



# Electrosynthesis of furan-2,5-dicarbaldehyde by programmed potential electrolysis

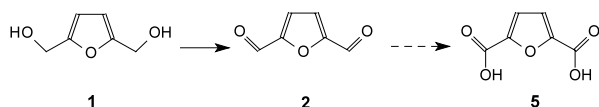
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**Abstract**—Electrocatalytic oxidation of 2,5-bis-dihydroxymethylfuran in alkaline medium on platinum electrode modified by lead adatoms lead to 80% furan-2,5-dicarbaldehyde with 63% faradaic yield. © 2002 Elsevier Science Ltd. All rights reserved.

Manganese and chromium oxides are known act as catalysts to oxidise 2,5-bis-hydroxymethylfuran (**1**) into furan-2,5-dicarbaldehyde (**2**).<sup>1–3</sup>

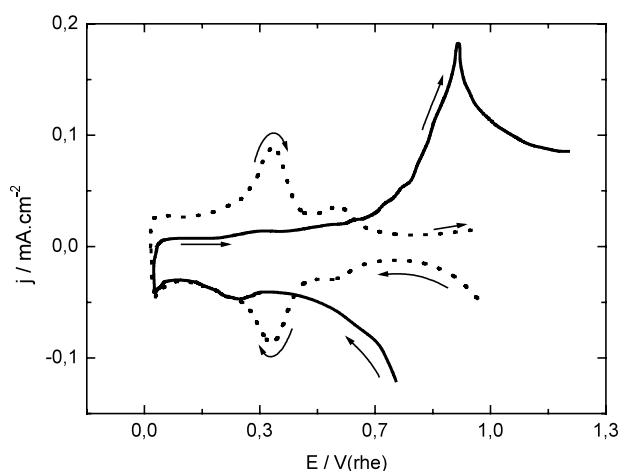


Cottier et al. have described the synthesis of **2** by oxidation of 5-silyloxymethyl-2-furfural.<sup>4</sup> The reaction was promoted by *N*-bromosuccinimide in the presence of azoisobutyronitrile. Such transformations are performed with stoichiometric amounts of mineral or organic oxidants. For our part, we are interested in the generation of carbonyl compounds via the electrochemical oxidation of alcohols. In this connection, a key objective in the electrosynthesis is the development of the concepts and the methods of heterogeneous catalysis associated with those of interfacial electrochemistry. In aqueous medium electrochemical oxidation of alcohols lead mainly to the carboxylic acids because of the nature of the electroactive sites (metal oxides at high potentials). However, aldehydes generated as primary products can be intercepted before further oxidation using a biphasic system.<sup>5</sup> A novel solution to the selective electrooxidation of alcohols into the corresponding aldehydes is to perform the electrolyses at low potentials. The interesting discovery is that noble metals, being inactive at low potentials due to poisoning processes, can be activated by under potential deposition (upd) of foreign adatoms.<sup>6</sup> We have shown that the upd

of lead adatoms has a positive effect on the electrocatalytic activity of platinum towards the oxidation of numerous alcohols, particularly at low potentials.<sup>7</sup>

Here we report the synthesis of **2** from the controlled potential oxidation of **1** on upd-lead modified platinum electrode.

In the supporting electrolyte, the system investigated by cyclic voltammetry clearly exhibits during the negative sweep the upd of  $\text{Pb}^{2+}$  (Fig. 1, solid line) allowing the determination of a fractional coverage of 40%. The adatoms desorption is displayed during the positive sweep by an oxidation peak with a maximum at 0.9 V.



**Figure 1.** Under potential deposition of Pb on platinum. Voltammograms recorded at  $50 \text{ mV s}^{-1}$  in 70 mL of  $0.1 \text{ mol L}^{-1}$  NaOH; (···) in the absence of  $\text{Pb}^{2+}$ ; (—) in the presence of  $5 \times 10^{-6} \text{ mol L}^{-1}$   $\text{Pb}(\text{ClO}_4)_2$ .

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As anticipated, during the positive sweep of the potential, bright platinum is weakly active towards the oxidation of **1** (Fig. 2, dashed line). In contrast, when  $\text{Pb}^{2+}$  ions are under potentially deposited onto the electrode, the electrochemical behaviour of **1** is dominated by a wide oxidation wave from 0.6 to 1.5 V with a maximum at 0.92 V (Fig. 2, solid line). The catalytic effect is caused by the upd-lead submonolayers, which change the local work function and provide new sites. As a result, the increasing of the oxidation rate suggests a weaker adsorption of the intermediates.

