Journal of Applied Electrochemistry (2006) 36:147–151
DOI 10.1007/s10800-005-9042-6

Electrocatalytic oxidation of lactose on gold nanoparticle modified carbon in carbonate buffer

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Received 17 March 2005; accepted in revised form 28 July 2005

Key words: Au colloids, electrocatalytic oxidation, electrolysis, lactobionic acid, lactose

Abstract

The electrocatalytic oxidation of lactose has been studied on nanolength scale Au-colloids (5 nm) embedded in carbon felt as electrode (Au-NMC). A preliminary investigation by cyclic voltammetry, used to determine the optimized conditions of electrolysis, showed that the current densities were higher than those obtained on a gauze electrode of gold (Au-GE) with a surface area three times greater. Long-time electrolyses were carried out using a two potential plateau program with different values for the oxidation potentials. Chromatographic and NMR analyses showed that the oxidation of lactose led mainly to lactobionate (91%).

1. Introduction

The electrosynthesis of lactobionic acid from the electrocatalytic oxidation of lactose has been the subject of several studies [1–7]. The main process was to indirectly oxidize lactose on a graphite electrode in calcium carbonate medium in the presence of Br^-, which was converted *in situ* to bromide. Lactobionic acid produced from lactose has potential applications as a food ingredient [8] but can also be used in the pharmaceutical industry due to its chelating properties [9–12]. Some investigations performed on massive gold electrodes showed that lactose was oxidized to lactobionic acid. By *in situ* IR spectroscopy, lactone was identified as the primary reaction product, which further underwent hydrolysis in aqueous medium to give lactobionic acid [7–13].

In the present work, the aim is concentrated on the electrocatalytic oxidation of lactose in aqueous medium on carbon modified by gold nanoparticles. Various reports have described the preparation of nanoparticles-based electrodes for diverse applications [14–16]. The electrocatalytic oxidation of carbohydrates on this type of electrode is attractive because of interest in sugar–oxygen fuel cell application, as well as sugar sensors for the medical and food industry [17–19].

2. Experimental

2.1. *Preparation of the colloidal gold solutions*

The preparation of nano-scale gold particles was carried out according to the procedure described by slot and Geuze [14]. We obtained 5 nm gold particles. About 100 cm^3 of solution was prepared by mixing, at 60 °C, 80 cm^3 of a gold chloride solution (1 cm^3 $HAuCl_4$ + 79 cm^3 ultra pure water) and 20 cm^3 of a reducing mixture (4 cm^3 1% tri sodium citrate $\cdot 2H_2O$ + 0.5 cm^3 of 1% tannic acid + ultra pure water to 20 cm^3). The final mixture of red colour was boiled for 15 min. Its UV–Vis spectrum, which was recorded with an ultroscan LKB (4050/4051), is represented in Figure 1.

This figure shows a peak at 540 nm which is indicative of the formation of gold nanoparticles in the colloidal solution; this is in agreement with the results described in the literature [14, 16, 17].

2.2. *Voltammetry and electrolysis*

The electrocatalytic property of Au-NMC electrodes were examined by measuring cyclic voltammetric responses for the oxidation of lactose. These experiments were carried out in a filter press cell (flow cell, Electrocell AB) (Figure 2). The anolyte (30 cm^3 of 10 mM lactose in carbonate buffer) and the catholyte (0.1 M carbonate buffer) were circulated separately by a Masterflex peristaltic pump with a flow rate of 5 $cm^3\ s^{-1}$. To avoid lactose degradation, carbonate buffer was used. This supporting electrolyte is easily removed by neutralization with cationic resin (Amberlite IRA 200 from Sigma). The two compartments of the cell were separated by an ion exchange membrane (Nafion® 423). The electrochemical measurements were recorded by using a saturated mercury| mercurous

