Journal of Applied Electrochemistry (2006) 36:233–238
DOI 10.1007/s10800-005-9056-0

Electrocatalytic oxidation of monosaccharides on platinum electrodes modified by thallium adatoms in carbonate buffered medium

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Received 17 March 2005; accepted in revised form 31 August 2005

Key words: electrocatalytic oxidation, monosaccharides, platinum, thallium adatoms

Abstract

The effect of modification of polycrystalline platinum by Tl adatoms on the electrocatalytic properties of the electrodes towards the oxidation of monosaccharides was investigated. Significant electrocatalytic effect towards glucose and methylglucoside oxidation was observed on Pt–Tl electrodes as displayed by an enhancement of the oxidation current densities. Different carboxylic acids produced by the electrolysis of carbohydrates were analyzed by ionic chromatography. The electrooxidation of glucose on Pt–Tl gave gluconic and keto-gluconic acids, successively. When the anomeric carbon is protected (methylglucoside), the first oxidation step of the monosaccharide was carried out on the primary alcohol following the same path as that of methanol oxidation.

1. Introduction

A number of organic molecules have shown reactivity on platinum electrodes [1–9]. To oxidize carbohydrates, polycrystalline platinum sites are too active and in most cases lead to a dissociative adsorption. This oxidation process, which breaks some carbon–carbon bonds can be avoided by modifying the superficial structure of the Pt electrode using underpotentially deposited metallic adatoms [2, 10]. These transition metals have no electrocatalytic effect when, under the same conditions of potential, they are used alone to carry out a selective transformation of sugars such as glucose. The chemical preparation of gluconic acid uses chlorine or bromine to oxidize glucose. This method is not satisfactory because a large amount of the halogen salt seriously interferes with the separation of the reaction products. Other electrochemical processes were developed, where free bromine is produced by electrolysis of a bromide solution at the anode. Then, bromine reacts with the carbohydrate to give gluconic acid but also produces hydrobromic acid in the solution [11, 12]. Electroenzymatic processes have also been investigated. Despite their selectivity, by using glucose oxidase (GOD) [13, 14], the reaction take so many days that it can not compete with the electrocatalytical procedure. Indeed, the underpotential deposition of lead, thallium, bismuth etc. on a platinum electrode enhanced appreciably current densities of carbohydrate oxidation [15, 16]. These metal adatoms are supposed to preferably occupy the poisoning sites of the electrode surface, thus enabling it to keep its activity much longer than when platinum is not modified [16]. This electrocatalytic effect is important in achieving high activities in the oxidation of monosaccharides and for applications using glucose-oxygen fuel cells.

The present work shows that non noble metals such as thallium promote the activity of a platinum electrode, when adatoms were underpotentially deposited on its surface. These systems (Pt–ad) were used to selectively oxidize glucose and methylglucoside in carbonate buffer [17]. Polarimetric measurements carried out at room temperature in this electrolyte medium showed that D-glucose undergoes a mutarotation giving two chemical stable anomers: the α and β D-glucopyranose forms, which in aqueous solution, correspond to an equilibrium of approx. 33% and approx. 67%, respectively. The difference between the two anomers originates from the carbon C-1, the OH functional group being axial for the α form and equatorial for the β form. Previous investigations have shown that β-D-glucose is electrochemically the most reactive isomer [18]. As methylglucoside undergoes hydrolysis in acidic medium and glucose isomerizes into D-fructose (interconversion) in alkaline solution, a carbonate buffer (pH = 9.82) was chosen in this work to stabilize the organic substrates.

