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Electrochemistry for the generation of renewable chemicals: One-pot electrochemical deoxygenation of xylose to δ-valerolactone

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Abstract

Electrochemical method is now widely recognized as a green and sustainable route for conversion of biomass to fuels and chemicals. However, most electrochemical biomass conversions that involve deoxygenation depend on intermediates from thermo-chemical and biological processes. At present, electrochemical deoxygenation of primary biomass feedstocks is rare. Thus, it is desirable to develop electrochemical methods for deoxygenation of primary biomass feedstocks into fuels and chemicals. In this study, we demonstrate the electrochemical conversion of xylose to δ -valerolactone via carbonyl intermediates. The conversion was achieved in aqueous media and at ambient conditions. We showed that a tandem anodic and cathodic conversion is a viable strategy for achieving electrochemical deoxygenation of biomass substrates. This is the first report on a one-pot electrochemical deoxygenation of xylose to δ -valerolactone.

Keywords: Xylose, δ -valerolactone, oxidation, cathodic reduction, deoxygenation

1 Introduction

Although fossil fuels remain the dominant primary energy resources that power socioeconomic activities in our modern society, increasing the share of renewable electricity generation in the global energy mix is an active pursuit towards curtailing climate change and global warming.^[1-2] Due to intermittent of nature solar and wind electricity generation, integration into convention electrical energy installations requires storage buffers.^[3-6] Rechargeable batteries are an established technology for storing electricity as chemical energy. The battery technologies depend on selection of appropriate reversible redox reactions for different applications. Lithium affords the most promising battery chemistry and it is presently the leading battery technology.^[7] Lithium battery products range from small to medium scale storage applications (such as from laptop to electric cars).^[8-10] However, there are still design constraints for grid scale storage applications.^[11] Fossil fuels which we currently depend on are products of energy storage of captured solar energy in covalent bonds during photosynthesis.^[12] Thus, taking inspiration from nature, transformation leading to formation of covalent bonds can affords large scale storage of renewable in portable forms such fuels and chemicals, especially when renewable energy is exploited to transform carbon dioxide into fuels and chemicals.^[13-14] This area is currently witnessing intense research activities,^[15-17] and it has the potential of helping to achieve the goals of energy storage and curtailment of global warming.

Industrial electrochemical processes such as chlor-alkali process, Hall-Heroult process etc. consume electricity at grid scale level to drive irreversible chemical reactions. These inorganic electrochemical processes are important for production of basic chemicals (NaOH,

Cl₂, and H₂) and aluminium metal respectively. At the turn of the century electricity had been used to drive industrial production of a number of organic chemicals.^[18] While most of the industrial organic electrochemical processes have been displaced by thermochemical methods, due to cheap availability of petroleum, there is a renaissance of interest in organic electrochemical processes using biomass substrates for production of fuels and chemicals as a means of biomass valorisation and storage of excess renewable electricity. Thus use of renewable resources (biomass and renewable electricity) for production of chemicals and fuels is one of the goals of sustainable chemistry.

Generally, the main goal in conversion of a carbohydrate biomass derived substrate into a fuel compound entails an increase of the hydrogen/oxygen ratio with minimal loss of carbon atoms of the substrate. For instance, in fermentation of glucose to ethanol: $C_6H_{12}O_6 \rightarrow$ $2C_2H_5OH + 2CO_2$, the increase of the hydrogen/oxygen ratio in ethanol is accomplished by a loss of two carbon atoms per unit of the starting glucose converted. Partial dehydration of carbohydrates e.g., xylose and glucose is a promising path, but the resulting products (furfural, hydroxymethylfurfural, levulinic acid) are yet suitable as fuel because they contain reactive groups (unsaturation, carbonyl and carboxylic acid).^[19-23] Further conversion processes of the partial dehydration intermediates into fuel suitable molecules require high temperature and hydrogenation process. high pressure Electrochemical hydrogenation/reduction at ambient conditions is now recognised as an environmentally benign process for converting furfural, hydroxymethylfurfural and levulinic acid into fuel suitable molecules.^[24-31] However, the electrochemical routes to biofuels are largely as complementary to thermochemical methods so far as the scope of substrates is limited to the above intermediates from thermochemical partial oxidation processes. It is desirable to expand the scope of substrates to primary carbohydrate biomass derived feedstocks and the robustness of electrochemical conversions as a means of storing excess renewable electricity. Thus, in this communication we demonstrate deoxygenation of xylose into delta valerolactone, a valuable chemical intermediate, using a one-pot electrochemical process.

