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Biomass Electrochemistry : from cellulose to sorbitol

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Outlook

In the project of “Biomass electrochemistry: from cellulose to sorbitol”, we were aiming at single-cell synthesis of sorbitol from cellulosic material by generating glucose as an intermediate species. This thesis has demonstrated the separate reactions of cellobiose hydrolysis to glucose by acid and hydroxyl radical on an anode (Chapter 6) and glucose hydrogenation to sorbitol on a cathode (Chapter 7) in an electrolysis cell. The glucose generated from anode can be transferred to the cathode inlet for further hydrogenation to sorbitol. Our work allows us to point out some factors that make the combination of two reactions in a cell currently still not a viable route towards cellulose valorisation.

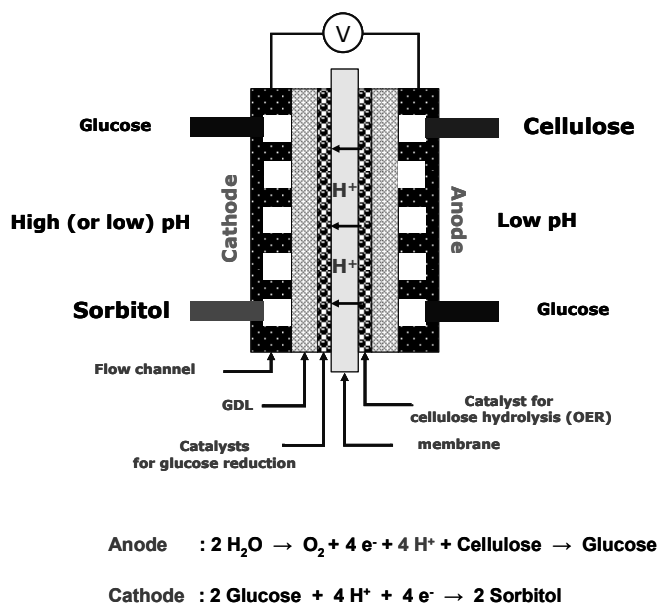


Figure 1. Schematic diagram of cellulose conversion to sorbitol in an electrolyzer.

First of all, for breaking the glycosidic bond to glucose by acid-catalyzed hydrolysis in cellulosic material, including cellobiose and cellulose, requires high temperature (around 200°C), which is not easily achievable under standard electrochemical conditions. From the study of cellobiose hydrolysis by electrochemically generated acid in Chapter 6, we observed a lower selectivity towards glucose than that of acid-catalyzed hydrolysis at 80°C due to the decomposition of glucose by the activated electrocatalyst or by-product formation by molecular O₂ generated during oxygen evolution reaction (OER). Therefore, an electrode with high activity for OER and low activity for glucose decomposition at high temperature is necessary for such an application. Future work should also investigate high pressures.

In contrast to acid hydrolysis, hydroxyl radical requires a lower temperature for cellobiose hydrolysis on boron-doped diamond (BDD) since the high temperature accelerates the reaction rate towards decomposition of glucose to smaller aldoses and their corresponding acids. Therefore, the application of hydroxyl radicals may be a promising technique with lower activation energy than that of the acid-catalyzed reaction, provided the hydrolyzed glucose is immediately separated from the active radical.

Compared to the cellulose hydrolysis to glucose at the anode compartment, glucose hydrogenation on a cathode is relatively well established. In Chapter 7, we could clearly show the trend of hydrogenation activity on solid metals in the Periodic Table. Especially, Pb electrode shows a high activity to form sorbitol with high selectivity (> 87%) and high yield (< 0.7 mM cm⁻²). Therefore after optimization of cellulose hydrolysis at the anode, it should be possible to achieve one-pot electrosynthesis of sorbitol from cellobiose or cellulose.

