

## Recent progress in electrochemical oxidation of saccharides at gold and copper electrodes in alkaline solutions

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### Abstract

This article reviews the progress made in the past 10 years, on electrochemical oxidation of saccharides in alkaline media for gold and copper electrodes. The mechanism and processes associated with the electrochemical oxidation of saccharides at native and surface coated electrodes continues to be of great interest. Despite the effort and various mechanisms proposed, still the need for an electrochemically active material that understands the complexity associated with saccharides continues to increase as their detection poses a challenge for bioanalytical chemistry and liquid chromatography.

### 1. Background

Carbohydrates, by nature are some of the most abundant compounds as they form more than 80% of the available biomass. The structural architecture of the carbohydrate polymers depends very much on the saccharides, which can be mono-, disaccharides, dextrans or oligosaccharides. The unit composition of a particular polymer will vary depending upon the nature or origin of the carbohydrate (softwood, hardwood and straw or cereals) [1]. For example lignocellulose consists of cellulose, hemicelluloses, lignin and other constituents. Hemicelluloses and cellulose are both of interest as they are used to produce fuel ethanol, whilst lignin is a fuel for the process. Cellulose is composed of glucose units bound by  $\beta$ -(1-4)-glycosidic linkages to form straight and parallel chains which are linked via hydrogen bonds [2]. According to Timell, hemicelluloses are complicated low molecular-weight cellulosic as well as non-cellulosic heteropolysaccharides called polyoses [3]. Hemicelluloses from softwood as well as hardwood plants, mainly consists of monomer units of d-galactose, d-glucose, d-mannose, d-xylose, l-arabinose, 4-O-methylglucuronic acid, d-galacturonic acid and glucuronic acid. Hemicelluloses can be classified by their

monomer constituent residues; xylose (xylan) and mannose (mannan) respectively. The sugar residues found in cereals like whole-wheat starch show a variety of linkages for d-galactose, d-glucose, d-xylose and l-arabinose units. Starch is the most abundant carbohydrate after cellulose, as it constitutes 40–90% of cereals by dry weight [3]. In the food industry, medical diagnosis as well as the paper and pulp industry, it is necessary sometimes to break down these polymers either by alkaline or enzymatic processes. The breakdown of these polymers leads to the formation of units consisting of various linear and possibly branched groups that if identified, can give an indication to the structural composition of the parent polymer, or in other cases, for the hydrolytic properties of a novel enzyme.

Prof. Gorton's group was involved with the ethanol from the lignocellulose project where the role of analytical chemistry was to monitor saccharide production for the purposes of either characterisation of enzymes or process optimisation by monitoring saccharification processes [4]. The challenge in this work was to employ analytical systems that provided an in-situ sampling and sampling clean-up step, a high-resolution separation step for carbohydrates of varying linkage and degree of branching as well as unequivocal identification. In order to achieve in-situ sampling, microdialysis sampling was employed and coupled on-line to high performance anion exchange chromatography with integrated pulsed electrochemical detection (HPAEC–IPED) or mass spectrometry [5].

There are two challenges one faces when employing microdialysis-HPAEC–IPED, as shown in Fig. 1, detection of carbohydrates on a gold electrode shows different molar and monomer unit sensitivity [6] and [7]. Secondly, because the basis for electrochemical oxidation of saccharides on a gold electrode is preceded by an adsorption step, detection of analytes beyond the linear range necessitates a step where selective cutting of the chromatogram is employed [7]. The approach means that the same chromatogram has to be analysed at least twice and hence fouls the on-line process. For example, if one is monitoring the hydrolytic activity of enzymes (see Fig. 2), it is necessary to get a true reflection of the processes taking place, though this cannot be achieved through the available commercial systems [8]. There is a need to manually process the data so as to give a correct picture that accounts for the different sensitivities as well as the concentrations that might be beyond the quantitative detection range.

