Electrosynthesis of *p*-hydroxybenzaldehyde from sodium *p*-hydroxymandelate

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The electrosynthesis of *p*-hydroxybenzaldehyde (PHB) from sodium *p*-hydroxymandelate (SPHM) was investigated and good synthesis conditions were obtained. The electrochemical reactor was a divided filter-press with carbon felt electrodes (anode and cathode). Two different anolytes were used depending on the membrane employed. Thus, a 0.6 M SPHM 2.7 M NaOH solution was used in conjunction with a cationic Nafion® 117 membrane while a 0.6 M SPHM in 1.8 M NaOH solution was employed with an anionic Ionac® MA-3475 membrane. The electrolysis was carried out at a constant current density of 100 mA cm^{-2}. A material yield of approximately 90% was obtained at an energy cost of 1.4–1.5 kWh kg^{-1} PHB and a production of 49 kg PHB m^{-2} day^{-1}.

List of symbols

c_i concentration of i (mol dm^{-3})
j current density (A m^{-2})

Q charge (faraday mol^{-1})
X_i fractional conversion of i
θ_i material yield of i
ϕ_i current efficiency of i

1. Introduction

p-Hydroxybenzaldehyde (PHB) is used for the synthesis of various pharmaceutical products such as trimetoxibenzamide, amoxiglicine and amoxicillin. It is also used for the production of dyes, synthetic fibres, pesticides and condiments. Different processes can be used for the chemical synthesis of this product. Thus, using the Reimer–Teimann process [1], PHB can be obtained by condensation of phenol and chloroform in a NaOH medium. This process leads to a mixture of ortho/para isomers with a yield of 60–80% based on phenol. Thoer *et al.* [2] carried out the synthesis using phenol and chloroform in a basic medium obtaining a mixture of salycilaldehyde (61%) and PHB(14%). Wakayama [3] carried out the same reaction but with polyethylene glycol as the catalyst obtaining salycilaldehyde and PHB (21%) and Hamada and Suzukamo [4] realized this reaction in an organic medium with higher yields. Starting from phenol and glyoxilic acid, Kalikar *et al.* [5] first obtained *p*-hydroxymandelic acid that was later oxidised to PHB in an alkaline medium using Cu(OH)$_2$ and air. The condensation reaction and the oxidation reaction have a high yield (76% and 78%, respectively). The synthesis of PHB from *p*-hydroxymandelic acid was also carried out by Nagai *et al.* [6] and Bauer and Steuer [7] using different oxidants, while Campo *et al.* [8] obtained PHB from the oxidation of *p*-cresol in basic medium. Thiault and Leguen [9] carried out the synthesis from *p*-anisaldehyde and

UBE Industries [10] by oxidation of *p*-hydroxy phenylglycine.

There are also several electrochemical syntheses of PHB. Doi *et al.* [11] carried out the electrosynthesis by anodic oxidation of *p*-hydroximandelate in a basic medium using a very low current density of 1–3 mA cm^{-2} and a carbon anode. Kai-Qi *et al.* [12] used the same initial product but the synthesis was carried out at a constant potential (0.4V vs SCE) on a carbon felt anode with a yield of 90%. This synthesis has also been studied from a more basic point of view. Thus, Gomis *et al.* [13] studied the oxidation of *p*-hydroxymandelic acid on different electrodes and at different pH using voltammetry and SNIFTIR spectroscopy showing that the oxidation process is strongly inhibited in acid media. However, in basic media the voltammetry does not show the existence of inhibition, the current peak being controlled by diffusion.

It is well known that paired syntheses are a good example of the power of the electrochemical synthesis of different products. We have started a study of the paired synthesis of *p*-hydroxyphenylacetic acid and *p*-hydroxybenzaldehyde from *p*-hydroxymandelic acid. This paper presents the results obtained for the oxidation of *p*-hydroxymandelate in a non-paired process in order to clarify the behaviour of the anodic process. The aim of the present work is the study and optimization of the synthesis of *p*-hydroxybenzaldehyde (PHB) by anodic oxidation of sodium *p*-hydroxymandelate (SPHM).