2. Experimental

Electrochemical experiments were carried out at room temperature (21 ± 1 °C) in a two-compartment glass cell (volume = 20 cm^3 for each compartment) separated by a membrane Nafion 423. The working electrode consisted of a platinum gauze (99.9% Alfa Aesar-Johnson Matthey) having an active surface area of 3.5 cm^2 calculated by the integration of the hydrogen region of a reference voltammogram recorded in 0.1 M NaOH. After a series of measurements of voltammograms in the presence of thallium, the platinum electrode was cleaned with aqua regia (1/3 HNO_3 + 2/3 HCl). It was then rinsed with ultra pure water (Millipore Milli-Q System) before recording a voltammogram of Pt in 0.1 M NaOH for reference. The electrolytic solutions were deaerated by bubbling nitrogen (U Quality from Air Liquide). A $Hg/Hg_2SO_4/K_2SO_4$ (MSE) saturated electrode and a Pt gauze (36 cm^2) served as reference and counter electrode, respectively. The reference electrode was separated from the solution by a Luggin–Haber capillary tip. The analysis of products was performed using ion exchange liquid chromatography (Dionex 4500 i). It works with a ternary gradient of elution and includes an ion-exchange column (AG 11 + AS 11) and a conductimetric detector followed by a refractive index detector.

Programmed potential electrolysis was used in this work. It consists in controlling the oxidation potential which is also a parameter of selectivity for the reaction. The potential programs were composed of three potential plateaus (Figure 1). After adsorbing the organic molecule at low potential (E_{ads} = −1.0 V(MSE)) for 0.2 s, the oxidation reaction was performed at a potential plateau, chosen at $E_{ox}(-0.6 \leq E_{ox} \leq -0.4$ V/MSE) for 12 s. The third potential pulse (E_{des}), set at 0.4 V(MSE) for 0.2 s, allowed for reactivation of the electrode surface by clearing out the poisoning species. A coulometer was used to record the quantity of electricity consumed during electrolysis (Q_{exp}).

Working solutions were prepared from ultra pure water. $NaHCO_3$ and Na_2CO_3 were purchased from Merck with the best purity available. D-glucose and methylglucoside were purchased from Sigma. The Tl sulphate (Tl_2SO_4) salts used for depositing adatoms at the electrode surface were purchased from Fluka. Electrolysis solutions were constantly stirred magnetically and deaerated to avoid glucose degradation by dissolved oxygen [19]. They were prepared with 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 (pH = 9.82).

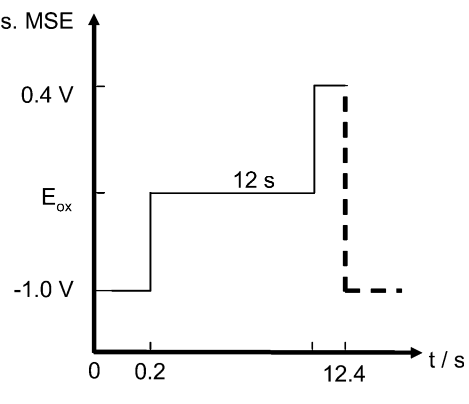


Fig. 1. Potential program used for long-time electrolysis of monosaccharides.

3. Results and discussion

The voltammograms of Pt, recorded at 50 mV s^{-1} and at room temperature in the supporting electrolyte alone (0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3) and in the presence of the carbohydrates, are given in Figure 2. In the presence of 50 mM glucose, the voltammogram (Figure 2(b)) exhibits four oxidation peaks, three of them (A, B and C) during the positive potential sweep, and then another peak D, followed by a shoulder (E) can be observed during the negative scan of potential. Figure 2(c) shows the voltammogram of Pt in the presence of 50 mM methylglucoside. Two oxidation peaks can also be seen during the positive scan of potential while one followed by a hump is noticed during the negative variation of potential.

Glucose appears to be more reactive electrochemically if we consider the current densities of peak A associated with the dehydrogenation of the anomeric carbon C-1 which is protected in methylglucoside. Peaks B, C and D reach current density of ca. j = 0.3 mA cm^{-2} in the region where the platinum surface starts oxidizing.

