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Biomass Electrochemistry : from cellulose to sorbitol

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Citation

Kwon, Y. (2013, September 5). *Biomass Electrochemistry : from cellulose to sorbitol*. Retrieved from <https://hdl.handle.net/1887/21649>

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Title: Biomass electrochemistry : from cellulose to sorbitol

Issue Date: 2013-09-05

Electrocatalytic hydrogenation and deoxygenation of glucose on solid metal electrodes

Abstract

This chapter addresses the electrocatalytic hydrogenation of glucose to sorbitol or 2-deoxysorbitol on solid metal electrodes in neutral media by combining voltammetry and online product analysis with high-performance liquid chromatography, which provides both qualitative and quantitative information of the reaction products as a function of potential. Three groups of catalysts in the 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, W, 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 ($< 0.7 \text{ mM cm}^{-2}$). 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. The mechanism to form 2-deoxysorbitol from glucose and/or fructose is discussed according to the observed reaction products. The yield and selectivity of hydrogenated products is highly sensitive to the chemical nature and state of the catalyst surface.

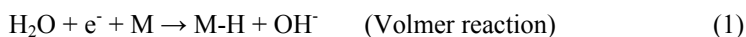
The contents of this chapter have been published: Y. Kwon, M. T. M. Koper, *ChemSusChem*, **2013**, 6, 455-462.

7.1 Introduction

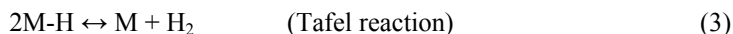
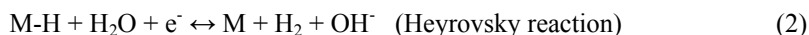
Catalytic conversion of biomass to fuels and chemicals has attracted great attention as one of the future technologies for mitigating global warming and for building up a carbon-neutral energy cycle.^[1,2] Glucose, as the monomer of the cellulose, plays a central role in biomass conversion. In particular, hydrogenation of glucose to sorbitol is a very important reaction from the 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.^[3] 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^[4,5] or poor metals at moderate pH (3~11)^[4,6-8] and temperature (<60°C)^[4-8] in a flow reactor.^[4-6,9] Especially controlling pH and temperature during hydrogenation process is a key issue to obtain high yield of sorbitol since strong acid leads to only H₂ formation and alkaline pH and high temperature cause mutarotation of glucose to by-products. Although electrocatalytic synthesis of sorbitol from glucose was once applied on an industrial scale,^[10] since 1950 sorbitol has been produced by catalytic hydrogenation on Raney-Ni and with modifiers (W, B, P etc.)^[3,11-13] or noble metals such as Ru^[14-16] under hydrogen pressure (1~350 atm) at various temperatures (ambient to 400°C).^[17]

Recently, one-pot conversion of cellulose into sorbitol under high H₂ pressure has been introduced,^[18,19] which consists of the hydrolysis of cellulose to glucose *via* water-soluble oligo-saccharides, followed by the hydrogenation of glucose to sorbitol.^[19] Precious metals such as Pt, Rh, Ir etc. on oxidic supports promote the rate-determining step of the hydrolysis of cellulose to glucose and subsequently reduce glucose to sorbitol.

In addition to Raney-Ni^[4,5], the most applied catalysts for the electrocatalytic hydrogenation of glucose are poor metals such as Pb,^[6-8] Hg,^[20] Pb(Hg)^[6,20], and Zn(Hg)^[4,20] since they suppress the hydrogen evolution reaction (HER). In electrocatalytic glucose hydrogenation, the chemisorbed hydrogen on electrode surface (M-H) is generated by electroreduction of water (under ambient pressure and temperature) as follows:



In competition with electrochemical (Eq. 2) and chemical (Eq. 3) hydrogen generation, adsorbed glucose on the electrode surface (M-glucose) is hydrogenated to sorbitol (Eq. 4) or deoxygenated to 2-deoxysorbitol (Eq. 5) following:



where we have assumed that glucose reacts in its adsorbed state with hydrogen adsorbed on the metal catalyst. Because of the co-production of hydrogen, careful selection of the electrocatalyst as well as the applied potential/current is very important in order to obtain high yield and selectivity towards sorbitol, since the overpotential for water reduction (Eq. 1~3) and the adsorption energy of glucose depend strongly on the nature of catalyst. Although electrocatalytic glucose hydrogenation to sorbitol has been applied on an industrial scale,^[10] 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. For instance, conventional bulk electrolysis requires a long operating time to find the optimum potential or current for a high yield of sorbitol,^[6-9] and moreover such studies yield little insight into the mechanistic aspects of the reaction. We believe this lack of insight into the mechanistic aspects of glucose reduction, and sugar compounds in general, hampers the application of electrochemical methods in their conversion, and therefore a detailed study, such as reported herein, is warranted.

In this chapter, we investigate the electrocatalytic glucose hydrogenation to sorbitol or 2-deoxysorbitol on a large number of pure solid metal electrodes from across the Periodic Table, aiming at understanding the activity and selectivity of catalysts by correlating the voltammetry and online product analysis. Glucose reduction is carried out in neutral solution deliberately as the local alkalinity generated during H₂ evolution helps in mutarotating glucose into an electro-active form, whereas the pH neutrality of the bulk

avoids product degradation. Acidic solutions are not active for glucose reduction. Reaction products are determined both quantitatively and qualitatively by using a combination of voltammetry and online high-performance liquid chromatography (HPLC).^[21-26] Since the expected products are soluble, HPLC is the most suitable analysis technique. The application of in situ spectroscopic techniques such as in situ Infrared or Raman spectroscopy is problematic due to concurrent hydrogen evolution. Finally, a possible mechanism of electrocatalytic hydrogenation of glucose is discussed based on the observed reaction products and the pH changes during electrolysis.