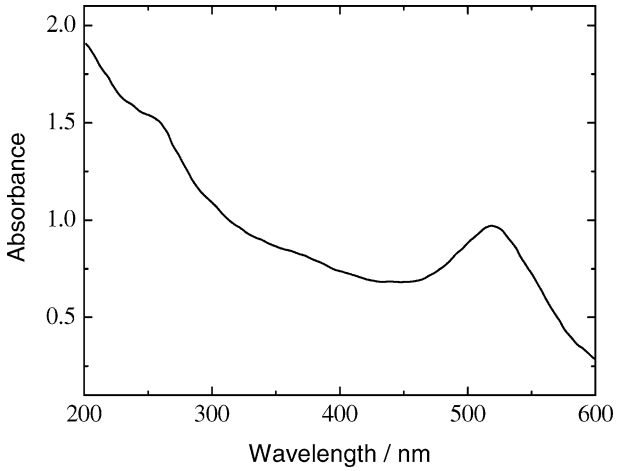

Fig. 1. UV–Vis spectrum of the Au-colloid solution obtained for preparing the electrode.

sulphate electrode (MSE) as reference. In both voltammetry and electrolysis studies, the electrode potentials indicated in the text are quoted on the reversible hydrogen electrode (RHE) scale. To prepare the working electrode, a carbon felt (from Carbon Lorraine, geometric area $S = 5 \times 10$ cm^2) was dipped in a 25 cm^3 of colloidal gold solution for 15 min and dried at room temperature. The electrical connexion was established between a gold wire and a conducting carbon paste. Its active surface area was $A = 9.94$ cm^2. The counter electrode was a platinized titanium plate (surface area $A = 36$ cm^2).

The electrochemical instrumentation consisted of a Hewlett Packard Arbitrary Waveform Generator (HP 33120A) coupled to a Potentiostat (Wenking Model HP 88). The potential program used during electrolysis was established with the HP BenchLink Software and then transferred to the function generator. Acquisition of experimental data (applied potential, current density and charge) was performed by a microcomputer equipped with an AD/DA converter (Keithley DAS 20) using a software package developed by Keithley (Viewdac).

2.3. *Analysis of the oxidation products*

Analysis of the reaction products was carried out during the electrolysis by Ionic Chromatography (Dionex). This apparatus works with a ternary gradient of elution and includes an ion exchange column (AG11 + AS11) and a double on-line detection, i.e., a conductimeter followed by a refractometer.

After electrolysis, NMR spectra, run on a WP 200 SY Bruker spectrometer, completed the identification of the reaction products. For this, the electrolytic solution was first neutralized with a cation exchange resin (Amberlite IRA-200 from Sigma). The aqueous solutions of the electrolyzed products, free from inorganic ions, were then lyophilized. The organic substrate was then heated at 40 °C in ethanol containing 0.2 M KOH. The remaining starting lactose was soluble and the precipitated lactobionate was recovered by filtration.

Supporting electrolytes were prepared with ultra pure water (MilliQ Millipore system) and Suprapur Na_2CO_3 and pro-analysis $NaHCO_3$ purchased from VWR. Lactose ($C_{12}H_{22}O_{11}$, H_2O) was also purchased from VWR. Other chemicals ($HAuCl_4$, Tri sodium citrate $\cdot 2H_2O$, tannic acid) were purchased from Sigma. The electrolytic solutions were purged in the reservoirs with nitrogen gas (quality U from Air Liquide) for at least 20 min prior to electrochemical measurements. All the experiments were performed at room temperature (21 ± 1 °C).

