyceraldehyde as the first reaction product. In addition, 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 oxidation pathway of glycerol toward 'secondary alcohol', since the primary alcohol oxidation is always dominant on monometallic catalysts in Chapter 2 and 3, we introduced Bi as an adatom on Pt/C catalyst. A Pt/C electrode in a bismuth saturated solution at a carefully chosen potential is capable of oxidizing glycerol to dihydroxyacetone

with 100% selectivity. In the absence of bismuth, the primary alcohol oxidation is dominant. Using a combination of online HPLC and in situ FTIR, it is shown that Bi blocks the pathway for primary oxidation but also provides a specific Pt-Bi surface site poised for secondary alcohol oxidation.

The role of the alkaline medium and the gold electrode during alcohol oxidation is investigated in Chapter 5. 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. The base catalysis follows a Hammett-type correlation with pK_a, and dominates overall reactivity for a series of similar alcohols. The high oxidation activity on gold compared to platinum for some of the alcohols is related to the high resistance of gold toward the formation of poisoning surface oxides. These results indicate that base catalysis is the main driver behind the high oxidation activity of many organic fuels on fuel cell anodes in alkaline media, and not the catalyst interaction with hydroxide.

Based on fundamental understanding of the electrocatalysis of biomass derived alcohols with online HPLC in Chapters 2~5, we extended our interest to the challenging topic of cellobiose conversion to sorbitol.

For cellobiose conversion to sorbitol, cellobiose hydrolysis to glucose is first investigated in Chapter 6. Platinum and boron-doped diamond (BDD) electrodes were employed to generate acid (H^+) and hydroxyl radicals ($OH\cdot$), respectively, the results of which were compared with the hydrolysis promoted by conventional acid (H_2SO_4) and $OH\cdot$ from Fenton's reaction. Cellobiose hydrolysis follows a first-order reaction obeying Arrhenius' law over the temperature range from 25°C to 80°C with different activation energies for the acid- and radical-promoted reaction, i.e. ca. 118±8 kJ mol^{-1} and ca. 55±1 kJ mol^{-1}, respectively. The high local acidity with electrochemically generated acid (H^+) on the Pt anode increases the rate of glucose formation, however the active electrode (PtO_x) interacts with glucose and decomposes it further to smaller organic acids. The hydroxyl radical

(OH•) generated on a BDD anode first hydrolyzes the cellobiose to glucose, but rapidly attacks the aldehyde on glucose, which is further decomposed to smaller aldoses and finally formaldehyde, which is subsequently oxidized electrochemically to formic acid.

As a coupled reaction of cellobiose hydrolysis to glucose, the glucose hydrogenation to sorbitol in neutral solution on solid metal cathodes is described in Chapter 7. Three groups of catalysts in a Periodic Table regarding to reaction products clearly show their affinities toward: 1) hydrogen formation on early transition metals (Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, We, and Re) and platinum group metals (Ru, Rh, Ir, and Pt), 2) sorbitol on late transition metals (Fe, Co, Ni, Cu, Pd, Au, and Ag) and Al (sp metal), and 3) sorbitol and 2-deoxysorbitol on post-transition metals (In, Sn, Sb, Pb, and Bi) as well as Zn and Cd (d metals). Ni shows the lowest overpotential for sorbitol formation from -0.25 V whereas Pb generates sorbitol with the highest yield (< 0.7 mM cm^{-2}). Different from a smooth Pt electrode, a large surface-area Pt/C electrode hydrogenates glucose to sorbitol from -0.21 V with relatively low current, which emphasizes the importance of the active sites and the surface area of the catalyst. In combination with the ability of potential-controlled electrolysis on anode (Chapter 6), it may be possible to achieve one-pot electro-synthesis of sorbitol from cellobiose or cellulose.

As 5-hydroxymethylfurfural (HMF) is a by-product of glucose dehydration during acid-catalysed cellulose hydrolysis, the effect of the presence of glucose on the hydrogenation of HMF and vice versa is investigated in Chapter 8. Three groups of catalysts show different selectivity towards: (1) 2,5-dihydroxymethylfuran (DHMF) (Fe, Ni, Ag, Zn, Cd, and In), (2) DHMF and other products such as 2,5-dimethylfuran (Pd, Al, Bi, and Pb), depending on the applied potential, and (3) other products (Co, Au, Cu, Sn, and Sb) involving HMF dehydration. The rate of electrocatalytic HMF hydrogenation is not strongly catalyst dependent since all catalysts show similar onset potentials (-0.5 ± 0.2 V) in the presence of HMF. However the intrinsic property of the catalysts determines the reaction pathway towards DHMF or other products. Ag showed highest activity towards DHMF formation (max. 13.1 mM cm^{-2} with high selectivity > 85%). HMF hydrogenation is faster than glucose hydrogenation on all metals. For transition metals, the presence of glucose enhances the formation of DHMF and suppresses the dehydration of HMF. On poor metals, glucose enhances the DHMF formation on Zn, Cd, and In, however, its contribution to Bi, Pb, Sn, and Sb is limited. Remarkably, in the presence of HMF, glucose hydrogenation itself is largely suppressed or even absent. The first electron transfer step of HMF reduction is not metal dependent suggesting a non-catalytic reaction with proton transfer directly from water in the electrolyte.

This thesis has shown the potential of electrochemistry and electrocatalysis toward generating sustainable chemicals from biomass by combining voltammetry and chromatography. This simple and innovative approach enables the monitoring of soluble reaction products during voltammetry with chromatographic techniques, and thereby allows for new insights into the mechanisms of complex multi-step electrode reactions.