2 Experimentals

2.1 Chemicals

All chemicals used in this study were of analytical grade. For qualitative and quantitative analysis, reference materials and solvents were used as purchased, without purification.

2.2 Electrode materials

Ag/AgCl sat. KCl electrode (SE11, Sensortechnik Meinsberg, Germany, 0.197 vs standard hydrogen electrode (SHE) as reference. All used electrodes are listed in Table 1 with their respective purity and surface area.

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Electrode material	Purity	Electrode surface (cm ²)
Lead (Pb) ^A	99.999	11
Zinc (Zn) ^A	99.99	11
Platinum (Pt) ^A	99.9	11
Ruthenium based das anode (RUA) ^B		

Table 1. Purity and surface area of electrode materials used

(A) ChemPUR, Germany B) Umicore Galvanotechnik GmbH, Germany(B) Ti Anode Fabricators Pvt. Ltd, Chennai - 126, India

2.3 Electrochemical procedure

All electrochemical reactions were conducted under potentiostatic control using a potentiostat/galvanostat SP50 (Bio-Logic SAS, Claix, Frankreich). All experiments used a three-electrode configuration and were stirred continuously with a magnetic stirrer. The undivided cell is a single 40 ml chamber cyclic glass cell with a 1cm neck window fitted with a Teflon® stopper bearing the anode and cathode terminals 2 cm apart. The divided cell was a 40 ml each two-chamber H-type glass cell. The anode and cathode terminals were 10 cm apart, the anode and the cathode chambers was separated via a cation exchange membrane (fumasep FKE, Fumatech, Germany)

2.4 Analysis

Qualitative analyses were carried out using gas chromatography-mass spectrometry (GC-MS) (Trace GC Ultra, DSQ II, Thermo Scientific, Germany) equipped with a TR-Wax MS (30 m x 0.25 mm ID x 0.25 mm film GC column, Thermo Scientific, Germany). Routine quantitative analyses were performed by high performance liquid chromatography (HPLC), by means of a refractive index (IR) detector (Spectrasystem P4000, Finnigan Surveyor RI Plus Detector, Fischer Scientific) equipped with HyperREZ XP carbohydrate H+8 μ m (S/N: 026/H/012-227) column. Sulphuric acid (0.005N, flow rate 0.5 ml min-1) as eluent. The column was operated at different temperature depending on sample composition, the refractory index detector was operated at 25°C.

3 Results and discussions

3.1 Conversion of hydroxyl to carbonyl in divided cell

Carbohydrates possess a carbonyl group and several hydroxyl groups. Thus, deoxygenation of carbohydrates would entail transforming its carbonyl group and hydroxyl groups to a methylene bridge. The exploitation of Clemenson-type cathodic reductions of aldehyde and ketone groups is well documented. Also, hydroxyl group(s) at alpha position(s) to a carbonyl group can be converted to methylene bridge.^[32-34] But direct reduction of a normal hydroxyl group and a carboxylic group are electrochemically inaccessible in aqueous media. Hence the level of deoxygenation that can be achieved in a carbohydrate substrate by direct cathodic reduction is limited. To achieve higher level of deoxygenation, a complementary anodic selective conversion of the hydroxyl groups to carbonyl becomes imperative. Anodic oxidation of polyols has been an active area of research for fuel cell applications where the target is exhaustive or complete oxidation of substrate to carbon dioxide. However, selective anodic oxidation of polyols is just receiving attention of late. Some of reported electrodes for selective anodic oxidation of secondary alcohols include Ru, Bi, Sb promoted platinum.^[35-37] While these electrodes possess desired selectivity, they suffer from stability issues which render them unsuitable for use in an undivided cell. Leaching and migration of Ru from RuO₂-Pt anode to the cathode had been reported in a fuel cell system.^[38-39] Bi-Pt and Sb-Pt anodes are likely to be prone to similar stability challenges. Our attention is drawn to hypochlorite (HClO) as a selective oxidant for conversion of alcohol group to carbonyl group(s).^[40] According to the Pourbaix diagram of aqueous chlorine, hypochlorite is stable in the pH range 3-6. The standard organic chemistry hypochlorite recipe is NaClO/CH₃COOH, and NaClO can be generated via electrolysis of NaCl. So we opted to explored in-situ generation of active oxidant from a suitable electrolyte.