3. Results and discussion

3.1. *Voltammetric behaviour of lactose on gold electrode*

Figure 3 represents the voltammogram for a Au nanoparticle modified carbon felt electrode (Au-NMC) in the

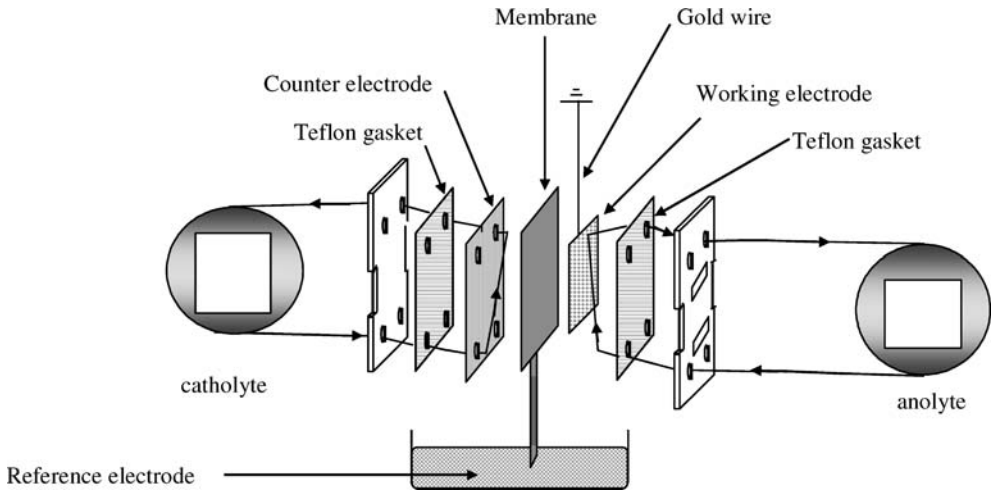

Fig. 2. Scheme of the filter press cell used to perform the electrochemical measurements.

absence (Figure 3a) and in presence of 10 mM lactose in carbonate buffer (Figure 3b). Four oxidation peaks can be observed, A and B, during the positive going scan, and two others denoted C and D, during the negative potential sweep. Peak B corresponds to the higher current density of the lactose oxidation during the formation of oxygenated layers while peak C appears as soon as gold oxides are being reduced. Figure 3b can be compared to Figure 4 which shows for comparison the voltammogram of a gold gauze electrode (Au-GE) (S_A = 30 cm^2) recorded in a three electrode-cell and in the presence of 10 mM lactose. In the latter figure it can be seen that during the positive potential scan, there are three oxidation peaks B and D almost superimposed at ca. 1 V(RHE), conversely to those present in the same potential region on Figure 3b. Although the active surface area of Au-NMC is three times smaller than that of Au-GE, the current densities are higher when the particles of gold are nanodispersed in the carbon felt (1.1 mA cm^{-2} at 1.36 V). In any case the oxidation of lactose presents the same behaviour as that observed with glucose and other carbohydrates. The superior activity of the gold electrode over catalysts such as platinum toward carbohydrate oxidation in alkaline solution requires no further demonstration. This efficiency can be explained by the oxidation of the electrode surface, which is involved in the transformation of the reducing sugars [12]. The OH species participate in the reactivation of the catalytic sites by eliminating species strongly adsorbed at the Au surface [15, 20–23].