Our initial attempts focused on potentiostatic electrolyses. Efforts to perform electrolyses at constant potential between 0.6 and 1.1 V were met with frustration as the decrease of the corresponding current densities were found to be connected with electrode deactivation. Programmed potential electrolyses could avoid these problematic processes. This possibility consists of applying a sequence of three plateaus of potential to the working electrode (Fig. 3).

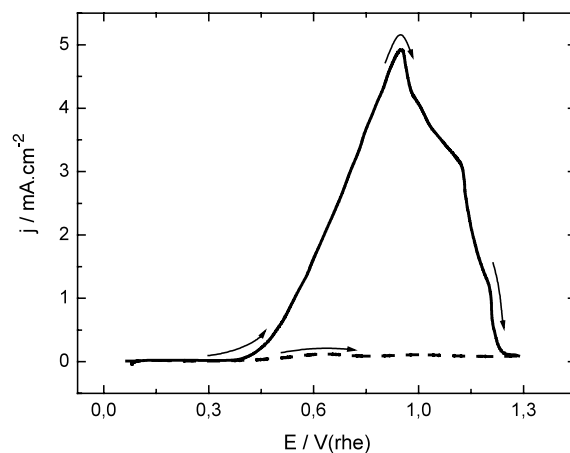
The adatom layer is deposited at 0.4 V ( $E_{\text{ads}}$ ). Oxidation of **1** is performed at 0.9 V ( $E_{\text{ox}}$ ) until the current density reaches its minimum then a reactivation process is achieved during a short pulse at more positive potential ( $E_{\text{des}} = 1.9$  V).

During electrolyses<sup>†</sup> the reaction mixture composition was followed by HPLC<sup>‡</sup> (Fig. 4). The system is described by consecutive first-order reactions where 5-(hydroxymethyl)-2-furaldehyde (**3**) is a primary product. **2** and 5-hydroxymethyl furoic acid (**4**) are secondary products. The rate formation of **2** seems to be proportional to the concentration of **3**, which indicate that **2** is not formed directly, but via intermediate **3**. At the end of the electrolysis 80 and 63% chemical and faradaic yields were obtained, respectively.

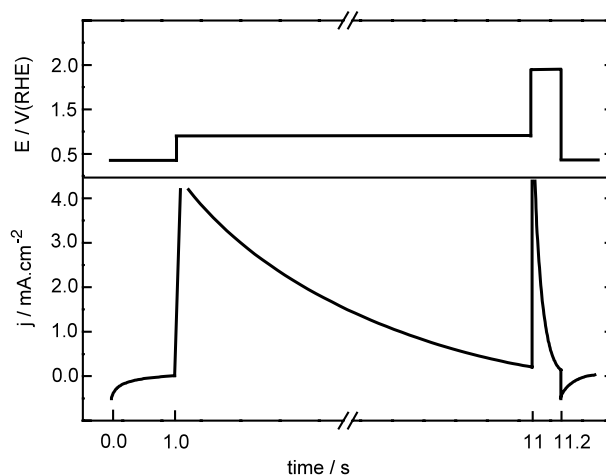
A final issue that must be addressed is the effect of the value of the oxidation plateau (0.8; 0.9 or 1.0 V). The results collected in Table 1 show that the best conversion yields are obtained at 0.9 V. At higher potential traces of 2,5-dicarboxylic acid (**5**) are obtained. We thus conclude that the electrode activity is dependant of the superficial concentration of lead adatoms. In fact, the submonolayer concentration decreases from 0.7 to 1.1

<sup>†</sup> 0.448 g of **1** were dissolved in aqueous supporting electrolyte (70 mL of 0.1 mol L<sup>-1</sup> NaOH, 5 × 10<sup>-6</sup> mol L<sup>-1</sup> Pb(ClO<sub>4</sub>)<sub>2</sub>). The solution was electrolysed at room temperature (21°C). After the electrolysis, the analyte was treated by a strongly acidic cation-exchange resin (10 mL, 17 mequiv. of Amberlite 200). The clear aqueous solution was then lyophilised without any further purification. The chemical yields were also estimated from <sup>1</sup>H NMR which corresponded to those in the literature.