Platinum is a stable anode for chloride ion oxidation to chlorine and carbonyl to methylene conversion had been demonstrated over lead electrode. So we investigated in-situ generation

of HClO using an undivided cell consisting of a mixture of NaCl and CH₃COOH/CH₃COONa buffer as electrolyte, platinum and lead as anode and cathode respectively. During the electrolysis, we observed deposition of lead oxide on the platinum anode. The same experiment with just NaCl without acetate buffer showed no lead oxide deposition at the platinum anode. Since lead acetate is very soluble in water, acetate ion can promote transport of lead (II) ions to the anode where they get further oxidised and deposited as lead oxide. In addition to leaching of lead cathode, presence of acetate in the electrolyte can also affect the selectivity of the electro-generation of the active oxidant. To avoid this unwanted effects of the acetate ion, we proceeded with just NaCl solution as electrolyte.

3.2 Conversions of model substrates in divided cell

Common carbohydrate substrates such as xylose and glucose are multi-hydroxyl substrates and can assume open chain or ring structure in solution. Monitoring the selective conversion of the hydroxyl groups in xylose and glucose to carbonyl group will be challenging. Moreover, because of the limitation of mimicking the established recipe for in-situ generation of HClO; we investigated the selectivity of the electrogenerated oxidant from NaCl solution on simpler substrates: 2,3-butanediol, 1,2-propanediol & glycerol. Figure 1 shows the conversion and the selectivity of the oxidation of 2,3-butanediol by the electro-generated oxidant. The substrate in scheme 1 contains only a secondary hydroxyl group, and the results in Figure 1 indicates absence of side reactions or deviations from the proposed pathway of oxidation of 2,3-butandiol in scheme 1. Thus, substrates containing only secondary hydroxyl groups are promising candidates for selective electrochemical deoxygenation via tandem selective oxidation and Clemenson-type cathodic reduction.



Figure 1: Conversion and selectivity of oxidation of 0.2M 2,3-Butanediol in a divided cell using Pt anode and cathode using 0.5M NaCl (potential 2.5V Saturated AgCl/Cl, temperature 25°C)



Scheme 1: Proposed pathway of electrooxidation of 2,3-butanediol by the electrogenerated oxidant from NaCl solution

Scheme 2 shows proposed pathways of the electrooxidation of 1,2-propandiol. The dash line divides the desired products (above) from the undesired products (below). Figure 2 shows the monitored oxidation products of 1,2-propandiol with the electrogenerated HClO. This substrate has a primary and a secondary hydroxyl group, hence, the product profile can give information about the selectivity of the electrogenerated oxidant on the type of hydroxyl groups. Figure 2 showed that the oxidant displayed preferential oxidation of the secondary over the primary hydroxyl group of the substrate. However, the sum of selectivities of monitored products does not account for the conversion of the substrate. The decrease in the material balance with time suggests that the main product undergoes other reactions outside the scheme. The carbonyl products (acetol and lactaldehyde) are prone to undesired aldol condensation reactions. The products are also prone to myriads of ester formations via their hydroxyl, aldehyde and acid groups.^[41-44]



Scheme 2: Proposed pathway of electrooxidation of 1,2-Propanediol by the electrogenerated oxidant from NaCl solution



Figure 2: Conversion and selectivity of oxidation of 0.25M 1,2-Propanediol in a divided cell using Pt anode and cathode using 0.5M NaCl. (potential 2.5V Saturated AgCl/Cl, temperature 25°C)