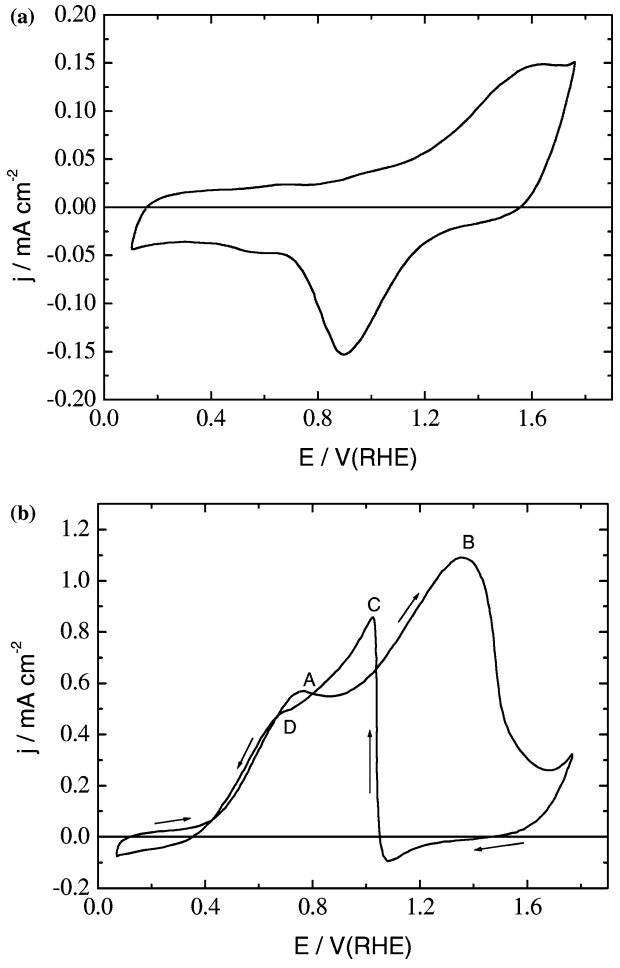

Fig. 3. Voltammograms of gold nanoparticles modified carbon felt electrode in carbonate buffer (pH 10.2) recorded at 50 mV s^{-1} (a) in the supporting electrolyte 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3 (b) in the presence of 10 mM lactose.

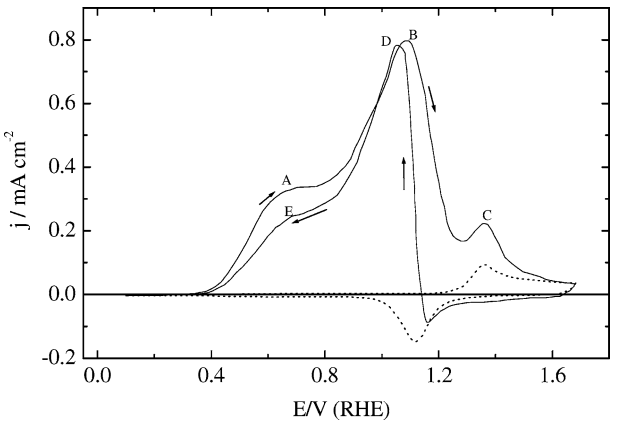

Fig. 4. Voltammograms of gold gauze electrode in carbonate buffer (pH 10.2) recorded at 50 mV s^{-1}. (- - - -) in the supporting electrolyte 0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3. (—) in the presence of 10 mM lactose.

3.2. *Electrolyses of lactose on gold nanoparticle modified carbon felt electrodes*

Electrolyses of lactose were carried out using the potential program shown in the inset of Figure 5b. For this, we took into account results previously obtained with voltammetric studies; a potential pulse, E_{ox}, was set at 1.1 and 1.2 V(RHE) for 15.8 s. As the current intensity decreased, because of both the consumption of the reactant and the poisoning of the electrode surface, a second and short potential plateau, E_{des}, was added in the sequence to clear *in situ* the adsorbed species from the Au-NMC sites. This was set at 1.6 V(RHE) for 0.2 s. The contribution of this reaction to the surface achieved 1.05 C i.e. 1.9% of the quantity of electricity is involved in oxidizing lactose. As mentioned above, the charge vs. time in Figure 5 shows that the conversion of lactose increases when the gold electrode surface is recovered by OH species.

