

Selective Electrocatalytic Oxidation of Sorbitol to Fructose and Sorbose

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A new electrocatalytic method for the selective electrochemical oxidation of sorbitol to fructose and sorbose is demonstrated by using a platinum electrode promoted by *p*-block metal atoms. By the studying a range of C4, C5 and C6 polyols, it is found that the promoter interferes with the stereochemistry of the polyol and thereby modifies its reactivity.

Given the depletion of oil resources and the continuously increasing demand for energy, the use of efficient and environmentally benign technologies for the utilization of renewable resources such as biomass has become highly topical in recent years.^[1] Sorbitol is considered as one of the 12 potential biomass-based platform chemicals as identified by the Department of Energy in the USA.^[2] Sorbitol can be obtained from the hydrogenation of glucose,^[1a,3] one of the main products of cellulose hydrolysis, and may be further processed to compounds such as alkanes, methanol, and hydrogen by aqueousphase reforming.^[1b,4] Sorbitol is also an interesting starting molecule for isosorbide, both as a building block for the polymer industry (e.g., polyethylene isosorbate terephthalate, PEIT) or as starting point for green solvents and fuel additives.^[5] Two particularly interesting selective oxidation products of sorbitol are fructose and sorbose, the ketose isomers of the corresponding aldoses glucose and gulose. Fructose is an important starting material for the production of furanics, including hydroxymethylfurfural (HMF) and 2,5-furandicarboxylic acid (FDCA), which are green building blocks for a large variety of products including plastics, fuel additives, as well as fine chemicals.^[6] It is well-documented that fructose is the preferred starting material over glucose in dehydration reactions.^[6] Interestingly, the activity and selectivity of the different ketoses towards HMF in acid-catalyzed dehydration is different, but the difference between fructose and sorbose is minor.^[7]

Industrially, fructose is produced from glucose by a xylose isomerase enzyme. However, this process requires a highly pure glucose source (i.e., starch) to avoid deactivation of the enzyme. To the best of our knowledge, the only known pro-

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cesses for the direct selective oxidation of sorbitol to fructose or sorbose are enzyme-catalyzed (by sorbitol dehydrogenase) or obtained by a noncatalytic chemical route reported many years ago.^[8]

In this Communication, we report a new electrocatalytic method for the selective oxidation of sorbitol to ketose isomers using a platinum catalyst in combination with a *p*-block metal promoter. Most previous works in electrochemistry have studied sorbitol oxidation on platinum as a potential anode reaction in fuel cells.^[9] In situ infrared studies have reported that CO_{ads} poisons the platinum surface and that glucose, glucono- δ -lactone, gluconic acid, and CO₂ are main non-adsorbed products.^[10] A prolonged electrolysis study confirmed that glucose is the predominant first oxidation product over the entire potential range.^[11] Here, we show that with suitable modification of the platinum surface, sorbitol can be oxidized to four different aldose/ketose intermediates/products: the aldoses D-glucose and L-gulose via primary alcohol oxidation and the ketoses D-fructose and L-sorbose via secondary alcohol oxidation, as illustrated in Scheme 1.



Scheme 1. Possible D-sorbitol oxidation pathways.

Figure 1 shows the linear-sweep voltammogram and corresponding product distribution of sorbitol oxidation on a carbon-supported platinum catalyst ("Pt/C") obtained at 1 mV s⁻¹. The online product analysis was performed using our combined voltammetry–HPLC setup.^[12] As can be seen from the product distribution, sorbitol is predominantly oxidized through the primary alcohol oxidation pathway to generate glucose and gulose in a 1:1 ratio at low potential ranges and



Figure 1. Sorbitol oxidation (0.1 μ) on Pt/C electrode in 0.5 μ H₂SO₄: (a) current density profile at a scan rate of 1 mV s⁻¹, (b) concentration changes of reaction products, and (c) selectivity (%) of products as a function of potential.

a somewhat higher selectivity to glucose at higher potentials. This suggests that there is no strong stereoselective effect for the electrocatalytic oxidation of sorbitol on the unmodified platinum catalyst, whilst the secondary alcohol oxidation is strongly suppressed. Interestingly, at the potentials of platinum surface oxide formation (> 1.0 V), the selectivity to formic acid increases via C–C bond cleavage as commonly seen in polyol oxidation^[11,13] in combination with an increased selectivity towards fructose; an effect that remains to be further understood.