To ascertain that the observed product selectivities are due to the electrogenerated oxidant, the oxidation of 1,2-propandiol was repeated using HCl and H_2SO_4 as electrolyte. The product profile obtained with HCl is nearly identical with that of NaCl but different from that obtained using H_2SO_4 as electrolyte (supplementary information). This shows the anodic reaction is independent of the nature of cation and different mechanism accounts for the electrooxidation of 1,2-propandiol in chloride and sulphate media. Chloride media displayed preferential oxidation of the secondary over the primary hydroxyl group of the 1,2-propandiol, but the reverse is the case in sulphate. Since sulphate ion is electrochemical refractory in aqueous media electrooxidation of 1,2-propandiol takes place on the platinum surface. But oxidation of chloride ion is possible on platinum and the resulting chlorine species, probably HClO, is the active oxidant in the oxidation of 1,2-propandiol in NaCl and HCl solution.

Scheme 3 depicts proposed pathways of electrooxidation of glycerol, a substrate with two primary and a secondary hydroxyl groups. Electrooxidation of glycerol was investigated in NaCl, HCl and H₂SO₄ as electrolytes. The three electrolytes displayed poor material balance with respect to the monitored products (supplementary information). The products profile obtained in NaCl and HCl/H₂SO₄ are similar to reported product selectivities of glycerol oxidation over platinum in alkaline and acidic media respectively.^[45] This shows that oxidation of glycerol occurred on the platinum surface. This suggests increasing number of hydroxyl group of the substrate increasing the strength of adsorption which promotes oxidation on the platinum instead of desired oxidation in the electrolyte through electrogenerated chlorine oxidant.



Scheme 3: Proposed pathway of electrooxidation of Glycerol by the electrogenerated oxidant from NaCl solution

3.3 Conversions of model substrates in an undivided cell

To achieve the intended deoxygenation objective, it is desirable to couple anodic oxidation and cathodic reduction in an undivided cell. It is anticipated that this arrangement will take advantage of the possibility of a combined transformation of carbonyl and alpha hydroxyl groups to methylene bridges to achieve high level of substrate deoxygenation. The results in section 3.2 satisfy the selective oxidation requirement, thus providing the reducible carbonyl intermediates for the cathodic half reaction. However, the cathodic conversion of the carbonyl compound in aqueous media is complicated due to keto-enol and hydrationdehydration equilibria.^[46] The keto-enol equilibria result in different reduction paths to different products. Species containing an alpha sp³ hydrogen atom to a carbonyl group are prone to keto-enol equilibria.^[47] Presence of an alpha hydroxyl group to a carbonyl group favours aldo-keto isomerisation as in the case of acetol-lactaldehyde equilibria.^[48] Theoretical studies had also suggested that HOCl, the most probable chlorine oxidant species in the HCl electrolyte, is a potential catalyst of keto-enol tautomerism.^[49] Also in aqueous media, carbonyl compounds react with water forming geminal diols. The geminal diol group is cathodic inactive.^[50-51] The hydration-dehydration equilibria favours hydration and the rate of the dehydration is usually slow.^[52-54] So the conversion of a hydrated carbonyl species at the cathode follows a CE mechanism, a pre-chemical dehydration of a germinal diol before electron transfer at the cathode. Thus, the results of in Figure 3 can be explained by selective oxidation 1,2-Propanediol to carbonyl intermediates and their subsequent transformations at the cathode presented in scheme 4. The cathodic reduction can follow a four protons-four electrons path or a two protons-two electrons path. Acidic media favour dehydration and the four protons-four electrons reduction path that leads to the desired deoxygenation.