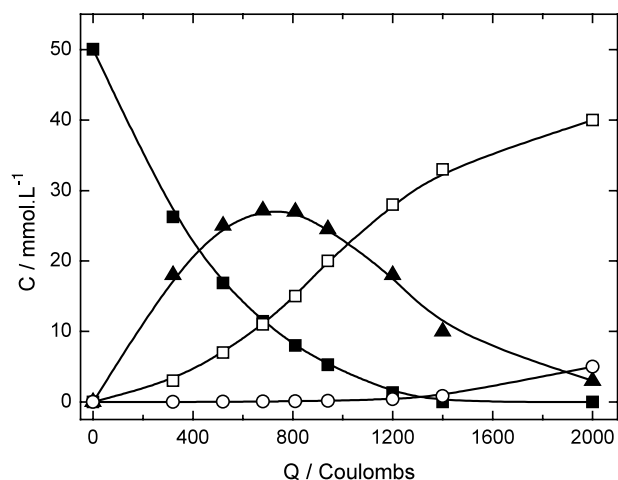
<sup>‡</sup> Analysis of the composition of the reaction mixture was carried out by HPLC which consisted of a pump (PU 980, Jasco) and two detectors settled online (UV 975 and RI 1530, Jasco). The partition was performed on a RP-18 column (Lichrosorb, Merck, water/ACN 85/15+TFA 0.2%, 0.6 mL min<sup>-1</sup>) and the quantitative analyses were carried out using the so-called 'external standard' method.



**Figure 2.** Effect of upd-lead on the electroreactivity of **1**. Voltammograms recorded at 50 mV s<sup>-1</sup> in 70 mL of 0.1 mol L<sup>-1</sup> NaOH: (---) in the absence of Pb<sup>2+</sup>; (—) in the presence of 5 × 10<sup>-6</sup> mol L<sup>-1</sup> Pb(ClO<sub>4</sub>)<sub>2</sub>.



**Figure 3.** Potential program used during electrolysis.



**Figure 4.** Concentration profile of the reactant and products during the programmed potential electrolysis of **1** at 0.9/V (RHE); (■) 2,5-bis-hydroxymethylfuran; (▲) hydroxymethyl furfural; (□) furan-2,5-dicarbaldehyde; (○) 5-hydroxymethylfurane-2-carboxylic acid.

**Table 1.** Electrocatalytic oxidation of 50 mmol L<sup>-1</sup> of **1** under the same conditions described in the first footnote.<sup>†</sup> Effect of the potential plateau on the distribution of the reaction product after passing 2000 Coulombs

<i>E/V</i> (RHE)	Product (%)	Faradaic yield (%)
0.8	(1): 8	38
	(2): 21	
	(3): 71	
0.9	(2): 80	63
	(3): 14	
	(4): 6	
1.0	(2): 31	60
	(3): 36	
	(4): 26	
	(5): 7	

V (see the voltammetric peak, Fig. 1) and optimum conditions required more or less 20% coverage, which is achieved at around 0.9 V.

In summary, the viability of a Pt/Pb-electrocatalysed oxidation has been demonstrated by the selective conversion of a primary alcohol group into its correspond-

ing aldehyde at controlled potential. It is expected that fine-tuning of the electrocatalytic conditions and the design of the electrochemical cell (opened reactor) should lead to new applications in heterogeneous electrosynthesis.

### References

- Oleinik, A. F.; Novitskii, K. Yu. *J. Org. Chem. USSR* **1971**, *6*, 2634.
- Bauer, S.; Spitteller, G. *Liebigs Ann. Chem.* **1985**, *4*, 813.
- Chmielewski, P. J.; Latos-Grazynski, L.; Olmstead, M. M.; Balch, A. L. *Chem. Eur. J.* **1997**, *3*, 268.
- Cottier, L.; Descotes, G.; Nigay, H.; Pardon, J.-C.; Grégoire, V. *Bull. Soc. Chim. Fr.* **1986**, *5*, 844.
- (a) Schneider, R.; Schäfer, H. *J. Synthesis* **1989**, 742; (b) Skowronski, R.; Cottier, L.; Descotes, G.; Lewkowski, J. *Synthesis* **1996**, 1291.
- Adzic, R. In *Modern Aspects of Electrochemistry*; Conway, B. E.; Bockris, J. O'M.; White, R. E., Eds.; Plenum Press: New York, 1990; Vol. 21.
- Belgsir, E. M.; Bouhier, E.; Essis-Yei, H.; Kokoh, K. B.; Beden, B.; Huser, H.; Léger, J. M.; Lamy, C. *Electrochim. Acta* **1991**, *36*, 1157.