7.2 Experimental

7.2.1 Electrochemical procedures

All measurements were carried out in a conventional single compartment three-electrode glass cell, which was cleaned by employing a standard procedure^[27] for removing traces of organic and inorganic contaminants. Oxygen was removed by bubbling argon through the solution prior to the voltammetric experiments. All transition and post-transition metals ($\geq 99.5\%$) used as working electrodes in the experiment were polycrystalline wires/rods/plates, which were mechanically polished with alumina (up to $0.05\ \mu\text{m}$) and cleaned ultrasonically in pure water (MilliQ gradient A10 system, $18.2\ \text{M}\Omega$) followed by electropolishing by cycling 5 times between -1.5 and $0\ \text{V}$ (vs. RHE) with a scan rate of $50\ \text{mV s}^{-1}$ in $0.1\ \text{M Na}_2\text{SO}_4$ solution in order to remove surface impurities and oxide before use.^[28,29] The surface area (cm^2) of the catalysts used to calculate the current density (mA cm^{-2}) and concentration yield of reaction products (mM cm^{-2}) was obtained based on geometric area except for Pt and Pt/C catalysts for which we considered the electrochemically active surface area by the hydrogen desorption charge in $0.5\ \text{M H}_2\text{SO}_4$. A thin-film electrode with $3\ \text{nm}$ Pt/C nanoparticles ($50\ \text{wt } \%$, Tanaka) was fabricated by loading $3\ \mu\text{L}$ and $20\ \mu\text{L}$ of nanoparticle suspension in water ($1\ \text{mg mL}^{-1}$) onto a polished Pt plate substrate, subsequently dried at room temperature. For the Pt and Pt/C catalysts, the electrochemically active surface area was recorded before experiment. In all experiments, a large platinum plate was used as a counter electrode while a reversible hydrogen electrode (RHE) was employed as a reference electrode. Glucose ($0.1\ \text{M}$, Merck) was dissolved into a solution of $0.1\ \text{M Na}_2\text{SO}_4$ (Merck, pH 7). Electrochemical cell potentials were controlled

with a potentiostat/galvanostat (μ -Autolab Type III). All experiments were carried out at room temperature.

7.2.2 Fraction collection and product analysis

For the detection of intermediates and products by HPLC, samples of the electrolyte solution were collected with a small Teflon tip (inner diameter, 0.38 mm) positioned close (10 μ m) to the center of the electrode surface, the tip being connected to a PEEK capillary with inner/outer diameters of 0.13/1.59 mm.^[21] The tip was cleaned in a solution of 0.2 M $K_2Cr_2O_7$ and rinsed thoroughly with ultrapure water before use. The sample volume collected in each well was 60 μ l on a 96-well microtiter plate (270 μ l/well, Screening Devices b.v.) using an automatic fraction collector (FRC-10A, Shimadzu). The flow rate of sample collection was adjusted to 60 ml min⁻¹ with a Shimadzu pump (LC-20AT). Collected samples were immediately neutralized by adding 60 μ l of 10 mM phosphate buffer. After collecting samples, the microtiter plate was covered by a silicon mat to prevent the evaporation of collected samples.

Samples collected during voltammetry were analysed using a Shimadzu Prominence HPLC. The microtiter plate with the collected samples was placed in an autosampler (SIL-20A) holder, and 20 μ l of sample was injected into the column. The column (Shodex SP0810) used for the analysis used pure water as the eluent. The temperature of the column was maintained at 80°C in an oven (CTO-20A), and the separated compounds were detected with a refractive index detector (RID-10A). The main reaction products analysed by HPLC, i.e. sorbitol and 2-deoxysorbitol, were confirmed by a FINNIGAN LTQ + LTQ ORBITRAP LC-MS equipped with two columns in series configuration (Aminex HPX 87-H+Shodex SH1011) using dilute sulfuric acid (5 mM) as the eluent at room temperature.

7.3 Results and discussion

Metal catalysts are divided into three groups based on the reaction products from glucose reduction; i) metals forming sorbitol, as well as some dihydrogen gas (Fe, Co, Ni, Cu, Pd, Au, Ag, and Al), ii) metals forming sorbitol and 2-deoxysorbitol, with very little hydrogen

(Zn, Cd, In, Sn, Sb, Pb, and Bi), and iii) metals forming solely H_2 (Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re, Ru, Rh, Ir, and Pt).

7.3.1 Sorbitol forming metals

Figure 1 shows the voltammograms of the glucose-free “blank” solution (dashed line) and 0.1 M glucose (solid line) reduction in 0.1 M Na_2SO_4 alongside the concentration profiles of the reaction product, sorbitol, on (a) Fe, Co, Ni, and Cu, and (b) Pd, Au, Ag, and Al. In general, the increase of cathodic current observed in the blank experiment is attributed to the evolution of H_2 and the solid line represents the formation of both sorbitol from glucose reduction and H_2 evolution. First of all, note that all catalysts in Figure 1 show different onset potential for H_2 evolution from blank scans, which clearly indicates that the formation of chemisorbed hydrogen (M-H, Eq. 1) and molecular H_2 (Eq. 2 and 3) is strongly dependent on the properties of the catalyst. For most metals, the cathodic current in the presence of glucose in solution is smaller compared to the reduction current in the blank, especially at high overpotentials, although the onset potentials are often quite close. From this observation, we can conclude that the presence of glucose inhibits hydrogen evolution, presumably by adsorbing onto the electrode surface. The two exceptions to this rule appear to be gold and especially copper, which exhibit higher cathodic currents in the presence of glucose. These are also the two metal electrodes with the highest sorbitol yield in their potential range of activity. Figure 1a also shows that the cathodic current on Ni increases from ca. -0.25 V, which is the lowest onset potential among all transition metals forming sorbitol, and the maximum concentration of sorbitol is observed at -0.41 V, after which it significantly decreases. This indicates that the optimum ratio between Ni-H and Ni-glucose is at -0.41 V, after which H_2 evolution becomes predominant. Although Raney-typed Ni catalysts are widely applied for heterogeneous hydrogenation reactions in industry, previous reports emphasize that Ni shows hardly any electrocatalytic activity for glucose reduction to sorbitol.^[6,7] However, the applied current ($> 10 \text{ mA cm}^{-2}$) or potential ($< -1 \text{ V}$ vs. RHE) in these works will yield only H_2 according to Figure 1a. Therefore, this observation confirms the importance of providing fundamental information correlating voltammetry and product formation. In addition to Ni electrode, Figure 1a shows that sorbitol is formed on Co, Fe, and Cu from -0.51, -0.63, and -0.75 V, and exhibit maximum yields at -1 V or -5 mA cm^{-2} for Co, -0.75 V or -2 mA cm^{-2} for Fe, and -1.3 V or -10 mA cm^{-2} for Cu electrodes, respectively. As mentioned, on a Cu electrode, the cathodic current