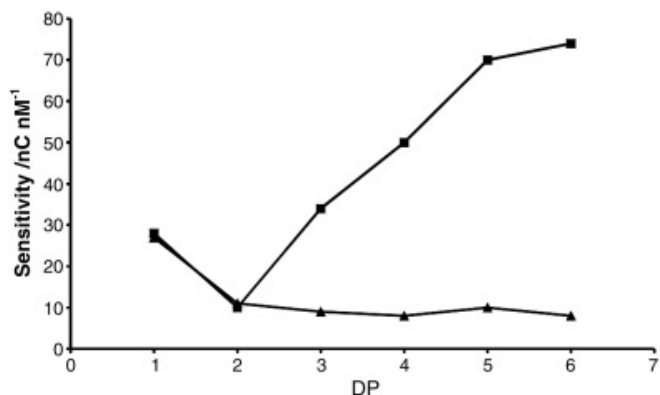


Fig. 1. The monomer (A) and molar (B) unit sensitivities for malto-oligosaccharides illustrate the challenge faced by a detection system. The sensitivities were evaluated from maltooligosaccharides on a gold electrode, where DP is the degree of polymerisation that reflects the number of glucose units equivalent for the particular saccharide [7].

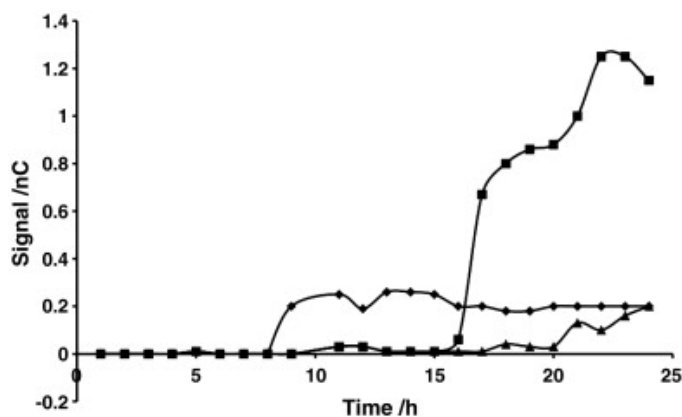


Fig. 2. A hydrolytic profile reflecting the production of monosaccharides (DP 1 ■), disaccharides (DP 2 ◆) and trisaccharides (DP 3 ▲) on studies of synergistic properties of enzymes over a continuous 25 h period. The challenge is to have a detector that can function with consistent sensitivity for 25 h, whilst giving a true reflection of the hydrolytic process (displaying similar sensitivities for the analytes) [8].

An understanding of the electrooxidation of saccharides is essential for any advancement in terms of seeking alternative detection systems. However there is also a compounding problem associated with the behaviour of saccharides in solution because of their readiness to undergo complex mutarotations. Studies aimed at elucidating these phenomena have been based on the rational involving acidity of OH groups [9], hydration numbers [10] and [11], the ratio of equatorial vs axial OH groups [12] and [13], anomeric effect [14], the hydrophobic or hydrophilic index [15], partial molar heat capacities, isothermal compressibilities and expansibilities [16] as well as various enthalpy measurements [17] that have been reported. A comprehensive and amicably agreed theory has yet to emerge. The task of understanding the electrochemical behaviour of saccharides for the very small fraction of time they reside on the electrode

surface (solution characteristics would affect stability and orientation at the electrode surface) after all the solution activities is overwhelmingly daunting. More important is also the knowledge of the behavioural characteristics of the electrode material in different electrolytes in the absence of analyte species.

Several investigations associated with the electrooxidation of saccharides and other related organic compounds have been carried out on metals in alkaline as well as acidic media. Notably studies on Ni, Pt, Au and Cu have received more attention. For example, Pletcher and co-workers investigated the oxidation of organics on a Ni electrode and proposed a mechanism involving the concomitant formation of NiOOH [18] and [19]. However Vertes and Hornayi presented a mechanism that excluded the catalytic role of NiOOH in their investigations on alcohols [20]. The alcohol oxidation peaks were observed at potentials much more positive than that of Ni(OH)<sub>2</sub>. Robertson supported the mechanism by Pletcher although he suggested that the reaction might be dependent on the concentrations of OH<sup>-</sup> ions, which would influence the Ni surface state [21]. Berchmans et al. [22] reported the electrocatalytic oxidation of sugars on Ni(OH)<sub>2</sub> ↔ NiOOH modified glassy carbon electrodes, following a similar mechanism as proposed by Pletcher. Despite these studies, Ni has not really been a subject for many investigations. However studies for Au have almost always been carried out with those for Pt, and indeed Au has shown the best promise in terms of delivery of a detection system. Cu on the other hand, has emerged as a possible alternative material for detection systems for carbohydrates. Therefore this review will focus on recent developments involving Au as well as Cu electrodes and will also give some remarks on modified electrodes that employ Au or Cu.