2. Experimental details

The global reaction of the synthesis is shown in Scheme 1. The electrolysis cell used was a divided filter-press cell. As separators, two different ionic exchange membranes, a cationic Nafion® 117 and an anionic Ionac® M-3475, were employed. The hydraulic circuit comprised two thermostatized tanks (for anolyte and catholyte) and two pumps. A gas meter and a CO_2 trap were placed at the outlet of the anolyte. Figures 1 and 2 show a diagram of the experimental set-up. The cathode used was always a carbon felt electrode while anodes of different materials, carbon felt, graphite, Ni, Ti–Pt, DSA chlorine and Ti–PbO_2 were employed. The electrolyses were carried out at constant current density. All the products used were Merck *pro analysi* with the
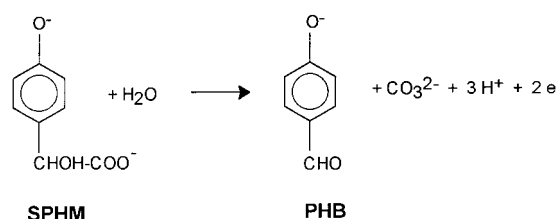
Scheme 1. Electrochemical reaction.

exception of the sodium *p*-hydroxymandelate (SPHM) whose purity was only 94%. The oxidation of SPHM was carried out in strong basic media because it has been demonstrated [13] that in this medium the oxidation process is not inhibited, the peak current being controlled by diffusion. Oxygen evolution from water oxidation and PHB oxidation with initial formation of sodium *p*-hydroxybenzoate (SPHB), that can in turn be transformed into more oxidized products, have been identified as the competitive processes to the oxidation of SPHM. These processes decrease the current efficiency and material yield of the synthesis.

The work up of the final solution was carried out by precipitating PHB by acidification with HCl or H_2SO_4 to pH 2. The solid was then filtered and collected. This solid had a light brown colour and a melting point of 114–117 °C (115–117 °C for PHB from tables). To purify this solid, it was dissolved in hot water, passed through active carbon and recrystallized. In solutions with high SPHM and NaOH concentrations, white crystals were obtained at the end of the electrolysis.

HPLC was used for monitoring the composition of anolyte at different electrolysis times. The column used was a B7499 Nucleosil 120-5C18 whose dimensions were 120 mm × 4 mm. The flow was 1 ml min^{-1} and the solvent used was a solution composed of 75% of the solution A (950 ml of H_3PO_4 1% in Millipore water and 50 ml of methanol for HPLC) plus 25% of the solution B (methanol for HPLC). The wavelengths used were $\lambda = 230$ nm for analysing SPHM (retention peak time 1.48 min) and $\lambda = 254$ nm for sodium *p*-hydroxybenzoate, SPHB (3.60 min) and PHB (4.10 min).

The techniques used for analysing the different products were elemental analysis, mass spectrometry, infrared spectroscopy and gas chromatography.

The results obtained for the light brown solid were as follows:

Elemental analysis: C(68.8%), O(26.2%), H(4.9%).
Mass spectrometry: $m/z = 121$, 93, 65.
^{1}H-RMN (CD$_3$COCD$_3$): $\delta = 9.80$, 9.25, 7.73, 6.93 against TMS.
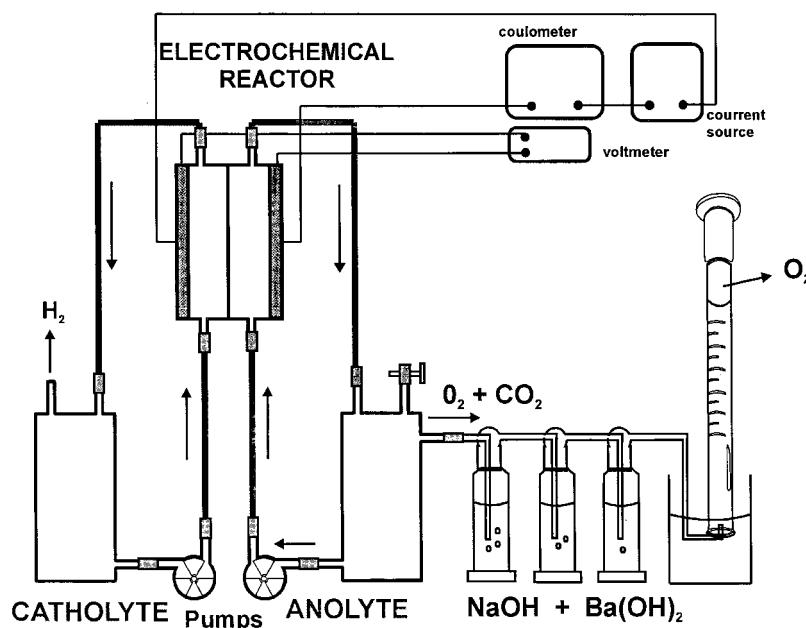^{13}C(MeOH/D$_2$O): ppm = 194, 163, 133, 129, 116.

Fig. 1. Schematic overview of the experimental set-up for the electrosynthesis of PHB.
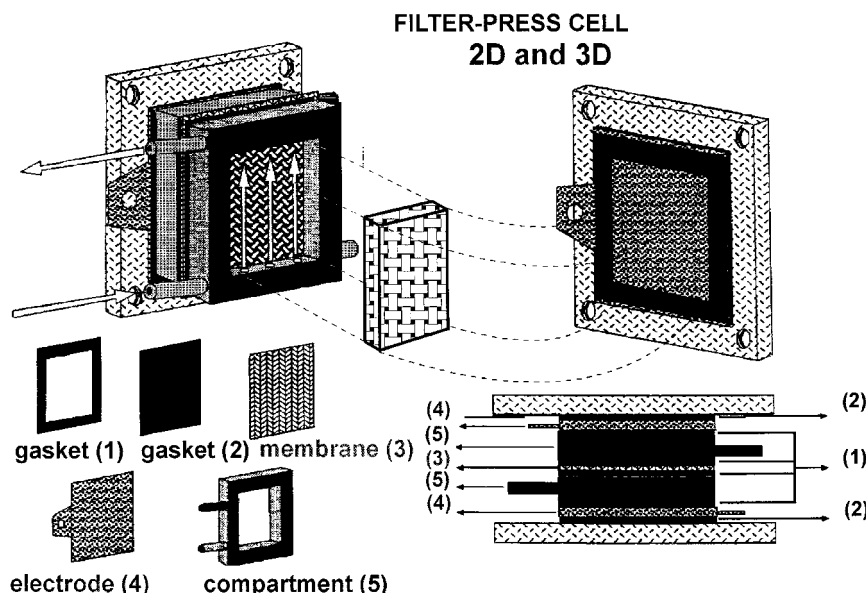
Fig. 2. Schematic view of the electrochemical reactor used in the synthesis of PHB. Electrode surface 20 cm^2; interelectrode gap 22 mm.

IR spectroscopy (KBr) [14]: 1650, 1570, 1430, 1200, 815 cm^{-1}.

All these results enabled the solid to be identified as PHB.

The results obtained for the white crystals were as follows:

Mass spectrometry: $m/z = 121, 93, 65$.

^{1}H-RMN (MeOD): $\delta = 9.25, 7.60, 6.58$ as against TMS.

^{13}C(MeOH/D$_2$O): ppm = 193, 177, 134, 123, 120.

IR (KBr): 1650, 1570, 815 cm^{-1}.

The product was identified as the sodium salt of the phenolate anion of *p*-hydroxybenzaldehyde ($pK_a = 7.8$).