with glucose in solution is significantly higher compared to blank, which must be mainly attributed to the formation of sorbitol.

Pd, one of the platinum group metals (Pt, Pd, Rh, Ir, Ru, and Os), adsorbs and also absorbs hydrogen, which changes the shiny surface to a highly porous structure after the cathodic reaction. On Pd, sorbitol is generated from -0.45 V and maximum concentration was observed at -0.87 V with a current density of -7 mA cm^{-2} , after which the concentration of sorbitol decreases (see Figure 1b). The special hydrogenation capacity of Pd, and also Ni, which have also been applied for electrocatalytic hydrogenation of ketone ($\text{C}=\text{O}$), aldehyde (CHO), alkene ($\text{C}=\text{C}$), and alkyne ($\text{C}\equiv\text{C}$) functionalities using i.e. Raney-type materials or supported nanoparticles,^[17] is often ascribed to absorbed hydrogen. Nogerbekov et al.^[30] showed that absorbed hydrogen in Pd black is able to carry out chemical hydrogenation of *p*-nitrophenol in 0.1 M NaOH to *p*-aminophenol and Sykes et al.^[31] observed subsurface hydrogen atoms in a Pd(111) surface by using low-temperature scanning tunnelling microscopy. Also in heterogeneous catalysis it is well known that Pd-based catalysts selectively hydrogenate the triple bonds of carbon in a mixture of alkynes and alkenes, governed by the population of either hydrogen or carbon on subsurface sites of Pd.^[32,33]

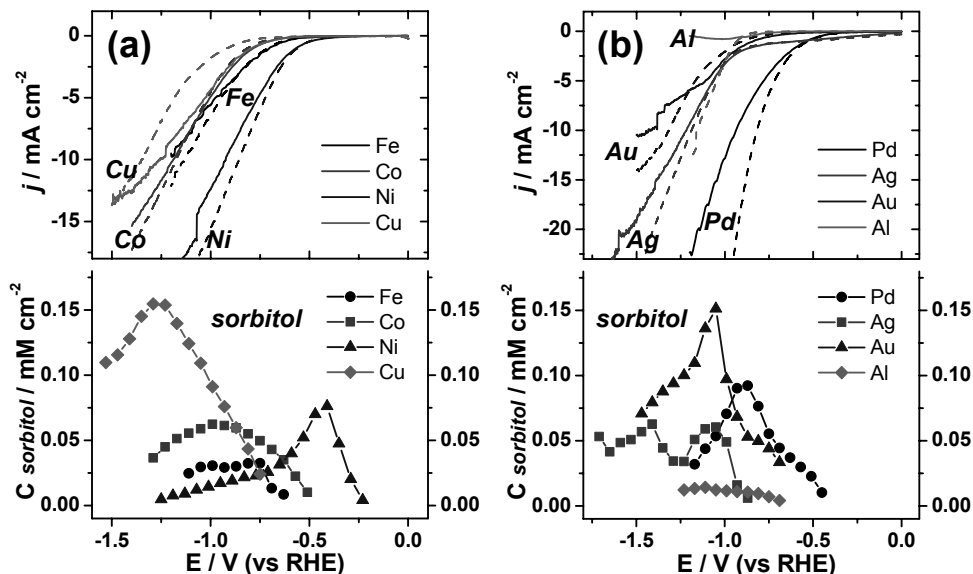


Figure 1. Electrocatalytic glucose (0.1 M) reduction on (a) Fe, Co, Ni, and Cu, and (b) Pd, Ag, Au, and Al in 0.1 M Na_2SO_4 . Current density profiles (upper panels) with (solid line) and without (dashed line) glucose in the solution during linear sweep voltammetry with a scan rate of 1 mV s^{-1} , and concentration profiles (lower panels) of corresponding reaction product, sorbitol, as a function of potential.

On Ag, sorbitol is detected from -0.9 V and two maxima in the production of sorbitol were observed at -1.05 V or -3 mA cm^{-2} and -1.41 V or -16 mA cm^{-2} . The potential at which sorbitol appears on Au and Al is -0.69 V , with -1.05 V the optimum potential for sorbitol formation on both metals with current densities of -3 mA cm^{-2} on Au and -3.5 mA cm^{-2} on Al, respectively. Although Al is the only *sp* metal in Figure 1, it shows some, albeit comparatively low, activity for glucose reduction to sorbitol.

As an intermediate conclusion, Ni exhibits the lowest potential, -0.25 V , to form sorbitol. Au and Cu show the highest yield of sorbitol (0.15 mM cm^{-2}) at -1.05 V and -1.3 V , respectively. Concerning the concentrations of sorbitol with corresponding current densities for each metal in Figure 1, we can conclude that each catalyst has an optimum potential or a current density to maximize the yield of sorbitol. Pd and Ni are active hydrogenation

catalysts in heterogeneous catalysis, and also require relatively low overpotentials for maximum sorbitol yield, but this is accompanied by the formation of H_2 at low overpotentials. Therefore, the efficiency of the electrochemical hydrogenation is determined by the competition between the glucose reduction to sorbitol (Eq. 4) and the evolution of hydrogen (Eq. 2 or 3).