Our previous work regarding the electrocatalytic oxidation of glycerol has revealed that Pt/C electrodes modified by bismuth or antimony enhance the catalytic activity and change the reaction selectivity toward secondary alcohol oxidation to generate dihydroxyacetone.^[13c,d] Previous work has shown that the product distribution obtained from voltammetric studies with online HPLC was consistent with a prolonged electrolysis at a chosen potential.^[13d] It is known that bismuth and antimony on the platinum surface block the CO formation and en-



Figure 2. Sorbitol oxidation (0.1 M) in 0.5 M H₂SO₄ on a Pt/C electrode in bismuth-saturated solution and a antimony-modified Pt/C (irrev., θ_{sb} = 90 %): (a) current density profile at scan rate of 1 mV s⁻¹, (b) concentration changes of reaction products, and (c) selectivity (%) of products as a function of potential.

hance the catalytic activity during oxidation of small organic molecules,^[13d, 14] but the mechanism through which the adatoms alter the selectivity during polyol oxidation has not yet been well established. Figure 2 shows how in a bismuth-saturated solution the Pt/C electrode enhances the sorbitol oxidation activity to ca. 180% compared to Pt/C in terms of maximum current density (which is proportional to the turnover frequency; TOF), and, more importantly, steers the product selectivity in favor of sorbose and fructose at potentials below 0.7 V_{RHF}. A similar effect is observed with an antimony-modified Pt/C: an antimony coverage of ca. 90% on Pt/C surface reduces the current of sorbitol oxidation with respect to Pt/C, but also in the presence of antimony, sorbitol is selectively oxidized to sorbose and fructose up to 0.9 $V_{\mbox{\tiny RHE}}$ with a corresponding significant suppression of the primary alcohol oxidation. Underpotential deposited bismuth and antimony on the platinum surface are in the metallic state and the stability of the adatoms has been demonstrated in direct formic acid fuel cells (DFAFC).^[14] For both bismuth and antimony, at higher potentials, voltammetric peaks may correspond to the adsorption of oxygenated species and finally to oxidative desorption of the adsorbed bismuth and antimony, as a similar product distribution as on unmodified Pt/C is obtained.^[15a, b, 16] Note that, in a real application, the promoter ions would be present in solution, so that the adsorption/desorption process would be reversible. In addition, lead, tin, and indium on Pt/C also enhance the catalytic activity and change the selectivity of sorbitol oxidation (see Supporting Information, Figure S1), whilst these adatoms do not alter the selectivity during glycerol oxidation.^[13c]

Interestingly, on all Pt/C electrodes modified by adatoms, we observe that the selectivity towards each primary (glucose vs.

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Figure 3. Arabitol oxidation (0.1 μ) in 0.5 μ H₂SO₄ on a Pt/C electrode (blank) in comparison with sorbitol (0.1 μ) and ribitol (0.1 μ) oxidation and arabitol oxidation on a Pt/C in Bi-saturated solution: (a) current density profile at scan rate of 1 mV s⁻¹, (b) concentration of reaction products of arabitol oxidation, and (c) corresponding selectivity (%) of products as a function of potential.

gulose) and secondary (fructose vs. sorbose) alcohol oxidation product is not identical. To study why the selectivity to glucose and sorbose is superior to that to gulose and fructose, we investigated how the molecular structure, especially the stereochemistry of the 2-carbon position, is related to the selectivity of the oxidation products. Figure 3 compares the electrocatalytic oxidation of two C5 polyols that is, p-arabitol and p-ribitol ($C_5H_{12}O_5$), on a Pt/C electrode in acidic solution, in absence and presence of bismuth in solution. The possible oxidation pathways of arabitol are shown in Scheme 2.