3. Results and discussion

To find an adequate value of the kWh kg^{-1} and kg m^{-2} day^{-1} parameters, (the kg PHB m^{-2} day^{-1} is the production of PHB at a given current density per m^2 and per day and the kWh kg^{-1} PHB is the energy consumption per kg of PHB) together with a good material yield, an optimization process was carried out in which the influence of the following variables was studied: type and nature of the anode, SPHM concentration, current density, NaOH concentration, type of separators and temperature.

For the following Tables, the different parameters are defined as follows:

Percentage fractional conversion of SPHM (X_{SPHM})

$$X_{SPHM} = \frac{[(\text{initial moles of SPHM}) - (\text{moles of SPHM at time } t)]}{\text{initial moles of SPHM}} \times 100 \quad (1)$$

Percentage material yield of PHB and SPHB (θ_{PHB} and θ_{SPHB})

$$\theta_{PHB} = \frac{(\text{moles of SPHM converted to PHB})}{(\text{total moles of SPHM consumed})} \times 100 \quad (2)$$

$$\theta_{SPHB} = \frac{(\text{moles of SPHM converted to SPHB})}{(\text{total moles of SPHM consumed})} \times 100 \quad (3)$$

Percentage current efficiency for oxygen formation (secondary reaction) ϕ_{O_2}

$$\phi_{O_2} = \frac{(\text{charge used in O}_2 \text{ formation})}{(\text{charge circulated})} \times 100 \quad (4)$$

3.1. Influence of the anodic material

To carry out this study a carbon felt cathode and a Nafion$^{®}$ 117 cationic exchange membrane separator were used. The temperature was 60 °C. The fractional conversion and material yield were measured at a charge two faradays per mol. The current density was 1000 Am^{-2}. The catholyte was a 2.7 M NaOH solution. The anolyte was a 0.6 M SPHM in 2.7 M NaOH solution. The different anodes studied were carbon felt, graphite, Ni foam, Ti/Pt, DSA for chlorine and Ti/Pt/PbO$_2$. Table 1 shows the results obtained.

These data show that a carbon felt (three-dimensional electrode) is a good choice. The use of this 3D electrode implies that the real current density used for the synthesis is very low. This improves the efficiency of the synthesis, increases the productivity of the cell and decreases the energy cost, not only because the overvoltage is low but also because the potential for the oxidation of PHMA, fixed by the current density corresponds to the foot of the voltammetric wave thus increasing the selectivity, the fractional conversion and the material yield.

Table 1. Results of the preparative synthesis of PHB showing the influence of anodic material

Carbon felt cathode; catholyte 0.1 dm^3 of a 2.7 M NaOH solution; anolyte 0.1 dm^3 of a 0.6 M SPHM in 2.7 M NaOH solution; membrane Nafion$^®$ 117; temperature 60 °C; current density 1000 A m^{-2}; charge passed 2.0 faradays per mol

Anode	Cell voltage /V	X_{SPHM}	θ_{PHB}	θ_{SPHB}	ϕ_{O_2}	Production /kg PHB m^{-2} day^{-1}	Energetic cost /kWh kg^{-1} PHB
Carbon felt	2.85	100	90	<0.5	0.0	49	1.4
Graphite	3.81	72	89	<0.5	0.0	35	2.6
Nickel	3.04	87	84	<0.5	1.3	40	1.8
Ti/Pt	3.85	68	60	<0.5	0.0	22	4.0
DSA chlorine	3.27	88	86	<0.5	0.0	41	1.9
Ti/Pt/PbO$_2$	3.10	90	87	<0.5	1.3	43	1.7

3.2. *Nature of the cathode*

Carbon felt was also chosen as the cathode, taking into account that with this electrode the real current density will be very low and thus the overvoltage for hydrogen evolution is also low. Moreover, this material can, if necessary, be easily catalysed with platinum thus decreasing hydrogen overvoltage. At the same time the use of a carbon felt as cathode and anode transforms the cell into a zero gap cell with low ohmic drop.

3.3. *Influence of the concentration of SPHM*

In this set of experiments, the behaviour of the synthesis for different SPHM concentrations was studied. The other experimental variables were the same as in Section 3.1. The results obtained are shown in Table 2.