Figure 6 represents the ^{13}C NMR spectrum of the dried reaction product, free from the supporting electrolyte. It was recorded in D_2O and the chemical shifts are given in ppm from tetramethylsilane (TMS) as internal reference. It can be seen that all carbon shifts belong to lactose except for the C_{12} position which is shifted to 177 ppm, i.e. in the carboxylic region. Another shift (a) present in the spectrum is attributed to the presence of the lactone form, which is usually in equilibrium with lactobionic acid in solution. The absence of impurities in the spectrum proves the efficiency of the neutralization protocol and above all the selective performance of

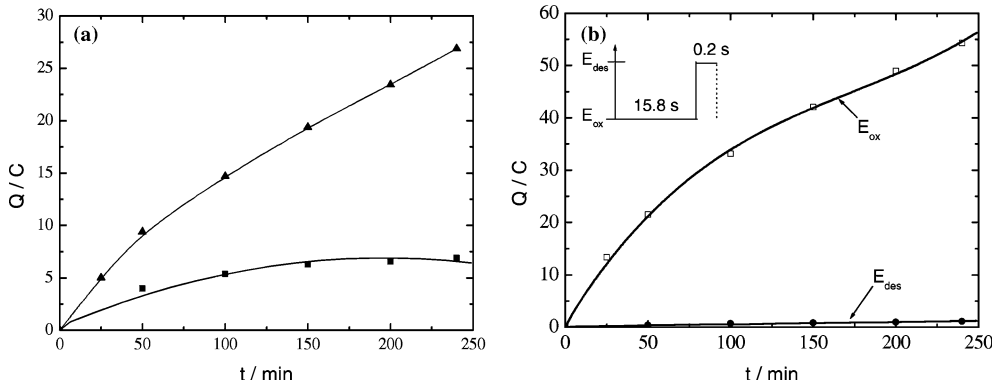

Fig. 5. Variation of quantity of electricity vs. time during electrolyses of 10.1 mM lactose on gold nanoparticle modified carbon felt electrode in carbonate buffer (pH 10.2); (a) (■) at 1.1 V; (▲) at 1.2 V(RHE). (b) (□) at 1.0 V(RHE) (the inset represents the potential program used during electrolysis); (●) charge due to the potential pulse of the reactivation of the electrode at 1.6 V(RHE).

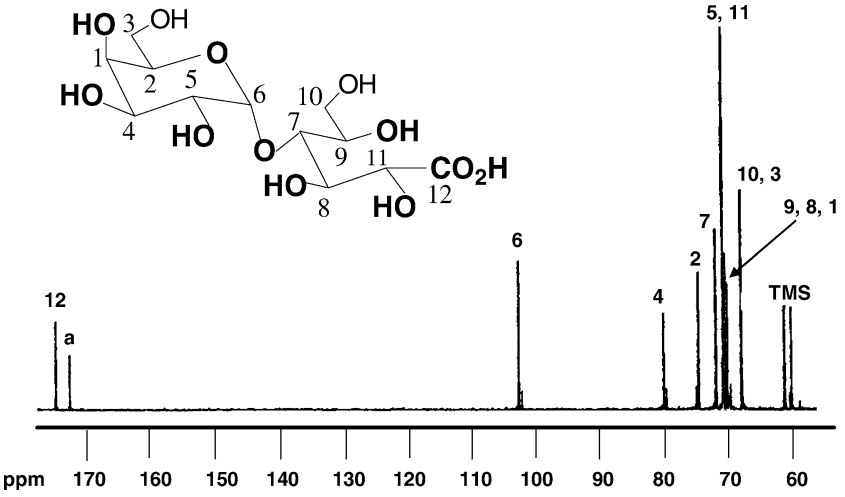

Fig. 6. NMR–^{13}C spectrum of the reaction product obtained at the end of electrolysis of 10.1 mM lactose on gold nanoparticle modified carbon felt electrode in carbonate buffer (pH 10.2) at 1.2 V(RHE).

Au-NMC to oxidize lactose to a sole reaction product. This result is in line with that of Tominaga et al. [15].