## 2. Electrochemical oxidation at the gold electrode

The studies on Au (as well as Pt) were developed through three routes due to research geared towards the production of fuel cells for the pace maker and that of glucose (carbohydrate) sensor/detector to determine blood sugar concentrations. The most significant contributions in this area were by Conway, Vesselyev as well as Johnson, although others also impacted on the understanding of the electrooxidation [23], [24], [25], [26], [27], [28] and [29]. Conway and workers extensively investigated the oxidation of Au in acidic as well as alkaline media where they identified the role of anion adsorbed on single crystals [22], [30], [31], [32], [33], [34] and [35]. They characterised the role of semi adsorbed anions as well as defined the time resolution of surface electrode processes occurring during oxidation. Studies that elucidate the electrochemical oxidation characteristics of possible electrode materials in various electrolyte media as well as the catalytic role of anions, are very important in the understanding of the mechanism of oxidation. This is because the initial stage of surface oxidation on noble metals is dependent on and is in competition with anion chemisorptions. Adsorption of the OH<sup>-</sup> ions from NaOH solution has to occur after displacement of

the hydrogen bonded water molecules in order to effect the catalytic oxidation of carbohydrates. For example the presence of chloride ions would interfere with the electrooxidation process.

The second route involved the work by Vassilyev and co-workers as they employed the surface chemistry knowledge of different electrodes (Au, Ag, Cu and Pt) so as to study the kinetics and mechanisms of glucose oxidation in neutral and alkaline solutions [34] and [35]. Their studies extensively investigated the electrooxidation of a wide range of glucose concentrations at different pH values and potential ranges of adions. They also investigated the effect of anions such as chlorides. The mechanism of adsorption and electrooxidation of glucose on Au was reported to be similar to that of elementary organic substances such as formaldehyde and formic acid [35]. However the third approach by Larew and Johnson involved the elucidation of the kinetics, mechanism and electrooxidation, accounting for the effective number of electrons transferred [36]. These studies led to the development of the pulsed electrochemical detection (PED) techniques for carbohydrates after their separation in their enolate form with HPAEC [37].

Several researchers continue to probe the electrochemical oxidation of carbohydrates on Au electrodes in order to elucidate the mechanisms and processes on the electrode surface. Ghanem et al. investigated the effect of microwave activation on the electrooxidation of glucose in alkaline media [38]. They reported increased current densities for Au compared to Cu and Ni in the oxidation of glucose to gluconolactone. Parpot et al. have recently systematically investigated the oxidation of d-mannose, d-galactose, d-sorbitol, d-gluconic acid, d-glucose-6-phosphate, d-glucuronic acid, 1,6-anhydro- $\beta$ -d-glucose, methyl- $\beta$ -d-glucopyranoside and 2-deoxy-d-glucose in 0.1 M NaOH solution [39], [40] and [41]. Their approach was based upon measuring the possible oxidation products rather than evaluate the number of electrons. Ideally it is preferred that the oxidation products and electron balance be carried out at the same time to facilitate mechanistic studies. However, most researchers have focussed on one component, with Parpot et al. reporting an impressive list of products after chromatographic analyses (see [Table 1](#)) [39], [40] and [41]. From their studies of galactose oxidation on Au, they concluded that the process was catalysed by the presence of hydrous gold oxides as already described by others. The product analyses by HPLC showed a high yield of galactonic acid after prolonged electrolysis [39]. In the case of mannose, the highest yield was observed for mannonic acid in agreement with previously suggested mechanism of mannose oxidation. Lamy et al. have also reported the oxidation products of d-glucose on pure and adatom modified gold electrodes in alkaline medium [42]. The products were analysed using ion exchange chromatography and it was observed that glucaric and keto-2-gluconic acids were produced with relatively high yields. Ideally one wants to examine the products directly after their production, due to mutarotation and other associated

saccharide characteristics in alkaline solution. However subjecting the oxidation products to chromatographic conditions does give a good indication as to their identity.

Table 1.