7.3.2 Sorbitol and 2-deoxysorbitol forming metals

In contrast to transition *d* metals which produce H_2 and sorbitol during glucose hydrogenation reaction, the post-transition *sp* metals also deoxygenate glucose to 2-deoxysorbitol as shown in Figure 2. Moreover, the higher overpotential or cathodic current applied to post-transition metals results in higher concentration of products in general. This high potential is made possible by the fact that these metals are typically poor hydrogen evolution catalysts. In the rest of this section, we will use the term ‘selectivity’ as the percentage of sorbitol or 2-deoxysorbitol generated from glucose, regardless of hydrogen generation.

Zn and Cd are included in Figure 2a, as they show similar reactivity as the other post-transition metals, although they are sometimes considered transition metals. Both Zn and Cd form reaction products from -1 V. Interestingly, the concentrations of sorbitol and 2-deoxysorbitol increase continuously as the cathodic potential increases, which is different from the sorbitol formation trend observed with the transition metals, which always show a maximum (Figure1). We note that the cathodic current on Zn is higher than that on Cd, however, the yield of reaction products on Cd is higher than on Zn, which indicates that Cd hydrogenates glucose more efficiently than Zn by suppressing the hydrogen evolution reaction. On Cd, the selectivity to sorbitol is $61\pm2\%$ vs. $39\pm2\%$ to 2-deoxysorbitol. On the other hand, 2-deoxysorbitol ($65\pm7\%$) is the preferred product on Zn vs. $35\pm7\%$ sorbitol. Even though Zn itself shows lower activity than Cd, adding Zn^{2+} to the solution significantly enhances the current efficiency by enlarging the surface area during electrodeposition or by accelerating the rate of the isomerisation of glucose.^[6]

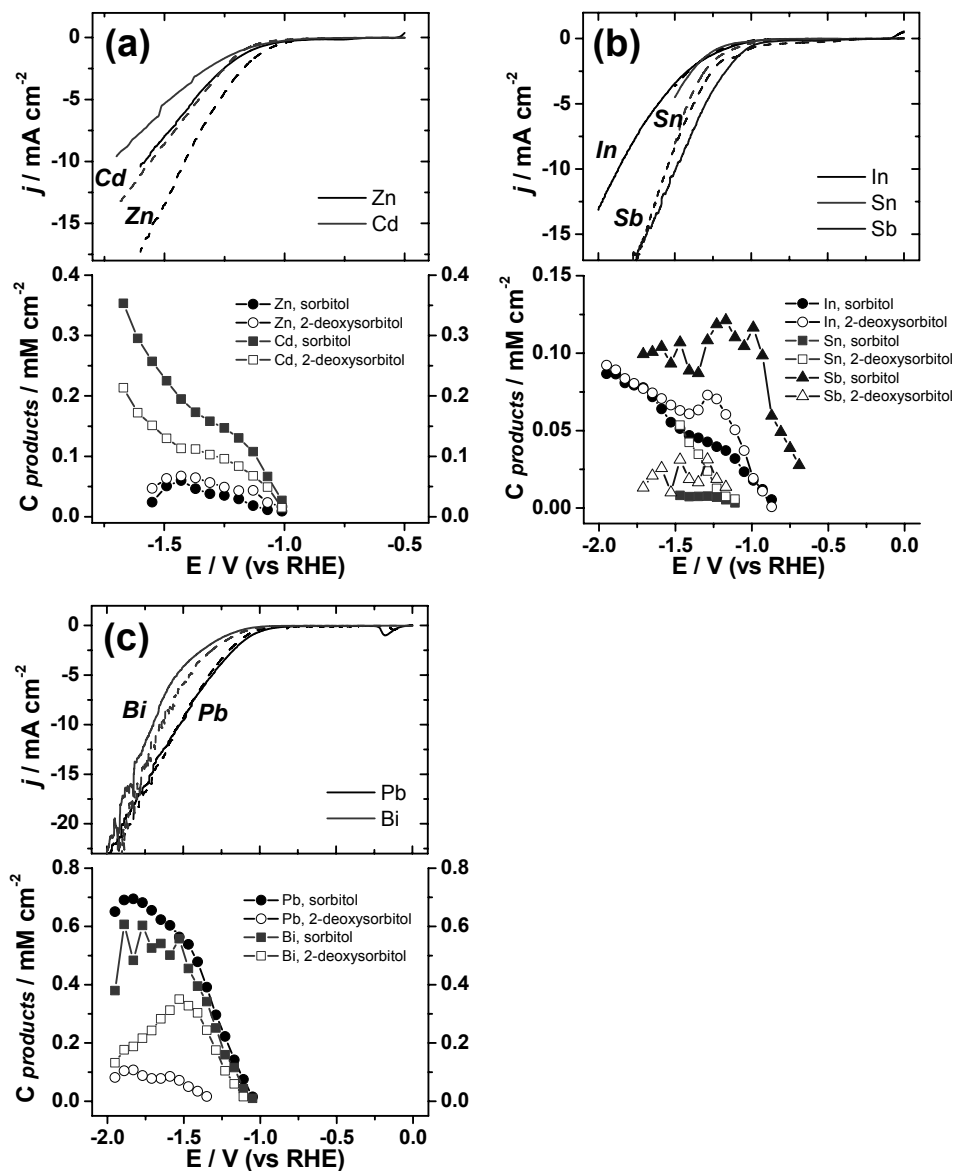


Figure 2. Electrocatalytic glucose (0.1 M) reduction on (a) Zn and Cd, (b) In, Sn, and Sb, and (c) Pb and Bi in 0.1 M Na₂SO₄. Current density profiles with (solid line) and without (dashed line) glucose in the solution during linear sweep voltammetry with a scan rate of 1 mV s⁻¹ and concentration profiles of corresponding reaction products, sorbitol and 2-deoxysorbitol, as a function of potential.