4. Conclusion

This study demonstrates that a Au-colloids modified carbon felt electrode allowed an increase in current densities in comparison to a Au-GE electrode. The explored oxidation potential range, from 0.4 to 1.6 V(RHE) indicated that the Au-NMC sites were less poisoned. Electrolysis at lower electrode potentials on Au hydroxides increased the production of lactobionic acid with a good yield (91% at 1 V(RHE)). The formation of AuOH species on the electrode surface is promoted in alkaline solution. In carbonate buffer the amount of hydroxides was lower than in NaOH; therefore one organic molecule interacted with one AuOH site to transform it into the corresponding lactone as a two-electron oxidation product [12, 15], which was then hydrolyzed in the bulk solution to give lactobionic acid. The amount of the organic substrate, accumulated by two electrolyses at 1.0 V(RHE), was identified as lactobionic acid by NMR spectroscopy. This proves the selectivity of the electrocatalytic process of sugars on gold nanoparticles.

References

1. M.L.S. Gupta, N. Bhattacharya and U.P. Basu, *Indian J. Technol.* **5** (1967) 152.
2. S.K. Dutta and K. Sanat, US Patent 4137397, 30 January 1979 (*Chem. Abstr.* 90, 174677).
3. H.V. Udupa, K.S. Udupa, P. Subbiah, J. Jarayaman, T.D. Blahirshnam and P. Thirunavakkarasu, Ind. Pat., IN154413, 1984, *Chem. Abstr.* 104, 26212m.
4. B. Jankiewicz and R. Soloniewicz, *Acta Pol. Pharm.-Drug Res.* **48** (1991) 7.
5. R.E. Shepherd, Y. Isaacson, L. Chensny, S. Zhang, R. Korkes and K. John, *J. Inorg. Biochem.* **49** (1993) 23.
6. H. Druliolle, K.B. Kokoh and B. Beden, *Electrochim. Acta* **3** (1994) 2577.
7. H. Druliolle, K.B. Kokoh and B. Beden, *J. Electroanal. Chem.* **385** (1995) 77.
8. J.L. Short, *N.Z.J. Dairy Sci. Technol.* 13 (1978) 181.
9. P.J. Simms, K.B. Hicks, R.M. Haines, A.T. Hotchkiss Jr. and S.F. Osman, *J. Chromatogr.* **667** (1994) 67.

10. G.G. Leppard and S. Ramamoorthy, *Can. J. Bot.* **53** (1975) 1729.
11. G.M. Escandar, A.C. Olivier, M. Gonzalez-Sierra and L.F. Sala, *J.Chem. Soc. Dalton Trans.* **8** (1994) 1189.
12. L.A. Larew and D.C. Johnson, *J. Electroanal. Chem.* **269** (1989) 167.
13. H.E.J. Hendriks, B.F.M. Kuster and G.B. Marin, *Carbohydr. Res.* **204** (1990) 121.
14. J.W. Slot and H.J. Geuze, *Eur. J. Cell Biol.* **38** (1985) 87.
15. M. Tominaga, T. Shiamzoe, M. Nagashima and I. Taniguchi, *Electrochem. Commun.* **7** (2005) 189.
16. B. Kutsch, O. Lyon, M. Schmitt, M. Mennig and H. Schmidt, *J. Non Cryst. Solid.* **217** (1997) 143.
17. G. Majumdar, M. Goswami, T.K. Sarma, A. Paul and A. Chattopadhay, *Langmuir* **21** (2005) 1663.
18. G.T.R. Palmore and H.-H. Kim, *J. Electroanal. Chem.* **464** (1999) 110.
19. A. Heller, *Phys. Chem. Chem. Phys.* **6** (2004) 209.
20. E.B. Makovos and C.C. Liu, *Bioelectrochem., Biogenet.* **15** (1986) 157.
21. R.R. Adzic, M.W. Hsiao and E.B. Yeager, *J. Electroanal. Chem.* **260** (1989) 475.
22. M.W. Hsiao, R.R. Adzic and E.B. Yeager, *Electrochem. Soc.* **143** (1996) 759.
23. S. Ben Aoun, G.S. Bang, T. Koga, Y. Nonaka, T. Sotomura and I. Taniguchi, *Electrochem. Commun.* **5** (2003) 317.