The difference between the structure of arabitol and ribitol is in the steric position of -OH on C_2 . Remarkably, on an unmodified Pt/C electrode, the oxidation activity of arabitol is strongly suppressed compared to that of sorbitol and ribitol.



Scheme 2. Possible oxidation pathways of D-arabitol and its structural comparison with D-ribitol.

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Arabitol is selectively oxidized to arabinose compared to lyxose regardless of the presence of bismuth (a scheme of the possible pathways and the results of ribitol oxidation are presented in the Supporting Information, Scheme S1 and Figure S2). We note that the presence of bismuth on Pt/C significantly enhances the oxidation activity of arabitol to the secondary oxidation product xylulose as the dominant product, with a lower selectivity to ribulose. The same observation was made for the oxidation of C4 polyols (see Supporting Information, Scheme S2, Figures S3 and S4): the placement of the primary and secondary OH on the same side of the carbon chain in the Fischer projection renders the polyol oxidizable on platinum; if, however, the OHs are placed on opposite sides, the polyol has a very low oxidation activity. A similar stereoselective oxidation activity has been observed before by Enea and Ango^[17] and Parpot et al.^[18] for polyol oxidation in alkaline media. Addition of bismuth to the reactive system removes this stereoselective oxidation activity (though some preference of one isomer over the other still remains), and leads to the selective oxidation of the secondary alcohol. This strongly suggests that the *p*-block-type promoter atoms interfere with the intrinsic stereochemistry of the polyol in such a way that the secondary alcohol is oxidized selectively. It has suggested before that metal cation can act as a Lewis acid capable of catalysing the ketose-aldose isomerisation.[19]

The above experiments were designed to demonstrate the principle possibility of selectively oxidizing the secondary alcoholic group on sorbitol by choosing carefully controlled electrochemical conditions in a half cell. It shows that by promoting the platinum surface by p-block metal atoms, one may steer the selectivity of polyol oxidation in a fundamental way. Application of this model approach to an electrolysis cell based on a carbon cloth diffusion layer would require the consideration and optimization of several parameters (e.g., catalyst loading, membrane, concentration of sorbitol, operating temperature). Our work here demonstrates the "proof-of-principle" that the *p*-block modified platinum electrode is the most promising catalyst for obtaining a high yield and selectivity for such an application. In fact, the actual practical application of this result may or may not involve an electrochemical setup, but would likely still use the catalytic system suggested here. Aqueous-phase heterogeneously catalyzed oxidation of sorbitol by a PtBi catalyst may in fact an industrially more convenient option (see, e.g., refs. [20]) for the selective oxidation of glycerol by PtBi using such a setup), but those experiments will not easily give the very detailed information collected in Figure 1-3. Still, it is useful to comment on the implications of reactivity that can be extracted from Figure 2. The experiment illustrated in Figure 2(a)-(c) took ca. 20 min, which is by far not long enough to report on conversion factors. The currents are stable on this time scale, but we have not tested the stability on the time scale of hours. The maximum current density in Figure 2 is ca. 0.1 mA cm⁻² at 0.5 V at room temperature, equivalent to a conversion of ca. 5×10^{-10} mol of sorbitol molecules per second per cm² of catalyst, from a 0.1 м solution. This implies that 1 g of platinum of 200 m²g⁻¹ surface area will yield 10⁻³ mol fructose plus sorbose in 1 second. This yield will be higher at higher temperature, though selectivity may be impaired by further oxidation of the ketoses.

In conclusion, we demonstrate the fundamental possibility of the selective electrochemical oxidation of sorbitol to fructose and sorbose by using a platinum electrode promoted by *p*-block metal atoms. This simple and robust approach would be easily scalable or translated into aqueous-phase heterogeneous catalysis, but the high selectivity and yield towards a single product as in conventional enzymatic synthesis is still challenging. Given the possibility of the electrochemical reduction of glucose to sorbitol,^[1a,3] the approach would also open up the way to (electro)catalytically convert glucose to its ketonic isomers. Furthermore, by studying a range of C4, C5, and C6 polyols, we provide evidence for the idea that the promoter interferes with the stereochemistry of the polyol and thereby modifies its reactivity. Still, the exact mechanism of promotion remains to be understood in detail.