The activity of the period 5 metals In, Sn, and Sb for glucose reduction is shown in Figure 2b. Based on current profiles, Sb shows the lowest overpotential and the main product on Sb, sorbitol, is observed from -0.7 V. The concentration of sorbitol on Sb increases until -1 V, after which it fluctuates mainly due to vigorous hydrogen evolution at higher overpotentials (< -1 V). 2-deoxysorbitol on Sb appears from -1.17 V with low selectivity ($< 20\%$) in the entire potential range, thus sorbitol is the dominant hydrogenation product ($> 80\%$) on the Sb electrode. On Sn the collected samples clearly show that sorbitol and 2-deoxysorbitol are generated from -1.1 V to -1.5 V, with 2-deoxysorbitol being the dominant product, although vigorous hydrogen evolution limits sample collection at high cathodic potential ranges. Note that the selectivity of 2-deoxysorbitol on Sn is higher than 90% at -1.5 V, even though the absolute concentration of 2-deoxysorbitol is not that high. On In, sorbitol and 2-deoxysorbitol appear at ca. -0.87 V and their concentrations increase roughly linearly as the cathodic potential increases. Between -1.4 V and -1 V the concentration of 2-deoxysorbitol is higher than that of sorbitol and the highest selectivity (65%) is reached at -1.3 V, whereas for $E < -1.5$ V the selectivities are approximately equal.

Figure 2c shows the results of glucose reduction on Pb and Bi catalysts. Sorbitol is observed as the first reduction product at -1.05 V on both electrodes, although the onset potential on Bi seems to be a bit more negative as compared to Pb. The concentration of sorbitol strongly increases until ca. -1.5 V, after which the sorbitol production slows down, mainly due to the hydrogen evolution reaction, and reaches to the highest concentration yield of 0.7 mM cm^{-2} on Pb at -1.83 V (or -17.5 mA cm^{-2}) and 0.6 mM cm^{-2} on Bi at -1.89 V (or -20 mA cm^{-2}), respectively. Note that the concentration of 2-deoxysorbitol on Bi follows the trend of sorbitol until -1.53 V with a selectivity of ca. 40%, after which it decreases as the cathodic potential increases. On the Pb electrode 2-deoxysorbitol is first observed at -1.35 V and reaches a maximum with ca. 13% selectivity as the cathodic potential increases. This makes Pb the most active and selective catalyst for glucose hydrogenation to sorbitol.

As a general conclusion, poor metals, both post-transition metals (“poor metals”) and Zn and Cd, show a high overpotential for the hydrogen evolution reaction, thus leading to a relatively high activity and selectivity toward glucose hydrogenation to sorbitol and 2-deoxysorbitol. The formation of sorbitol is highest on Pb ($> 87\%$ selectivity) with high yield ($< 0.7 \text{ mM cm}^{-2}$). The Sn electrode has the highest selectivity towards 2-deoxysorbitol

(> 90%) though the overall yield is rather low. Figure 2 does not show a clear trend of reactivity and selectivity of the various surfaces based on their electronic structure. As an important difference to the reactivity of transition metals, the concentration of reaction products on poor metals tends to continuously increase as the cathodic potential increases.

7.3.3 Metals producing only H₂

Non-active catalysts for glucose hydrogenation can be divided into two groups; 1) early transition metals (Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, and Re) as shown in Figure 3a~c and 2) platinum group metals (Ru, Rh, Ir, and Pt) as shown in Figure 3d. Early transition metals require high overpotentials for the hydrogen evolution reaction (dashed line, blank) and the onset potentials are in between -0.8 and -0.5 V (vs. RHE). Although in 0.1 M glucose solution, the current densities near the onset potentials on Ti, V, Cr, Mo, Nb, Mo, Hf, W, and Re are a bit higher than those of the blank, similar to the general trends of sorbitol forming catalysts in Figure 1, we did not observe any trace of sorbitol either due to the inactivity of the catalysts or to the limitation of the HPLC analysis (a concentration of > 1 μ M is required). Therefore, we conclude that although a certain minimum applied overpotential is important to obtain hydrogenation products, as shown in Figure 1 and 2, a highly negative potential itself does not automatically imply glucose hydrogenation and needs to be accompanied by a reaction product analysis.