These data show that an initial concentration of 0.6 M is a good value for the synthesis.

3.4. *Influence of current density*

The current density was changed between 100 and 2000 A m^{-2} while the other experimental parameters were the same as in Section 3.1. Figure 3 shows the results.

These data show that a current of 1000 A m^{-2} can be considered as adequate. The selectivity and conversion are high and no oxygen is evolved. Current densities higher than 2000 A m^{-2} cause oxygen evolution. This reaction not only decreases current efficiency but also causes corrosion of the carbon felt, shortening the life of the anode. This is an important parameter in developing a competitive industrial process.
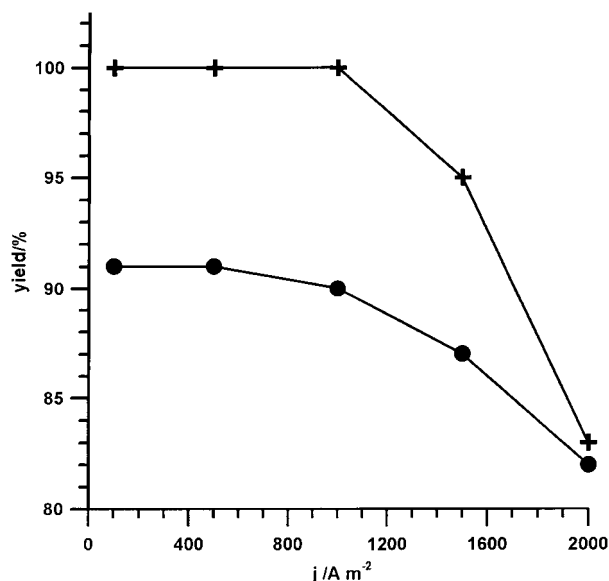

Fig. 3. Results of preparative synthesis of PHB showing the influence of current density. Carbon felt cathode; catholyte 0.1 dm^3 of a 2.7 M NaOH solution; carbon felt anode; anolyte 0.1 dm^3 of a 0.6 M SPHM in 2.7 M NaOH solution; Nafion$^®$ 117 membrane; temperature 60 °C; current density 100–2000 A m^{-2}; charge passed 2.0 faraday mol^{-1}. Key: (+) Fractional conversion (%) of SPHM (●) Material yield (%) of PHB.

The small amount of SPHB detected can be explained using the voltammetric results [13] showing that SPHB is oxidized at potentials less positive than that corresponding to the oxidation of PHMA. It is possible that the oxidation of SPHB yields quinonic products (the nature of which has not been determined) that can easily be oxidized. The identification and detection of these products is difficult.

A study of the evolution of the material yield and fractional conversion for different values of the

Table 2. Results of the preparative synthesis of PHB showing the influence of SPHM concentration

Carbon felt cathode; catholyte 0.1 dm^3 of a 2.7 M NaOH solution; carbon felt anode; anolyte 0.1 dm^3 of a 0.6–1.0 M SPHM in 2.7 M NaOH solution; membrane Nafion$^®$ 117; temperature 60 °C; current density 1000 A m^{-2}; charge passed 2.0 faradays per mol

c_{SPHM} /mol dm^{-3} (M)	Cell voltage /V	X_{SPHM}	θ_{PHB}	θ_{SPHB}	ϕ_{O_2}	Production /kg PHB m^{-2} day^{-1}	Energetic cost /kWh kg^{-1} PHB
0.6	2.85	100	90	<0.5	0.0	49	1.4
0.7	2.83	100	90	<0.5	0.0	49	1.4
0.8	3.01	100	88	<0.5	0.0	48	1.5
0.9	3.10	100	88	<0.5	0.0	48	1.6
1.0	3.20	100	88	<0.5	0.0	48	1.6

Table 3. Results of the preparative synthesis of PHB showing the influence of charge passed