Some oxidation products for galactose and mannose after extended electrolysis.\*

Product	d-galactose chemical yield (%)		d-mannose chemical yield (%)	
	0.1 V vs SCE	- 0.1 vs SCE	0.1 V vs SCE	0.25 V vs SCE
2,3,4,5-Hydroxy-pentanoic acid			2	4
Formic acid	ND	ND	1.2	4
Galactose	20	13		
Galactonic acid	51	86		
Galactaric acid	8	3		
Glycolic acid	1	1	2	4
Glyceric acid	1.5	1	1	3
Glyoxylic acid			4	6
Mannose			15	45
Mannonic acid			42	10
Mannaric acid			2	2
Mannuronic acid			2	ND
Oxalic acid	1	ND	6	12
Tartaric acid	6	1	4	6
Tartronic acid	ND	ND	4	4

\* Adapted from Parpot et al. [39], [40] and [41], where ND represents not quantifiable products. A concentration of  $1.05 \times 10^{-2}$  M for galactose and  $1.0 \times 10^{-2}$  M for mannose, all in a 0.1 M NaOH solution were used. Products were analysed using gas chromatography with a CP-Sil 8 (Chrompack) capillary column (95% dimethyl-8% diphenyl polysiloxane bonded) with a flame ionisation detector (FID) for both galactose and mannose. Further quantitative work was carried out with HPLC employing UV-VIS, refractometer and conductivity detection.

Parpot et al. [41] and Tominaga et al. [43] also reported studies on structure–reactivity relationships for monosaccharide oxidation and surface poisoning during electrocatalytic monosaccharide oxidation, respectively. Both these studies have ramifications for example on bioprocess monitoring where a large number of such saccharides might be present at the same time. The subtle difference in structure which impacts on separation as well as detection poses a challenge for quantitative work (see Fig. 1 and Fig. 3).