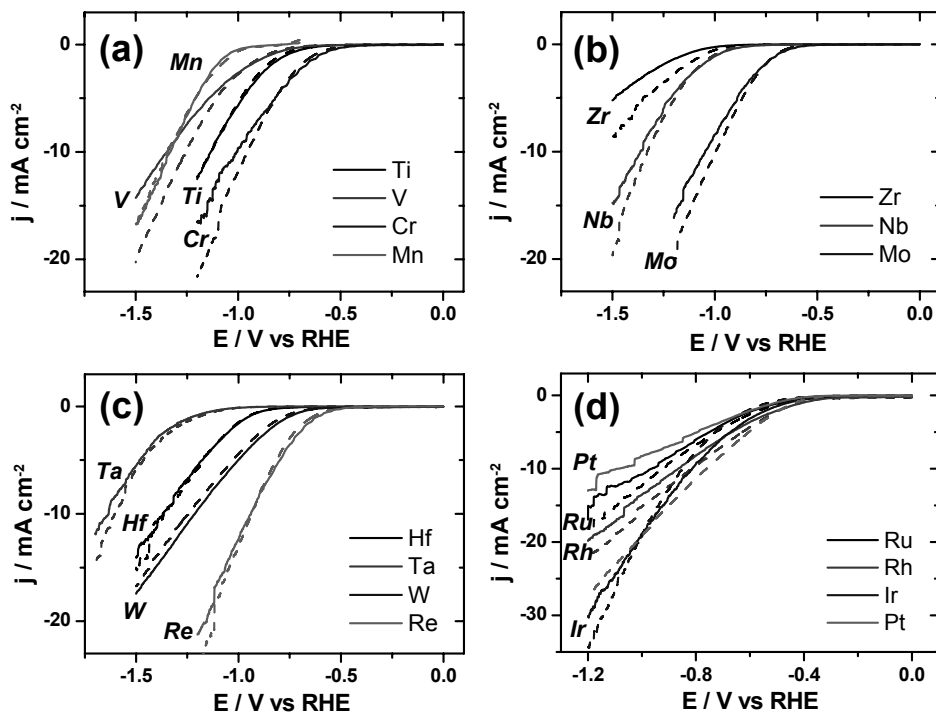


Figure 3. Voltammograms of electrocatalytic glucose reduction (0.1 M) on (a) Ti, V, Cr, and Mn, (b) Zr, Nb, and Mo, (c) Hf, Ta, W, and Re, and (d) Ru, Rh, Ir, and Pt in 0.1 M Na₂SO₄. Current density profiles with (solid line) and without (dashed line) glucose in the solution during linear sweep voltammetry with a scan rate of 1 mV s⁻¹.

In contrast to the early transition metals, the onset potential for hydrogen evolution reaction on platinum group metals is less negative (close to -0.4 V) as shown in Figure 3d. Interestingly, Pt^[18,34] and Ru^[3,14,18,34,35] are the most well-known active catalysts in the heterogeneous glucose hydrogenation reaction, however there is no evidence in our experiments that glucose is hydrogenated to sorbitol or 2-deoxysorbitol under electrochemical conditions at room temperature. The general hydrogenation mechanism considered in the heterogenous catalysis literature is that the adsorbed hydrogen on active Pt or Ru under high H₂ pressure hydrogenates the C=O bond stabilizing glucose to its hydrogenated alcohol form, i.e. sorbitol.^[18,19] The inactivity of Pt and Ru during electrohydrogenation might be due to the fact that the kinetics of hydrogen evolution (H₂,

Eq. 2 or 3) is faster than the hydrogenation reaction (Eq. 4 or 5). However, it is known that e.g. cinnamic acid can be only reduced on platinized, i.e. rough, platinum.^[36] In general, the hydrogenation of carbohydrates is carried out on platinized Pt in organic solvents such as methanol.^[37]

To investigate the influence of the catalyst surface condition or the number of active sites, the activity of carbon-supported Pt nanoparticles with the identical active surface area (3 μg Pt/C loading) compared to smooth Pt for glucose hydrogenation was studied separately, and we could only observe the trace of sorbitol. In order to clarify the influence of the active surface area of the catalyst, a 7 times higher loading of Pt/C (20 μg) was also investigated, the results of which are shown in Figure 4.

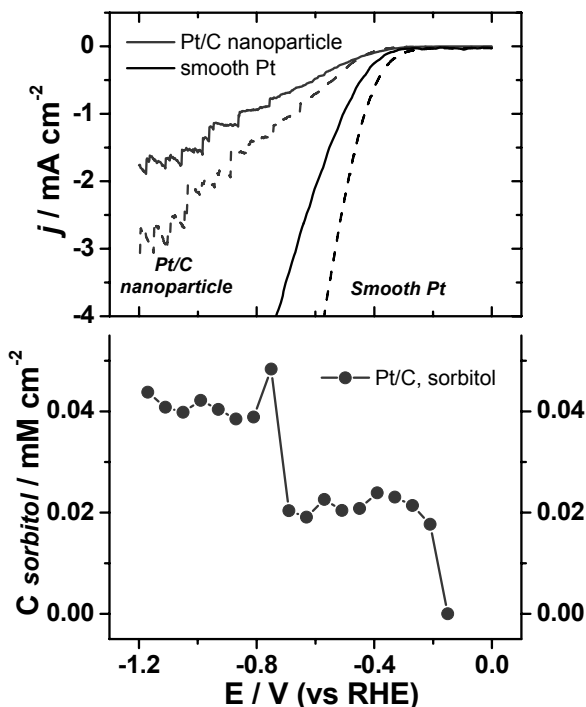


Figure 4. Electrocatalytic glucose (0.1 M) reduction on Pt/C in 0.1 M Na_2SO_4 . Current density profiles with (solid line) and without (dashed line) glucose in the solution during linear sweep voltammetry with a scan rate of 1 mV s^{-1} and the concentration profile of sorbitol as a function of potential.

Although the current density on Pt/C with glucose in solution (solid line) is ca. 4 times lower than on smooth Pt (at -0.6 V) due to the loss (ca. 70%) of Pt/C and the formation of hydrogen bubbles which adsorb stronger than on the smooth surface, we can observe the formation of a small but significant amount of sorbitol from -0.21 V. A sudden increase of the concentration of sorbitol was observed from -0.75 V, which was mainly due to the removal of a hydrogen bubble from the catalyst surface. Below -0.75 V, the yield of sorbitol stabilizes to ca. 0.04 mM cm⁻². Therefore this observation implies that a large active surface area on Pt is necessary for glucose hydrogenation as well as a roughened catalyst surface in order to generate a measurable amount of sorbitol in our HPLC. Owobi-Andely et al.^[9] reported that a Pt-Rh catalyst, which was prepared by calcination after substituting Sn ions for Pt and Rh on the electrode, electroreduces fructose selectively to mannitol (60%) and sorbitol (40%) with a 60% conversion of fructose at -1.25 V (SCE) in an electrocatalytic membrane reactor, which supports our observation, although there is no explicit evidence that the synthesized Pt-Rh catalyst is Sn-free. Apart from metallic catalysts, we tested boron-doped diamond (BDD), a material which shows a high overpotential for water electrolysis but also some electrocatalytic activity toward nitrate reduction,^[38] for glucose hydrogenation. However, BDD does not generate sorbitol or 2-deoxysorbitol in spite of the negative onset potential of -1.2 V (RHE) for hydrogen evolution, which clearly emphasizes again that the feasibility of glucose hydrogenation is mainly determined by the nature of catalyst, and much less by the applied overpotential.