Experimental Section

Electrochemical measurements were carried out in a standard three-electrode cell controlled by a potentiostat/galvanostat (μ -Autolab Type III). A thin-film electrode with 3 nm Pt/C nanoparticles (50 wt%, Tanaka) was fabricated by loading defined amounts of a nanoparticle suspension (10 μ L) in water (1 mg mL⁻¹) onto a polished glassy carbon substrate, subsequently dried by purging Ar at room temperature. In order to confirm the electrochemically active surface area of the loaded catalyst, a blank voltammogram was recorded before each experiment. A large platinum plate was employed as a counter electrode and a reversible hydrogen electrode (RHE) as a reference. Oxidation of polyols (sorbitol and arabitol) was performed in a mixture of polyols (0.1 m, analytical grade) and 0.5 m H₂SO₄ under deaerated conditions by purging Ar.

For the Pt/C surface modification, analytical grades of bismuth (Bi₂O₃, Sigma-Aldrich), antimony (Sb₂O₃, Sigma-Aldrich), lead (Pb(ClO₄)₂, Acros), tin (SnCl₂·2H₂O, Merck), and indium (In₂(SO₄)₃, Sigma-Aldrich) were used. Irreversible adsorption of adatoms was performed by placing the freshly prepared Pt/C electrode in contact with antimony-saturated 0.5 м H₂SO₄ solutions and 1 mм solution of tin for 3 min.^[13c] After rinsing the electrode with water, each coverage is determined by recording the suppression of the hydrogen region,^[21] and then transferred to the electrochemical cell. For reversible adatom adsorption/desorption, 1 mм adatoms (lead and indium) and a sufficiently large amount of Bi2O3, which corresponds to a concentration of ca. 10^{-5} – 10^{-4} M, were introduced directly into the electrochemical cell. A freshly prepared Pt/C electrode was kept at a constant potential of 0.1 V for 3 min,^[13c] after which the surface coverage is measured by the suppression of the hydrogen region in a blank solution, before applying it for sorbitol oxidation.

The reaction products during voltammetry were collected in a microtiter plate with a fraction collector and collected samples were analysed with an HPLC system (online HPLC), which provides qualitative and quantitative information as a function of potential as described in our previous work.^[12, 13d,22] Sample volumes of 30 μ L were injected into the four columns in series of an Aminex HPX 87-H (Bio-Rad) and three columns of Sugar SH1011 (Shodex) with diluted sulfuric acid (0.5 mM) as eluent. The selected temperature of column oven was 85 °C. Details of system configuration are described elsewhere.^[12, 13]