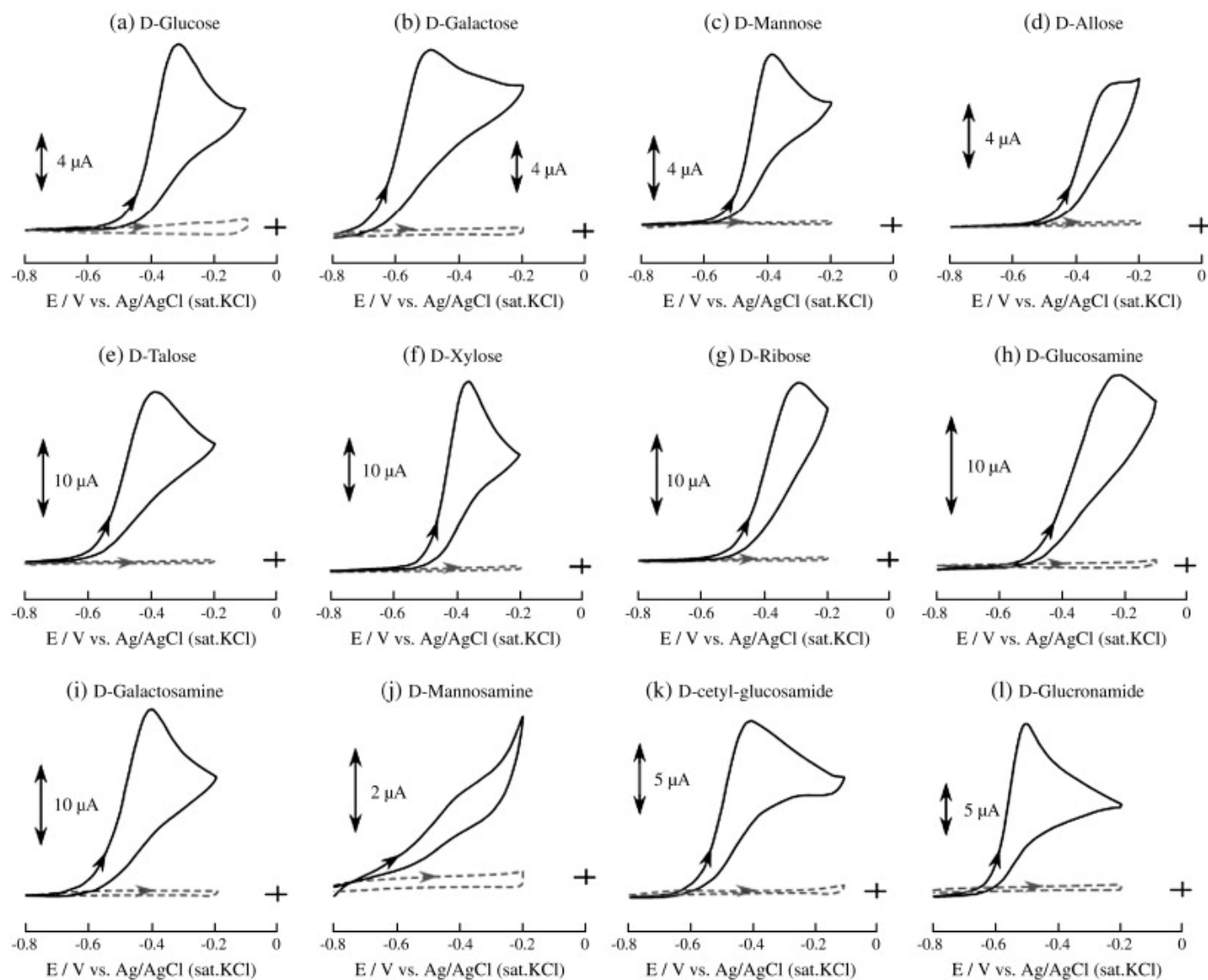


Fig. 3. The cyclic voltammograms for various saccharides and glucose derivatives reflect the impact of the subtle difference in these compounds in terms of the oxidation potential and the resultant current. The figure was adapted from Ref. [58], where  $5 \text{ mmol dm}^{-3}$  concentrations of aldohexoses (a–e) and aldopentoses (f,g), and aminosugars (h–j) were investigated with acetyl-glucosamine and glucuronamide at a gold electrode in  $0.1 \text{ M NaOH}$  solution.

These studies were conducted by slowly sweeping ( $5 \text{ mV s}^{-1}$ ) glucose derivatives (10 mM) in 0.1 M NaOH solution in order to observe the effect of functional groups on electro-reactivity [41]. It was observed that the oxidation of hemi-acetal at C1 atom proceeded with less demand on potential, whereas the oxidation of the primary alcohol group was preceded by an adsorption step. The spatial orientation of the OH group was also shown to be important for the oxidation of the vicinal diols. Tominaga et al. on the other hand demonstrated that the oxidation of aldohexoses and aldopentoses type monosaccharides, aminosugars, acetyl-glucosamine and glucoronamide can be affected by surface poisoning of the electrode [43]. Although this does not sound like anything new, given the long recognition of passivity on the electrode surface, they proceeded to employ electrochemical quartz crystal microbalance (EQCM) to demonstrate that reaction products such as gluconic acid were adsorbed vertically forming a monolayer on the electrode.

Recently it has also been demonstrated that artificial neural networks aided the estimation of oxidation signals and thus facilitating the understanding of the electrochemical process on a gold electrode. Gopal and Dilmaghani demonstrated that neural networks are able to predict the electrooxidation peak potentials of monosaccharides in a linear sweep regime if molecular descriptors are defined [44]. The data showed good to excellent correlations for d-allose, d-glucose, d-arabinose, d-mannose, l-glucose and d-xylose.

### 3. Electrochemical oxidation at the copper electrode

Studies by Miller [45] defined the oxidation states of Cu in alkaline solutions and resulted thereafter in intensified efforts by others to understand the role of these oxidation states (oxides) for electrochemical oxidation of carbohydrates [46], [47], [48], [49], [50] and [51]. As in the case for Au, there have been several efforts to try and elucidate the mechanism of oxidation on freshly polished (designated as fresh electrode) as well as oxide modified Cu electrodes in alkaline media. Luo and Baldwin employed cyclic voltammetry, hydrodynamic voltammetry, coulometry and NMR to characterise the oxidation of glucose and related polyalcohols on a copper electrode [48]. They employed coulometry to evaluate the number of electrons transferred during oxidation at the Cu electrode. For example they evaluated the electrons for fructose, glucose, glucuronic acid and glucaric acid to be 14, 12, 10 and 10 respectively. They concluded that the observed electrons transferred with the absence of detected by-products as suggested in other mechanisms, probably indicated to a different oxidation process.