Based on the reactivities of the catalysts as reported above, the potential ranges for formation of sorbitol and/or 2-deoxysorbitol as well as hydrogen evolution are summarized in the Periodic Table in Figure 5. The metals forming only hydrogen shown in Figure 3 are the early transition metals with overpotentials of between -1.0 and -0.5 V, and the Pt group metals with hydrogen evolution potentials higher than -0.5 V. The other transition metals shown in Figure 1 hydrogenate glucose to sorbitol with low cathodic potentials (> -0.5 V) on Ni and Pd, and intermediate overpotentials (-1 V to -0.5 V) on Fe, Co, Cu, Ag, and Au catalysts. Post-transition metals (*sp* orbital) including Zn and Cd (*d* orbital) as shown in Figure 2 generate sorbitol and 2-deoxysorbitol in combination with suppressing the hydrogen evolution reaction resulting in a high overpotential (< -1 V).

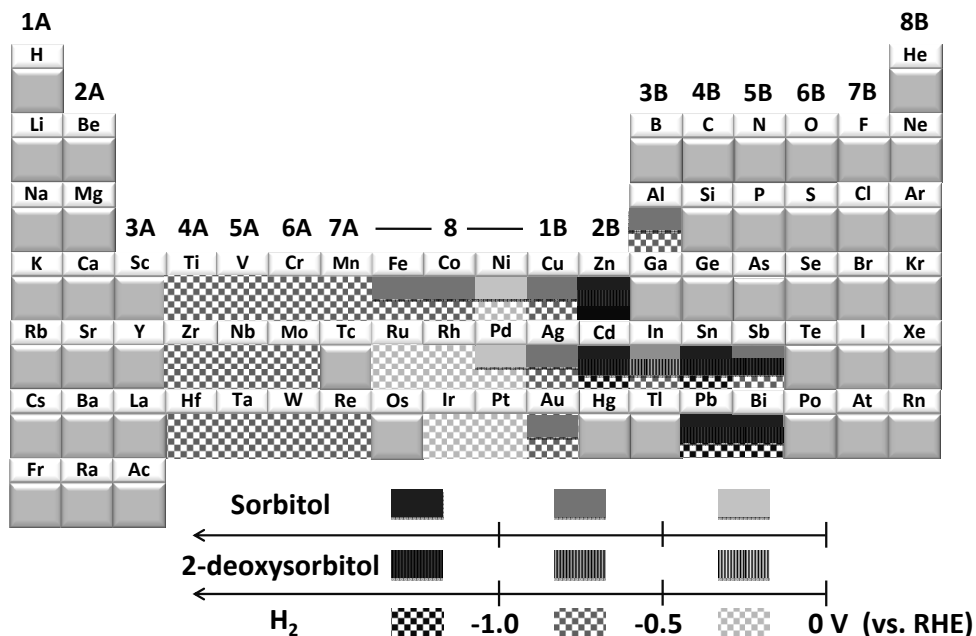


Figure 5. Periodic Table showing the trends of catalysts for hydrogen evolution and the glucose reduction of sorbitol and 2-deoxysorbitol at ambient operating conditions in 0.1 M Na₂SO₄.

7.3.4 A mechanistic view of glucose reduction

From the relationship between voltammetry and reaction product analysis under identical experimental conditions as shown in Figure 1~4, we could clearly show that the electrocatalyst plays a crucial role in glucose hydrogenation. In addition, pH changes on electrode surface during electrolysis should be considered. These aspects were also emphasized recently for the electrochemical oxidation of hydroxymethylfurfural.^[39] The pH on electrode surface increases during hydrogen adsorption (Eq. 1) and especially during hydrogen evolution (Eq. 2) due to the generation of OH⁻, leading to a deviation of the interfacial pH from the pH of the bulk solution (0.1 M Na₂SO₄). The rate of generated OH⁻ is determined by cathodic current. The effect of the high pH near the electrode surface is that the cyclic (inactive) form of glucose easily changes to the linear (electroactive) form, which is considered as a rate-determining step.^[4,6,20] However, long-time electrolysis would increase the pH in the bulk solution, which generates base-catalyzed by-products, i.e. fructose and mannose as isomers of glucose, and poly-ols, i.e. mannitol, reduced from

mannose or fructose.^[9,20] Unsurprisingly, we could observe a trace of fructose, an isomer of glucose at high cathodic current in all experiments, even though the collected samples ranging in pH from 7 to 10 were immediately neutralized by adding 10 mM phosphate buffer solution. To probe the effect of a high pH on glucose isomerization to fructose or mannose, we investigated the time-dependent degradation of glucose by adding 10 mM glucose in 0.1 M NaOH under O₂-free conditions, which clearly showed that ca. 5% of glucose was converted to fructose in an hour, but not to mannose. Based on this observation, we believe that the trace of fructose derives from isomerization of glucose by the increase of pH on the electrode surface during water electrolysis. Therefore the formation of 2-deoxysorbitol on *sp* metals, which Nobe et al. believed to be formed from fructose as the ketone group is in the 2-position,^[4] can be generated through the base-catalyzed process of forming the ‘enediol’ as an intermediate species, which can subsequently be transformed to fructose as shown in Figure 6. However, we must emphasize that postulating fructose as the precursor to 2-deoxysorbitol is an assumption. Our recent work on the dehydrogenation of 2-carbon atom oxygenates showed that the C-O bond prefers to break in a C-OH group next to a C=O group.^[25] If this holds for glucose as well, glucose itself would be the precursor to 2-deoxysorbitol. In addition, the absence of mannitol, an isomer of sorbitol, in the product spectra supports the model of deoxygenation from glucose since the chiral carbon (ketone-C in fructose) is hydrogenated in general into two isomeric alcohols with similar ratio (sorbitol 40% and mannitol 60%), as demonstrated by Owoby-Andely et al.^[9] We also emphasize that the formation of 2-deoxysorbitol, is an electrocatalytic reaction that occurs only on *sp* metals, for reasons that remain to be understood. The existence of OH⁻ near electrode surface is a necessary but not sufficient condition since the hydrogenation reaction is catalyst dependent. Importantly, acidic pH (0.5 M H₂SO₄) does not lead to glucose hydrogenation even on catalysts such as Pb, Co, and Cd, which are active in neutral media. Metals such as Ti and Ru that are not active in neutral media also remain inactive in acidic media. Therefore the presence of OH⁻ is a necessary factor in electrocatalytic glucose hydrogenation, but bulk alkalinity is unfavorable as it generates too many side products. This explains the importance of working in unbuffered neutral media.