Electrocatalytic oxidation of carbohydrates by Pt-adatoms was observed through cyclic voltammetry (Figure 3). The activity of the platinum electrode (S = 3.5 cm^2) was modified by adding precursor salts of the adatom to the working solution, which also contained the supporting electrolyte and the electroactive organic compound.

The comparison of the voltammograms of Pt recorded in the supporting electrolyte alone and, in the presence of Tl adatoms and the organic substrate, shows a shrinkage of the hydrogen region, which is caused by the adsorption of the latter species. When the anomeric carbon is protected (methylglucoside) the electrochemical reactive group of this monosaccharide is the primary alcohol (in C-6 position). Its reactivity appears similar to that of methanol [16]. The maximum of desorption of adatoms from the electrode surface occurs at −0.04 V(MSE). However, the Pt oxides region is still modified in comparison to that of Pt in the supporting electrolyte alone. This indicates that the adatoms were not totally stripped off the electrode surface, as can be seen in Figure 3(a) during the negative potential scan. The maxima of the current densities in the presence of glucose (Figure 3(b)) and methylglucoside (Figure 3(c)) are located at potentials between −1.0 and −0.2 V(MSE), which shows that adatoms contribute to the increased activity of platinum. The electrocatalytic activity of platinum increased by a factor of 14.2 for the oxidation of glucose

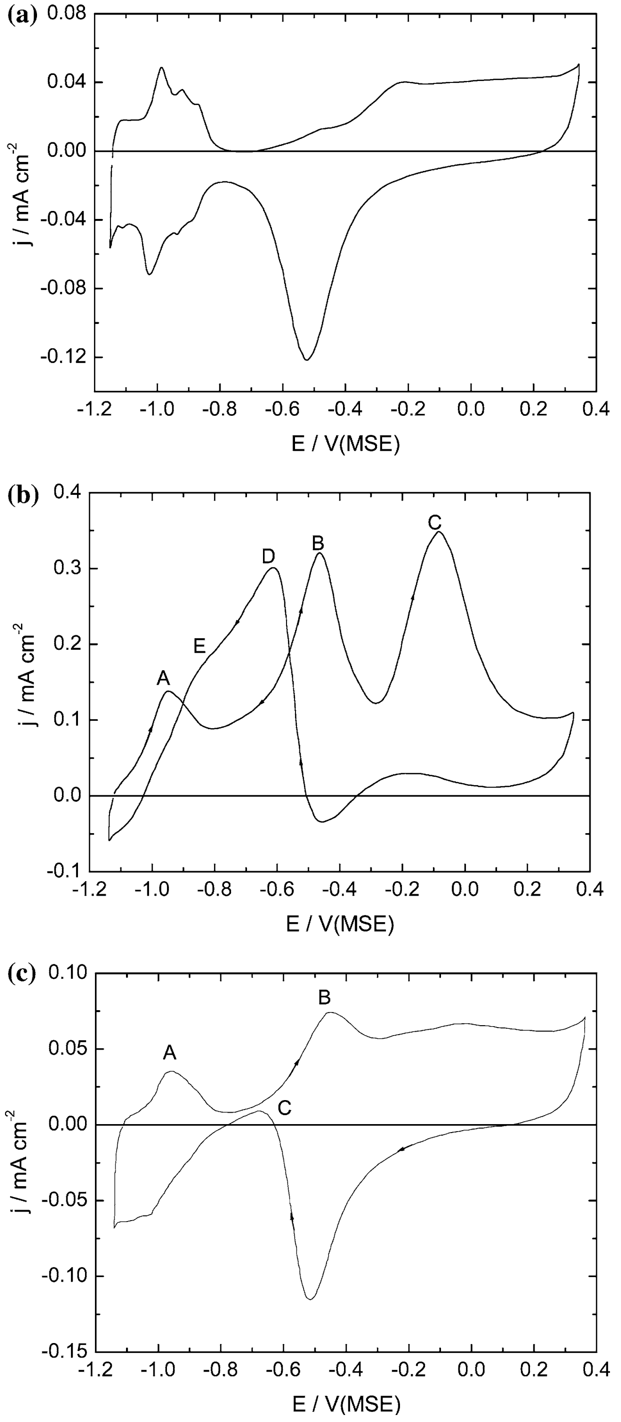


Fig. 2. Voltammograms of platinum recorded at 50 mV s^{-1} and at room temperature (a) supporting electrolyte 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 (b) in the presence of 50 mM glucose (c) in the presence of 50 mM methylglucoside.