Carbon felt cathode; catholyte 0.1 dm³ of a 2.7 M NaOH solution; carbon felt anode; anolyte 0.1 dm³ of a 0.6 M SPHM in 2.7 M NaOH solution; membrane Nafion® 117; temperature 60 °C; current density 1000 A m⁻²; charge passed 0.5–2.0 faradays per mol

Q /F mol⁻¹	Cell voltage /V	X_{SPHM}	θ_{PHB}	θ_{SPHB}	ϕ_{O_2}
0.5	2.44	24	100	< 0.5	0.0
1.0	2.48	49	98	< 0.5	0.0
1.5	2.52	76	95	< 0.5	0.0
1.9	2.65	97	92	< 0.5	0.0
2.0	2.85	100	90	< 0.5	0.0

charge passed expressed as number of faradays per mol of SPHM is shown in Table 3.

3.5. *Influence of NaOH concentration*

The previous voltammetric study [13] showed that for high current densities and avoidance of inhibition of the oxidation, the solution must be strongly alkaline. The NaOH concentration was changed from 2.4 to 3.6 M. Because of the decrease in pH produced during the oxidation either of the SPHM or water, the quantity of NaOH must be sufficiently high to maintain the anolyte in a pH interval that avoids the inhibition of the reaction. All the experimental parameters were the same as in the preceding paragraph with the current density 1000 A m⁻². Table 4 shows the results obtained for an electrolysis charge of two faradays per mol.

The concentration 2.7 M was considerate as adequate for the synthesis. Higher concentrations of NaOH produce an increase in the quantity of HCl needed for the separation of the PHB. Some crystals were obtained during the cooling of the anolyte at the

end of the electrolysis. These crystals were identified as the sodium salt of the phenolate of *p*-hydroxybenzaldehyde.

To avoid the acidification of the anolyte during the oxidation reaction and to employ an initial NaOH concentration lower than 2.7 M, that will decrease not only the cost of the process but also the quantity of NaCl in the effluents, an anionic exchange membrane was used. This membrane permits the transfer from the catholyte to the anolyte of the OH⁻ generated during the cathodic evolution of hydrogen. This transfer will maintain the pH of the anolyte constant (small variations can be observed due to the fact that the transport number of H⁺ through the membrane is slightly smaller than 1). Thus the initial NaOH concentration can be decreased. The membrane used was an Ionac® MA-3475. The experiments were carried out using the same experimental conditions as in Section 3.1. Table 5 shows the results.

These results clearly show that only an initial concentration of NaOH of 1.8 M is needed. We consider that the small increases in the energy cost caused by the decrease in NaOH concentration is compensated by the cost reduction due to the lower NaOH concentration involved, and to the lower cost of HCl for the precipitation of PHB. Moreover, the smaller amount of reactants employed produces effluent with lower salinity and, therefore, with less environmental impact upon disposal. The only negative point is the possibility that the membrane MA-3475 does not withstand strong alkaline medium in long term electrolysis.

3.6. *Influence of temperature*

In this set of experiments the influence of the temperature was studied. The other experimental variables were the same as in Section 3.1.

Table 4. Results of the preparative synthesis of PHB showing the influence of the concentration of NaOH (cationic exchange membrane)

Carbon felt cathode; catholyte 0.1 dm³ of a 2.7 M NaOH solution; carbon felt anode; anolyte 0.1 dm³ of a 0.6 M SPHM in 2.4–3.6 M NaOH solution; membrane: Nafion® 117; temperature 60 °C; current density 1000 A m⁻²; charge passed 2.0 faradays per mol

c_{NaOH} /mol dm⁻³ (M)	Cell voltage /V	X_{SPHM}	θ_{PHB}	θ_{SPHB}	ϕ_{O_2}	Production /kg PHB m⁻² day⁻¹	Energetic cost /kWh kg⁻¹ PHB
2.4	4.79	81	86	< 0.5	0.8	38	3.0
2.7	2.85	100	90	< 0.5	0.0	49	1.4
3.0	2.78	100	90	< 0.5	0.0	49	1.4
3.6	2.72	100	90	< 0.5	0.0	49	1.3