Torto et al. described the electrochemical oxidation of mono- and disaccharides at fresh as well as oxidized Cu rotating disk electrode (RDE) in alkaline media [52]. The monosaccharides investigated included glucose, galactose, mannose and the disaccharides were cellobiose, isomaltose, laminaribiose, mannobiose and maltose. In this study the aim was to link the knowledge generated for studies on monosaccharides to



that of disaccharides especially by evaluating the effective number of electrons transferred during the oxidation step. The studies assumed contribution by both the kinetically limited as well as diffusion limited currents as shown in Eq. (1);

$$1/I=1/I_{\text{kin}}+1/I_{\text{diff}}.$$

Eq. (1) is a combination of the Levich ( $I_{\text{diff}}$ ) and Koutecky ( $I_{\text{kin}}$ ) equations which were used to evaluate the effective number of electrons transferred where;

$$I_{\text{kin}}=nFAkC_s$$

$$I_{\text{diff}}=0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}(C_b-C_s)$$

and  $n$  represents the number of electrons transferred,  $F$  is the Faraday constant ( $C \text{ mol}^{-1}$ ),  $A$  is the electrode area ( $\text{cm}^2$ ),  $k$  is the heterogeneous rate constant ( $\text{cm s}^{-1}$ ),  $C_b$  and  $C_s$  are concentrations of species to be oxidized in the bulk and on the surface of the electrode ( $\text{mol cm}^{-3}$ ),  $D$  is the diffusion co-efficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $\omega$  is the angular velocity of the disk electrode ( $\text{rad s}^{-1}$ ) and  $\nu$  is the kinematic viscosity of NaOH ( $\text{cm}^2 \text{ s}^{-1}$ ).

From these studies, the number of electrons transferred during the oxidation of glucose, galactose and mannose, within experimental error were 12 for all monosaccharides. These results were in agreement with previously reported coulometric and RDE studies. The oxidation of glucose derivatives (glucaric, gluconic and glucuronic acid) proceeded by a transfer of 9–12 electrons and were also in agreement with coulometric studies. The data seemed to agree with the proposed mechanism suggested by Luo and Baldwin which saw no evidence of a stepwise oxidation process [48].

Torto et al. also examined the oxidation of disaccharides in comparison with that of monosaccharides [52]. Studies were carried out on cellobiose, isomaltose, laminarbiose as well as maltose using a freshly polished Cu RDE. The aim of these investigations was to understand if the mechanism of disaccharides was similar to those of aldohexoses or their acid derivatives. One would expect that if the electrooxidation of disaccharides proceeded as that of aldohexoses, at least 22 electrons would be transferred during the process. Results obtained during the electrooxidation of disaccharides at freshly cleaned Cu RDE resulted in a transfer of between 2 and 9 electrodes. The number of electrons observed for cellebiose, isomaltose,

laminaribiose and mannobiose were;  $n = 6.2 (+/-1.3)$ ,  $8.8 (+/-0.3)$ ,  $5.9 (+/-0.3)$ ,  $2.9 (+/-0.2)$ , respectively [52].

From these studies of disaccharides it could only be formally concluded that a single unit of the disaccharide was involved in the electrooxidation process as less than 12 electrons were transferred. Because electrooxidation of glucose was shown to be dependent on the NaOH concentration, further studies on disaccharides were conducted at 50, 100 and 150 mM NaOH concentrations as well as applied potential between 0.4 and 0.6 V vs Ag/AgCl/KCl<sub>sat</sub>. Except for cellobiose which increased the transferred electrons to  $n = 11.5 (+/-2.5)$ , the electrooxidation did not show a significant dependence on NaOH concentrations or potential.

As shown in Table 2, the electrochemical oxidation of glucose compared to that of maltose (disaccharide consisting of two glucose units) was found to be dependent upon surface oxides on the Cu electrode. Irrespective of surface treatment time of the electrode, within experimental error, only 11 electrons were transferred for glucose but the number increased with increased treatment for maltose. In their microwave activation study of the electrooxidation of glucose on a Cu electrode, Ghanem et al., observed that oxidation currents also showed a dependency on the thickness of the pre-formed oxide layer [38]. Kano et al., also reported that the presence of Cu(II) oxide on the Cu electrode surface was essential for the electrooxidation process as it served as a catalyst [53]. In these studies electrons transferred for the oxidation of xylose, glucose and sorbitol, after treatment at 2.0 V for 3 s, at a RDE were evaluated to be 10, 12 and 14 respectively. The role of copper oxide in the oxidation of glucose was recently demonstrated with copper oxide nanoparticles (after chemical vapour deposition) which produced the same glucose oxidation currents when compared with copper (II) oxide immobilised on pyrolytic graphite electrodes [54].

Table 2.