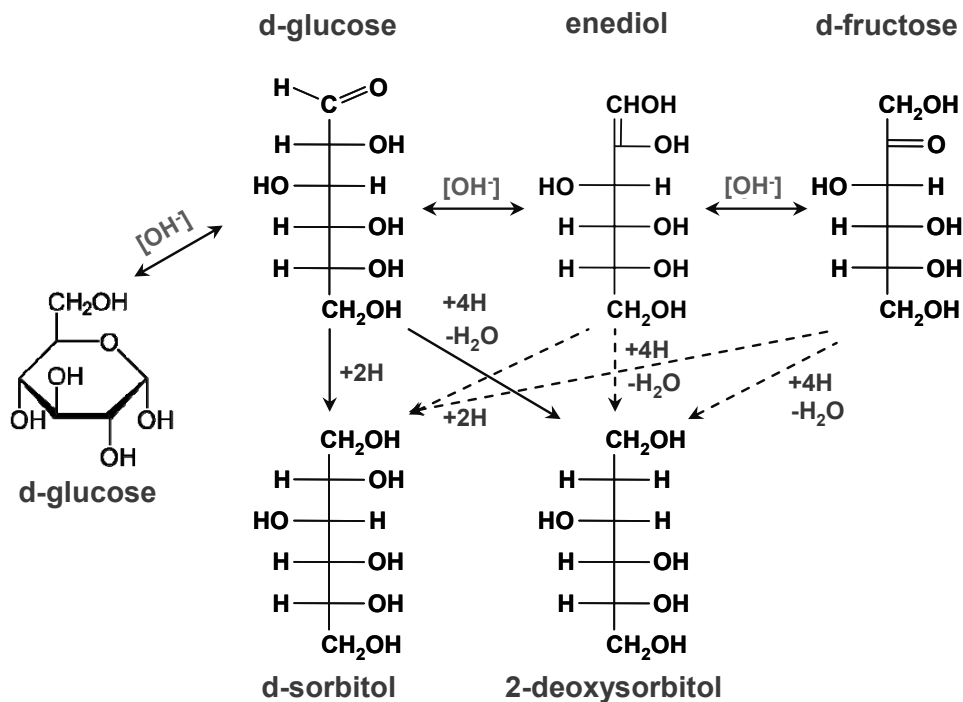


Figure 6. Suggested reaction pathways for glucose hydrogenation and deoxygenation. Solid lines/arrows are the suggested pathways, but the pathways indicated by the dashed arrows cannot be excluded.

7.4 Conclusions

This chapter has described the electrochemical glucose hydrogenation to sorbitol and deoxygenation to 2-deoxysorbitol on solid monometallic electrodes in neutral solution. We studied the activity and selectivity of the catalysts for glucose hydrogenation by correlating the voltammetric scan with online product analysis using high-performance liquid chromatography (HPLC), which provides qualitative and quantitative information of sorbitol or 2-deoxysorbitol formation as a function of potential. Three groups of catalysts regarding to reaction products are distinguished from this study. Hydrogen is the only product 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). Sorbitol and hydrogen are formed on late

transition metals (Fe, Co, Ni, Cu, Pd, Au, and Ag) and Al (*sp* metal). Sorbitol and 2-deoxysorbitol, with a high overpotential for hydrogen evolution, are formed on post-transition metals (In, Sn, Sb, Pb, and Bi) as well as on Zn and Cd (officially *d* metals). Among the late transition d metals, the lowest overpotential to form sorbitol is observed on Ni, sorbitol formation starting from -0.25 V, and Au and Cu show the highest yield of sorbitol (0.15 mM cm^{-2}) at potentials of -1.05 and -1.3 V, respectively. On poor (*sp*) metals, the formation of sorbitol is predominant, with Pb having the highest selectivity (> 87%) and high yield (< 0.7 mM cm^{-2}). Interestingly, the highest selectivity for 2-deoxysorbitol (> 90%) was observed on a Sn electrode with high overpotential (-1.5 V). Even though Pt and Ru are considered the most active catalysts for glucose hydrogenation under heterogeneous catalysis conditions (i.e. under hydrogen pressure and at higher temperature), smooth Pt and Ru electrodes do not show any hydrogenation activity under room-temperature electrochemical conditions. However on a Pt/C nanoparticle electrode with a high active surface area, the formation of sorbitol was observed from -0.21 V, albeit with low activity, suggesting that Pt does show some activity for glucose hydrogenation, either due to the specific surface sites on Pt nanoparticles or simply due to the higher catalytic surface area. From the mechanistic point of view, we believe that 2-deoxysorbitol is generated from glucose hydrogenation followed by a subsequent dehydration (or vice versa) on catalytically active post-transition metals, although we can not exclude the formation of 2-deoxysorbitol from fructose (as originally suggested by Nobe et al.^[4]) since electro-generated OH^- on the catalyst surface during water electrolysis isomerise glucose to fructose *via* the endiol intermediate. Based on these observations, we conclude that the yield or selectivity of hydrogenated products is mainly catalyst dependent combined with a minimum applied potential or current and suitable local pH conditions. In combination with the ability of potential-controlled electrolysis on anode, as recently demonstrated for the cellobiose hydrolysis to glucose,^[40] it may be possible to use the current work to achieve one-pot electrosynthesis of sorbitol from cellobiose or cellulose.

7.5 References

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