A similar electrolysis of 2,3-Butanediol gave very small amount reduced products (Figure 4) and the Pb cathode transformed into PbO₂. This is a signature of reaction of chlorine with Pb catalysed by presence of oxygen.^[55] Cathodic reduction of 2,3-Butanedione had been demonstrated using Hg cathode;^[56] and paired electrochemical conversion of 2,3-Butanediol to butanone in a divided flow cell using NaBr as electrolyte and Pb/Hg as cathode had been reported by Baizer et al.^[57] As illustrated in Figure 4, we carried out the electrochemical reduction of the products (2,3-Butanedione Acetoin & Butanone) using a Pb cathode in a divided cell. The products are readily reduced at the Pb electrode and a similar cathodic reduction paths as proposed in the case of 1,2-propanediol may be expected for the oxidized intermediate of 2,3-Butanediol (supplementary information Figure 4b, Scheme 5). So we inferred that the lack of reduced product in the 2,3-Butanediol electrolysis was due to HClO chlorine attack on the Pb cathode. While 1,2-Propanediol or its oxidized intermediates act as inhibitor of HClO attack on the Pb cathode.



Figure 3: Conversion and selectivity of oxidation of 0.25M 1,2-propandiol in an undivided cell using Pb as working electrode and Pt counter cathode using 0.5M HCl. (potential -1.8V Saturated AgCl/Cl, temperature 25° C)



Scheme 4: Proposed pathway of the cathodic transformations at a Pb electrode during electrolysis of 1,2-Propanediol (Pb as working electrode and Pt counter cathode using 0.5M HCl, -1.8V Saturated AgCl/Cl, temperature 25°C)



Figure 4: Conversion and selectivity of the oxidation of 0.25M 2,3-but andiol in an undivided cell using Pb as working electrode and Pt counter cathode using 0.5M HCl. (potential -1.8V Saturated AgCl/Cl, temperature 25° C)

3.4 Electrochemical deoxygenation of xylose

The results from the conversions of the model substrates suggests that electrochemical deoxygenations are more probable for primary biomass substrates that have no primary hydroxyl or minimal ratio of primary/secondary hydroxyl group via a sequential oxidation and reduction steps in a divided cell. Among the primary carbohydrate molecules xylose comes close to meeting these requirements. Xylose exists predominantly as xylopyranose in solution. xylopyranose is a six-membered ring, with an intramolecular hemiacetal formed between a hydroxyl (on C₅ carbon) and the aldehyde carbon (C₁). The remaining three secondary hydroxyl groups that can be selectively converted to ketones, and a two-step electro-deoxygenation of xylose to δ -valerolactone was envisaged. Xylose and δ -

valerolactone are the two extremes of a continuum of possible oxidised and reduced intermediates (see Scheme 4 in supplementary information). Since selective anodic oxidation is the critical step of the electrochemical deoxygenation, obtaining reduced intermediates is an evidence of successful selective oxidation step. Moreover, hydrophobicity of the intermediates increasing with increasing extent of reduction, therefore, extraction into ethyl acetate will allow identification of reduced intermediates using GC-MS.

Anodic oxidation of xylose in a divided cell using Pt working electrode (2.5V vs Ag/AgCl reference electrode) in 0.5M HCl, followed by cathodic reduction using Pb working electrode at (-1.8V vs Ag/AgCl reference electrode) gave no δ -valerolactone. Then we carried out xylose conversion in an undivided cell containing 0.25M xylose, 0.5M HCl, a Pt working electrode and Pb counter electrode at 2.5V vs Ag/AgCl reference electrode), followed cathodic reduction in a divided cell at -1.8V, Pb working electrode and Pt counter electrode. GC-MS analysis of ethyl acetate extract of the sequential electrochemical oxidation and reduction of xylose showed no compound. We interpreted the absence of reduced intermediates as non-selective oxidation of xylose. Anodic polarisation brings about surface oxide formation on platinum, and as explained in the case of glycerol oxidation, three hydroxyl groups of xylose will lead to strong interaction with the surface oxide on platinum. This strong adsorption of xylose on platinum surface may not only inhibits chloride ion oxidation but also promote xylose non-selective oxidation on the platinum surface. In order minimise non-selective oxidation we carried out the oxidation step at high current density and reduced reaction time (1h), followed by stirring for 2h before the reduction step. GC-MS analysis of ethyl acetate extract of the cell content after the reduction indicates a trace of δ valerolactone. This confirms that the platinum is not sufficiently chlorine selective in the presence of xylose, thus, a chlorine selective anode will lead to successful deoxygenation of xylose.