Role of oxide layer for electrochemical oxidation of glucose and maltose on a Cu RDE. \*

Treatment time/s	Glucose $n$	Oxidation $10^3 \text{ k/cm s}^{-1}$	Maltose $n$	Oxidation $10^3 \text{ k/cm s}^{-1}$
5	11.0	5.9	7.5	0.54
	10.8	4.9	12.2	1.28
35	10.9	4.6	10.0	1.48
	11.0	4.4	8.5	1.75

Treatment time/s	Glucose $n$	Oxidation $10^3 \text{ k/cm s}^{-1}$	Maltose $n$	Oxidation $10^3 \text{ k/cm s}^{-1}$
180	10.7	5.8	13.9	1.7
	11.1	3.9	12.0	1.8
	11.3	7.0	10.8	1.7
360	10.7	5.1	18.9	1.2
	10.8	6.6	13.2	1.6

\* The  $n$  and  $k$  values were evaluated using the same RDE for glucose and maltose in order to assess the impact of the oxide layer. Within experimental error, the number of electrons transferred for glucose was independent of the oxide layer and treatment time [50].

#### 4. Electrochemical oxidation at modified electrodes

There have been several reports of studies that have employed modified electrodes for the oxidation of saccharides in alkaline media, however only a few illustrative examples that employed a combination that includes Au or Cu will be discussed. Johnson et al. employed nickel–copper [55] and copper-alloy electrodes [56] for the study of both carbohydrates and other small organic molecules. These investigations were motivated by the desire to find an electrode material that exhibits and sustains high catalytic activity when used for amperometric detection at a constant potential. For the  $\text{Ni}_x\text{Cu}_{100-x}$  electrodes, they observed that  $\text{Ni}_{10}\text{Cu}_{90}$  exhibited the largest range of positive potential for voltammetric and amperometric applications for glucose in 0.1 M NaOH. The glucose response was reported to be significantly higher compared with pure Cu and Ni electrodes and this was attributed to the synergism between the Ni-sites and Cu-sites in the anodic response mechanism [55]. Further studies with CuMn (95:5) also showed significantly higher responses for pre-anodized CuMn compared with a pre-anodized pure Cu RDE with evaluated electron transferred according to Koutecky–Levich of 11.7 electrons for glucose on CuMn and 9.6 at a pure Cu RDE. Aoun et al. also reported the effect of metal ad-layers on Au (111) electrodes on the electrocatalytic oxidation of glucose in 0.1 M NaOH [57]. The studies investigated various ad-metals such as Cu, Ag, Ru, Pt, Pd and Cd. Of the metals investigated Ag adatoms exhibited the highest catalytic effect on the oxidation of glucose as this was associated with the shift in potential of zero charge of the electrode after the deposition of Ag to enable formation of the catalytic AuOH [57]. Tominaga et al., also reported on composition–activity relationships for AuAg nanoparticles in the oxidation of glucose in alkaline media. Homogeneously bimetallic  $\text{Au}_m\text{Ag}_{100-m}$  nanoparticles showed improvements in the electrocatalytic activity for glucose and the electrolysis products were dependent on the composition ratio of Ag [59], [60] and [61].

## 5. Perspective

Because of the complexity of saccharides in their monomeric or oligomeric form, the task of describing the electrochemical oxidation process at metal electrodes especially Au, Cu, Ni and Pt is still a subject for fundamental studies. Proposed mechanisms are good only to the conditions that were applied for the oxidation processes which are mostly electro-synthesis or analytically driven. A universal approach is still to emerge which can answer fundamental questions that should account for the incomplete oxidation of a monosaccharide unit in a disaccharide for instance. From an analytical perspective, what are seemingly similar compounds have such subtle differences that indeed require a detector that understands these characteristics. For example, variations in a homologous series such as aldoses, pentoses, ketoses, alditols and aldonic acids can be complicated further by configurational differences as observed in glucose, mannose and galactose or by various linkages (1,1; 1,3; 1,4 or 1,6) for disaccharides. However it is clear from literature that the mechanism of oxidation at Au or Cu electrodes depends on some catalytic process. However it remains a subject for further investigations if the oxidation of monosaccharides is a stepwise process as known for biological and chemical processes. Despite reports employing RDE, it is surprising that not so much has been done employing RRDE as this would enable in-situ oxidation of the primary products so as to indicate to electrochemical oxidation products at Au or Cu electrodes. One hopes that such experiments will add valuable information in addition to evaluating the electrons transferred as well as detect products after extended electrolysis times.

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