Apart from cellulose conversion to sorbitol, this thesis includes ‘glycerol oxidation’ in Chapter 2 ~ 4. Since glycerol is an important biomass-related compound, both as a model poly-ol compound, and as an abundant byproduct of biodiesel, the catalytic conversion of glycerol into value-added chemicals is a topic of significant current interest in biomass research. In electrochemistry, glycerol has been considered as a potential fuel for cell cells. From a recent review of electrochemical valorization of glycerol given by Coutanceau et al.^[1], glycerol is energetically more interesting reactant than water for the production of hydrogen in electrolysis cell. Furthermore, the fuelling of a fuel cell with the generated

hydrogen from glycerol electrolysis is more efficient from an energy-yield viewpoint than the direct oxidation of glycerol in a fuel cell, which brings us an idea to co-generate hydrogen and valuable chemicals (i.e. glyceraldehyde, glyceric acid, dihydroxyacetone, formic acid) depending on the applied potential in an electrolysis cell shown in Figure 2.

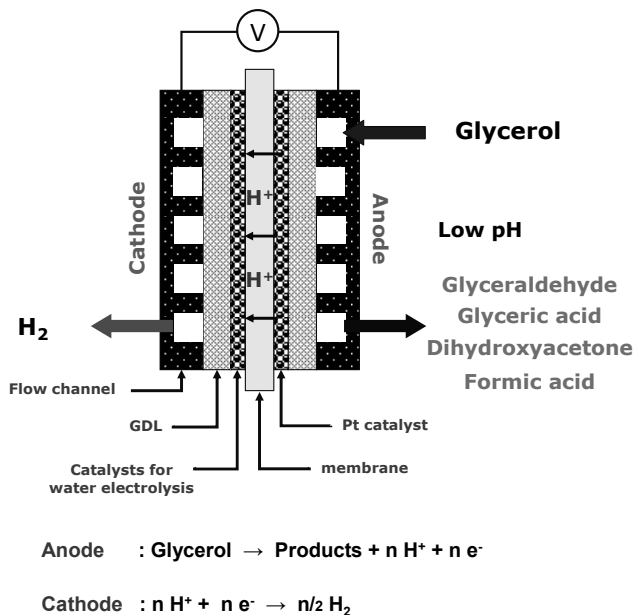


Figure 2. Schematic diagram of glycerol conversion to hydrogen and chemicals in an electrolyzer.

The selective oxidation of glycerol through the secondary alcohol oxidation pathway to generate dihydroxyacetone (DHA) was described in Chapter 4 using Bi as a modifier of the Pt catalyst. The role of Bi should be understood beyond the blocking the formation of poisoning species ‘CO’, which is preferentially formed from the terminal CH₂OH^[2]. From an extended study of other poly-ols [C4~C6] oxidation, the role of Bi is also applicable to bigger poly-ols and changes the reaction pathway toward secondary alcohol oxidation. In addition, we found that other adatoms i.e. Sb, Pb, can also control the reaction pathway mainly dependent on the surface coverage on the Pt catalyst.

An important achievement of this thesis is online HPLC, which has enabled the detailed product analyses in the thesis. More specifically, online fraction collector (FRC) was combined with electrochemical techniques and chromatographic techniques. The application of this technique is not only limited to the study of biomass conversion, but it

includes all possible analytical methods which may be combined with electrochemistry. For instance, online sampling technique can visualize the soluble reaction products i.e. nitrite, ammonium, hydroxylamine during nitrate (or nitrite) reduction by analyzing collected samples using ion chromatography, which has not been done before. Importantly, online sampling system is also accessible to gas evolution reactions, therefore I believe that this technique will contribute to the study of global carbon and nitrogen cycles.

References

- [1] M. Simoes, S. Baranton, C. Coutanceau, *ChemSusChem* **2012**, 5, 2106-2024.
- [2] P. S. Fernández, M. E. Martins, C. A. Martins, G. A. Camara, *Electrochem. Commun.* **2012**, 15, 14-17.