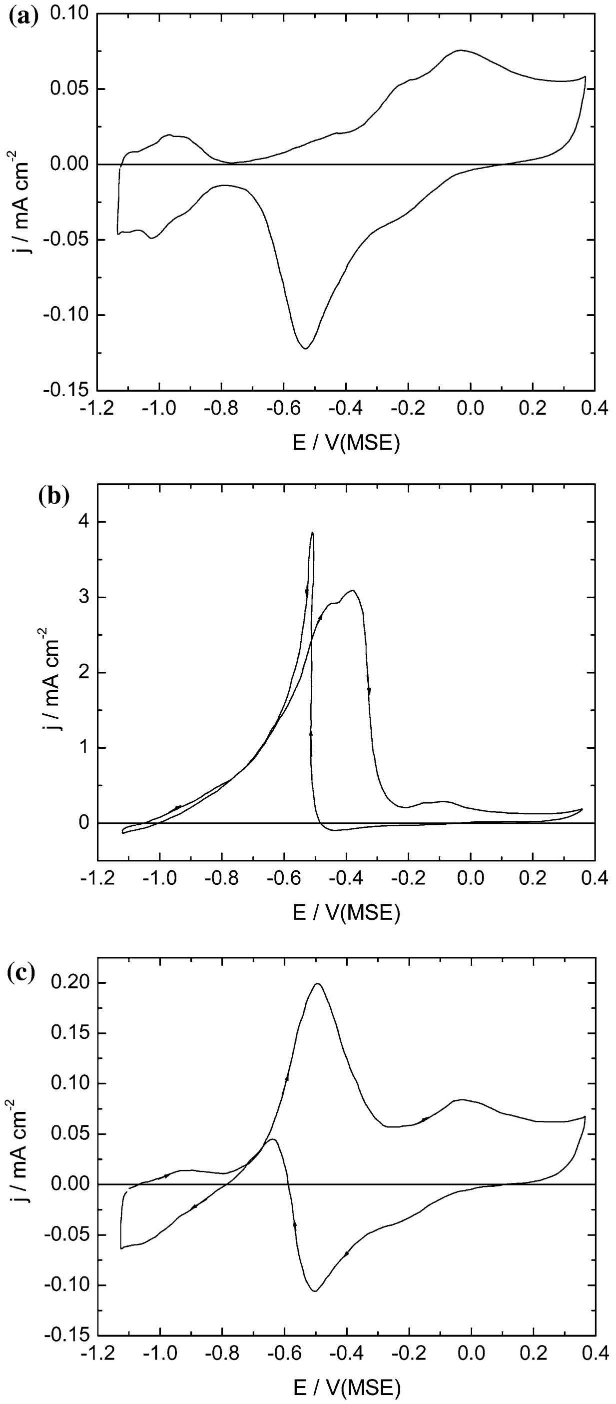


Fig. 3. Voltammograms of platinum recorded at 50 mV s^{-1} and at room temperature in 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 (a) in the presence of 10^{-6} M Tl^+ (b) in the presence of 10^{-6} M Tl^+ and 50 mM glucose. (c) in the presence of 10^{-6} M Tl^+ and 50 mM methylglucoside.