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- a) A. M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem. Int. Ed.* 2012, 51, 2564–2601; *Angew. Chem.* 2012, 124, 2614–2654; b) R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* 2002, 418, 964–967.
- [2] T. Werpy, G. Petersen, in Top Value Added Chemicals from Biomass. Results of Screening for Potential Candidates from Sugars and Synthesis Gas, Vol. 1, US Department of Energy, 2004.
- [3] Y. Kwon, M. T. M. Koper, ChemSusChem **2013**, 6, 455-462.
- [4] G. W. Huber, J. W. Shabaker, J. A. Dumesic, Science 2003, 300, 2075– 2077.
- [5] R. M. de Almeida, J. Li, C. Nederlof, P. O'Connor, M. Makkee, J. A. Moulijn, ChemSusChem 2010, 3, 325–328.
- [6] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* 2013, *113*, 1499–1597.
- [7] R.-J. van Putten, J. N. M. Soetedjo, E. A. Pidko, J. C. van der Waal, E. J. M. Hensen, E. de Jong, H. J. Heeres, *ChemSusChem* **2013**, *6*, 1681–1687.
- [8] W. R. Sullivan, J. Am. Chem. Soc. 1945, 67, 837-840.
- [9] A. Oyarce, C. Gonzalez, R. B. Lima, R. W. Lindström, C. Lagergren, G. Lindbergh, *Electrochim. Acta* 2014, *116*, 379–387.
- [10] a) L. Proença, M. I. S. Lopes, I. Fonseca, A. Rodes, R. Gomez, A. Aldaz, *Electrochim. Acta* **1998**, *44*, 735–743; b) L. Proença, M. I. S. Lopes, I. Fonseca, J. M. Leger, C. Lamy, *J. Electroanal. Chem.* **1997**, *432*, 193–198; c) L. Proença, M. I. S. Lopes, I. Fonseca, F. Hahn, C. Lamy, *Electrochim. Acta* **1998**, *44*, 1423–1430; d) J. M. Léger, F. Hahn, B. Beden, C. Lamy, M. F. Bento, I. Fonseca, M. I. S. Lopes, *J. Electroanal. Chem.* **1993**, *356*, 255–267.
- [11] L. Proença, M. I. S. Lopes, I. Fonseca, K. B. Kokoh, J. M. Leger, C. Lamy, J. Electroanal. Chem. 1997, 432, 237–242.
- [12] Y. Kwon, M. T. M. Koper, Anal. Chem. 2010, 82, 5420-5424.
- [13] a) Y. Kwon, K. J. P. Schouten, M. T. M. Koper, *ChemCatChem* **2011**, *3*, 1176–1185; b) Y. Kwon, S. E. F. Kleijn, K. J. P. Schouten, M. T. M. Koper, *ChemSusChem* **2012**, *5*, 1935–1943; c) Y. Kwon, T. J. P. Hersbach, M. T. M. Koper, *Top. Catal.* **2014**, *57*, 1272–1276; d) Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez, M. T. M. Koper, *ACS Catal.* **2012**, *2*, 759–764.
- [14] a) J. K. Lee, H. Jeon, S. Uhm, J. Lee, *Electrochim. Acta* 2008, 53, 6089–6092; b) S. Uhm, H. J. Lee, Y. Kwon, J. Lee, *Angew. Chem. Int. Ed.* 2008, 47, 10163–10166; *Angew. Chem.* 2008, 120, 10317–10320.
- [15] a) E. Herrero, J. M. Feliu, A. Aldaz, J. Electroanal. Chem. 1994, 368, 101–108; b) A. Fernandez-Vega, J. M. Feliu, A. Aldaz, J. Clavilier, J. Electroanal. Chem. 1989, 258, 101–113; c) S. P. E. Smith, K. F. Ben-Dor, H. D. Abruna, Langmuir 2000, 16, 787–794; d) S. Uhm, Y. Yun, Y. Tak, J. Lee, Electrochem. Commun. 2005, 7, 1375–1379.
- [16] S. H. Cadle, S. Bruckenstein, Anal. Chem. 1972, 44, 1993-2001.
- [17] O. Enea, J. P. Ango, *Electrochim. Acta* **1989**, *34*, 391–397.
- [18] P. Parpot, N. Nunes, A. P. Bettencourt, J. Electroanal. Chem. 2006, 596, 65-73.
- [19] a) B. E. Tilley, D. W. Porter, R. W. Gracy, *Carbohydr. Res.* 1973, *27*, 289–296; b) R. W. Nagorski, J. P. Richard, *J. Am. Chem. Soc.* 2001, *123*, 794–802.
- [20] a) H. Kimura, Appl. Catal. A 1993, 105, 147–158; b) W. Hu, D. Knight, B. Lowry, A. Varma, Ind. Eng. Chem. Res. 2010, 49, 10876–10882.
- [21] P. Rodríguez, J. Solla-Gullon, F. J. Vidal-Iglesias, E. Herrero, A. Aldaz, J. M. Feliu, Anal. Chem. 2005, 77, 5317–5323.
- [22] Y. Kwon, S. J. Raaijman, M. T. M. Koper, ChemCatChem 2014, 6, 79-81.

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