Dimensionally stable anode (DSA) anodes are platinum group metal oxide (PGM) coated titanium electrocatalysts. They are widely used in the chlor-alkali industry. They are more chlorine selective than platinum. So we explored a commercial ruthenium based DSA anode (RUA) in the two step electrochemical deoxygenation of xylose. GC-MS analysis of ethyl acetate extract confirmed dexygenation of xylose to δ -valerolactone. Encouraged by δ valerolactone formation, we attempted to integrate the two step into one-pot reaction. But taking into consideration the earlier experience of the problem of electrogenerated chlorine oxidant attack of the cathode when the undivided cell was used (with 2 cm separation between the anode and the cathode), we allowed sufficient gap between the anode and the cathode so as minimise the unwanted dissolution of the cathode by the oxidant. We used the divided cell without the membrane separation. This afforded a 10 cm gap between the anode and the cathode. The separation will create time gap for chlorine oxidant to react with xylose thereby preventing or minimising it migration to the cathode. A significant improvement of δ -valerolactone formation was obtained in the one-pot deoxygenation in the undivided twochamber H-cell (Figure 5). δ-valerolactone is a chemical intermediate used in production of polyesters. A conservative coulomb efficiency calculated with respect to reduction of three carbonyl groups to methylene groups is 18.4 %. Although coulomb efficiency obtained is rather low, the process is attractive from green chemistry perspective since the conversion was achieved in aqueous media and at ambient conditions and there is no harzardous waste generation. Improvement of the coulomb efficiency may be possible by exploring ways to increase the rate of the cathodic half reaction such as high surface area by use of porous lead electrode. Use of other hydrogen over-potential metal electrode such as cadmium or leadcadmium alloy, optimisation of educt and electrolyte concentration, may be explored for improving the cathodic half of the conversion. A proposed simplified pathway of the one-pot electro-deoxygenation of xylose to δ -valerolactone is shown in scheme 6.



Figure 5: One-pot electrochemical deoxygenation of xylose



Scheme 6: Simplified pathway of electro-deoxygenation of xylose to δ -valerolactone

Furan-2(5H)-one is also obtained as a side-product in the one-pot deoxygenation of xylose. The exact elementary steps from xylose to furanone is unclear now, the unsaturation suggests a dehydration step during oxidation in the HCl electrolyte. Furan-2(5H)-one is recently implicated as starting chemical for synthesis of insecticide,^[58] hence this study demonstrates possibility of using exclusive electrochemical routes for production of valuable renewable chemicals and fuels. Oxidation of hydroxyl groups in starch to carbonyls has been exploited for producing modified starch for different applications.^[59] This suggests similar direct one-pot electrodeoxygenation of starch to biofuels or chemicals could be possible. Also, the one-pot experiment is clearly a pointer to the possibility of integration of the separate electrochemical processes in a continuous membrane chlor-alkali type cell with HCl electrolyte. This will prevent unwanted competing dissolution of the cathode by the oxidant and to ultimately optimized energy efficiency of electrodeoxygenation reaction.

Conclusion

We have demonstrated of use electrochemistry for achieving deoxygenation of carbohydrate substrates into value-added chemicals intermediates and biofuels. The deoxygenation was achieved in a one-pot electrochemical process: partially separated selective oxidation via electrogenerated chlorine oxidant and cathodic reduction. Successful deoxygenation of a substrate depends on selective conversion of the hydroxyl groups in the substrate to corresponding carbonyl groups. Aldehyde is readily convertible into carboxylic acid by the oxidant, hence, primary hydroxyl groups are a selectivity weak link of the overall deoxygenation process. Where complete absence of primary hydroxyl groups is not possible, minimal ratio of primary/secondary hydroxyl groups is a desirable criterion for selection of substrates for this electrodeoxygenation process. The electrochemical deoxygenation can be further optimized using a continuous integrated process in a chlor-alkali type reactor system. While fulfilling the requirement for green chemistry, this study also adds to the electrochemistry options for storage of excess renewable electricity via production of renewable chemicals and biofuels.

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