(at −0.55 V(MSE)) and of 3.2 for that of methylglucoside (at −0.51 V(MSE)).This effect of Pt–M could be interpreted as due to the decreasing of the adsorbed intermediates that are poisonous since metallic adatoms occupied some Pt sites. The effect of the thallium coverage was studied by varying the concentration of the precursor salt from 10^{-7} to 10^{-5} M in the buffered solution. Optimum activity is obtained at $[Tl^+] = 10^{-6}$ M. In any case, it can be observed a shift of the optimum potential towards the more negative values in the presence of the monosaccharide. The coverage θ_M of the electrode surface by adatom M was calculated based upon the hydrogen region in the voltammograms of unmodified and modified Pt electrode, as follows:

$$\theta_M = 1 - \frac{Q_H^M}{Q_H^O}$$

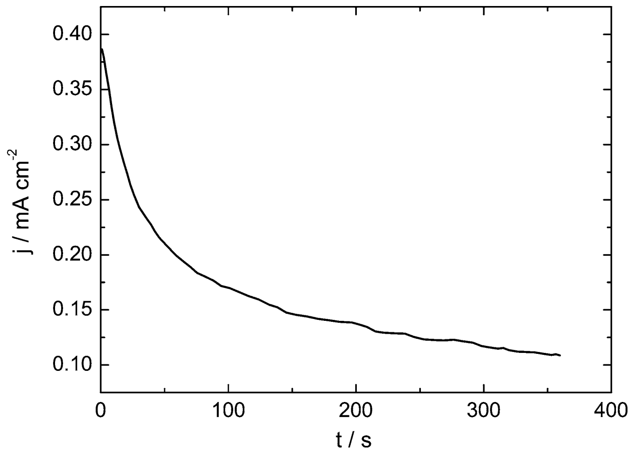


Fig. 4. Variation of the current density vs time during electrolysis of glucose at a fixed potential (−0.51 V(MSE)) on Pt–Tl.

where Q_H^O is the quantity of electricity determined when all the Pt sites are occupied by adsorbed hydrogen, and Q_H^M the quantity of electricity necessary to adsorb hydrogen atoms on the Pt sites free from metal adatoms M [20]. The value of θ_M obtained from the voltammograms of Pt in the supporting electrolyte is $\theta_{Tl} = 0.35$, which shows that the thallium adatoms occupy less than 50% of the active surface sites of platinum [15, 21].

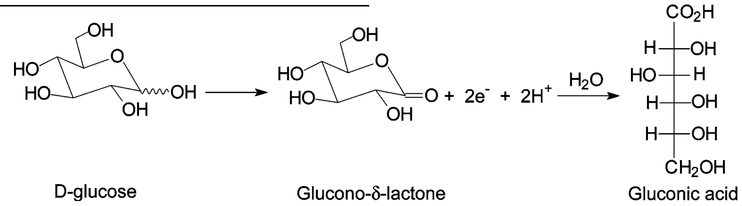
Figure 4 shows the variation of the current density vs time, when a fixed potential is applied at −0.51 V(MSE) to oxidize glucose on Pt–Tl. That the initial current density is 0.4 mA cm^{-2}, while at the same potential, Figure 3(b) shows a value 6 times higher. As the current density decreases quickly due to the poisoning species adsorbed at the Pt surface, a suitable potential program of Figure 1 is useful to increase the conversion of the monosaccharides up to 54% on Pt–Tl by long-term electrolysis.

When Tl adatoms were deposited at the Pt surface, it can be seen in Table 1 that, while the same reaction products were obtained, the distribution of the main compounds was modified depending on the electrode potential. Indeed 2-ketogluconic acid was synthesized at −0.4 V(MSE) with good selectivity, while no side-product from the cleavage of the C–C bond was detected in the bulk solution.

Based on the CV data (see Figures 2 and 3), long-term electrolyses were performed on a platinum electrode. The results were then compared to those obtained on modified electrodes at an optimized electrode potential. Under the same experimental conditions, methylglucoside (the hemiacetalic function of glucose was protected by methylation) was used in order to selectively oxidize the primary alcohol in the C-6 position. The results in Table 2 show that on bare platinum, methylglucoside was oxidized mainly to the corresponding glucuronic acid (ca. 97%). However, the conversion yield remained low after 24 h of electrolysis. In the presence of Tl adatoms, the enhanced current densities permitted electrolyses to be carried out over a shorter time (6 h) with higher conversion yields.