Table 5. Results of the preparative synthesis of PHB showing the influence of the concentration of NaOH (anionic exchange membrane)

Carbon felt cathode; catholyte 0.1 dm³ of a 2.7 M NaOH solution; carbon felt anode; anolyte 0.1 dm³ of a 0.6 M SPHM in 0.6–1.8 M NaOH solution; membrane IONAC® MA-3475; temperature 60 °C; current density 1000 A m⁻²; charge passed 2.0 faradays per mol

c_{NaOH} /mol dm⁻³ (M)	Cell voltage /V	X_{SPHM}	θ_{PHB}	θ_{SPHB}	ϕ_{O_2}	Production /kg PHB m⁻² day⁻¹	Energetic cost /kWh kg⁻¹ PHB
0.6	4.60	51	65	< 0.5	2.3	18	6.1
0.9	4.22	88	89	< 0.5	0.4	43	2.4
1.2	4.06	100	87	< 0.5	0.0	48	2.1
1.5	3.27	100	90	< 0.5	0.0	49	1.6
1.8	3.12	100	90	< 0.5	0.0	49	1.5

Fractional conversion, material yield and production remain unchanged in the temperature interval 30 to 60 °C. The energy cost decreases slightly with temperature increase, due to a decrease in the ohmic drop of the cell. However this decrease must be compared with the energy cost involved in the heating of the system. At 60 °C no white solid product was found. It was checked that a PHB solution in 2.7 M NaOH at 60 °C is stable over a time corresponding to the electrolysis period, that is, no aldolization reaction occurs.

4. Conclusions

Adequate conditions for the electrochemical synthesis at constant current of *p*-hydroxybenzaldehyde from sodium *p*-hydroxymandelate were identified as

Current density: 1000 A m^{-2}

Anode and cathode: carbon felt

Membrane: cationic (Nafion$^{®}$ 117) or Anionic (Ionac$^{®}$ MA-3475).

Anolyte: 0.6 M sodium *p*-hydroxymandelate in 2.7 M NaOH (Nafion$^{®}$ 117) or 1.8 M NaOH (Ionac$^{®}$ MA-3475).

Catholyte: 2.7 M NaOH.

Temperature: 30–60 °C.

Under these conditions, the material yield was 90%; the energy cost 1.4–1.5 kWh kg^{-1} and the production 49 kg m^{-2} day^{-1} (at a current density of 1000 A m^{-2}).

References

[1]   Reimer–Teimann, *USA patent 3 365 500* (1876).
[2]   A. Thoer, G. Denis, M. Delmas and A. Gaset, *Synth. Commun.* **18** (1988) 2095.
[3]   K.Wakayama, *Patent* JP1 038 039 A (1989).
[4]   K. Hamada and G. Suzukamo, *Patent EP 68725 A* (1983).
[5]   R. Kalikar, R. Deshpande and S. Chandalia, *J. Chem. Technol. Biotechnol.* **36** (1) (1986) 38.
[6]   S. Nagai, T. Enomiya and T. Nakamura, *Patent JP 76 128 934* (1976).
[7]   K. Bauer and W. Steuer , *Patent DE 2 115 551* (1972).
[8]   P. Campo, P. Cocolios, P. Dognin and H. Ledon, *Patent EP 323 290 A1* (1988).
[9]   G. A. Thiault and Y Leguen, *Patent FR 2 578 538* (1986).
[10] Ube Industries Kk., *Patent JP 57 108 034 A* (1982).
[11] K. Doi, H. Tsuruta and T. Yoshida, *Patent JP 52 027 739 A* (1977).
[12] P. Kai-Qi, Ch. Qi-Rui, Ch. Lan and Yiyao Gongye, **19** (7) (1988) 317.
[13] J. Gomis, E. Morallon, V. Montiel and A. Aldaz, *J. Electrochem. Soc.* **143** (1996) 3166.
[14] 'Merck FT-IR Atlas' (Merck, 1988), p. 473.