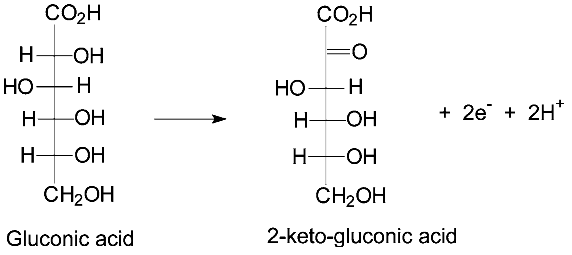
The formation of methylglucuronic acid was improved, and the synthesis of glucaric acid was ca. 16% selective on Pt–Tl.

To interpret these results, we propose that glucose was oxidized as follows:



(1)

D-glucose is transformed into gluconic acid by the oxidation of its hemiacetalic function [22, 23]. The formation of 2-ketogluconic acid may be explained by the oxidation of the secondary alcohol of gluconic acid as follows [24]:



(2)

Table 1. Distribution of reaction products resulting from the anodic oxidation of 50 mM glucose on Pt–Tl ([Tl$^+$] = 10^{-6} M) in 0.1 M NaHCO$_3$ + 0.1 M Na$_2$CO$_3$ at different electrode potentials

E_{ox}/V(MSE)	τ (%)	Q_{exp}/C	Reaction products detected /mM				
			Gluconic acid	2 Keto gluconic acid	Glucuronic acid	Glucaric acid	Oxalic acid
−0.60	54	78.5	25.0	1.1	0.08	0.03	2.82
−0.51	97	116.6	36.0	6.7	0.34		3.60
−0.40	93	140.6	27.6	14.1	0.30	0.40	

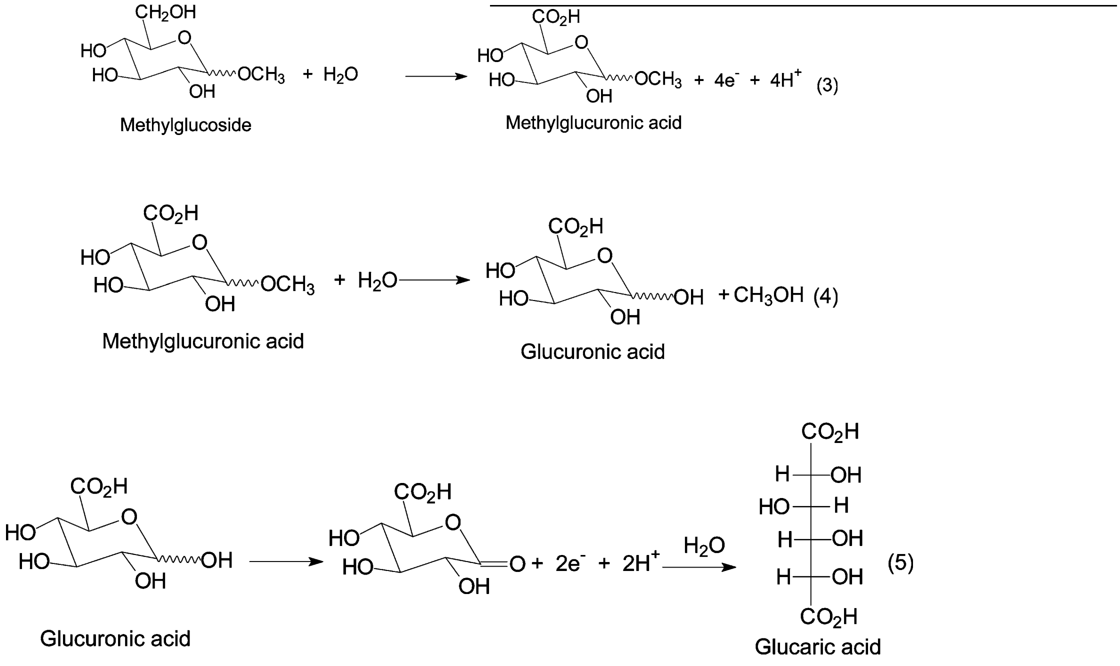
* The same potential program was used for performing each electrolysis. Only E_{ox} changed. τ (%) is the conversion yield: $\tau(\%) = \frac{C_0 - C}{C_0} \times 100$ where C_0 is the initial concentration of the substrate; C is its remaining concentration at the end of electrolysis. Q_{exp} is the experimental charge given by the coulometer.

Table 2. Distribution of reaction products resulting from the anodic oxidation of 10 mM methylglucoside on thallium ($[Tl^+] = 10^{-6}$ M) modified platinum electrodes in 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 at optimized electrode potentials

Electrode	E_{ox}/V(MSE)	t/h	τ (%)	Q_{exp}/C	Reaction products detected/mM (Selectivity (S_x/%))	
					methylglucuronic acid	Glucaric acid
Pt	−0.50	24	31.0	15.7	3.0 (97%)	
Pt–Tl	−0.60	6	49.5	29.0	4.0 (81%)	0.8 (16%)

* S_x(%) is the selectivity of a reaction product x. $S_x(\%) = \frac{C_x}{C_0 - C} \times 100$ where C_0 is the initial concentration of the substrate, C is the remaining concentration at the end of electrolysis and C_x, the concentration of the reaction product at this time.

The formation of methylglucuronic acid could be similar to the transformation of a primary alcohol (such as methanol) by an electrooxidation reaction:



Taking into account the occupation of some Pt sites by adatoms, it is likely that the oxidation of methylglucoside to glucaric acid proceeded through hydrolysis of the anomeric carbon. The unprotected hemiacetal, which is very active on platinum sites, is then easily transformed into glucaric acid (Eq.5) following the same pathway as that of glucose to gluconic acid (Eq.1) [25].

The catalytic effect due to the presence of adatoms was illustrated by a shift towards more negative potentials and the main oxidation peaks were located in the potential range where the platinum surface was partly covered by hydroxides species [26, 27]. According to the EQCM results obtained by Xia and Birss, PtOH species transformed fast to PtO [28]. Therefore, it can be assumed that glucose was oxidized on the Pt surface covered by oxides to δ-gluconolactone as a two-electron reaction product. Hydroxyls, present in the carbonate buffer, hydrolyzed the lactone to the corresponding carboxylate. It may be suggested that the underpotentially deposited adatoms not only modifies the bond strength of the reactant/intermediate molecules on the electrode, through electronic and structural changes, but also changes the water oxidation potential. These two combined effects may lead to improve catalytic effects of adatom–Pt over pure platinum for carbohydrate oxidation.

4. Conclusion

The modification of a Pt electrode surface by foreign metal adatoms resulted not only in enhanced current densities, but also in better product selectivity, when monosaccharides such as glucose and methylglucoside were anodically oxidized on platinum. In the best case, the electrocatalytic activity of platinum is increased by a factor of 14 for the oxidation of glucose (at −0.55 V(MSE) and of 3.2 for that of methylglucoside (at −0.51 V(MSE)). Although thallium adatoms contributed to the formation of α-keton carboxylic acid (2-ketogluconic acid with glucose), it also resulted in the hydrolysis of the protected hemiacetalic function. The oxidation of this anomeric carbon allowed the conversion of methylglucuronic acid to glucaric acid. The fact that no trace of gluconic acid was detected by ionic chromatography suggests that the hydrolysis and the production of glucaric acid were successive reactions.

Acknowledgements

The authors would like to acknowledge Professor C. Lamy for discussing this manuscript.

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