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Use of electrocatalytic membrane reactor for synthesis of sorbitol

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Abstract

The strategy of paired electrochemical synthesis of organic compounds in undivided cell process in which the reaction product at the anode and the reaction product at the cathode are simultaneously separated was performed. In order to evaluate the feasibility of the process the electrochemical oxidation of fructose to gluconic acid and the reduction of fructose to sorbitol and mannitol were paired in an electrocatalytic membrane reactor. However, only the results obtained on the electrochemical reduction are described in this work as it required catalysis to be performed successfully. The reactor is made with two coaxial tubes of membrane support. Some parameters which modify the electrocatalytic activity of the electrode are studied. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemical synthesis; Electrocatalytic reduction; Sorbital; Membrane reactor

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1. Introduction

During the recent years, research in inorganic membrane reactors for a variety of different reactions has been intensive. Even though some applications in the fields of biotechnology are described in the literature, the most important works are focused on catalytic hydrogenation and dehydrogenation reactions. As mentioned by Zaman and Chakma [1], the potential applications for membrane reactors include steam reforming of methane, water gas-shift and dehydrogenation of various hydrocarbons. Most of these applications are studied in gas phase at high temperature. The electrosynthesis of organic compounds is an interesting route to transform raw materials, typically the components of biomass such as alcohols, carbohydrates, etc., into more economically profitable products [2].

In this work, a membrane reactor with electrocatalytic activity has been used for the electrochemical transformation of fructose into sorbitol, mannitol and gluconic acid with Pt–Rh catalyst according to the following scheme of reaction:

$$\text{fructose} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{sorbitol} + \text{mannitol}$$
$$\text{fructose} \rightarrow \text{gluconic acid} + 2\text{H}^+ + 2\text{e}^-$$

The electrooxidation of glucose to gluconic acid and the electroreduction of glucose to sorbitol have been formerly combined into a paired synthesis in undivided flow cells by Pintauro et al. [3] and Park et al. [4]. Each of these processes has been carried out separately on an industrial scale. As an example, the reduction of glucose to sorbitol, a compound currently used in foodstuff industries, was commercially accomplished as an electroorganic chemical process [5]. But, for economic viability, this process was replaced since the war by the catalytic hydrogenation route at high pressure (50–60 bars) and temperature between 130 and 160°C. By this way the electrooxidation and

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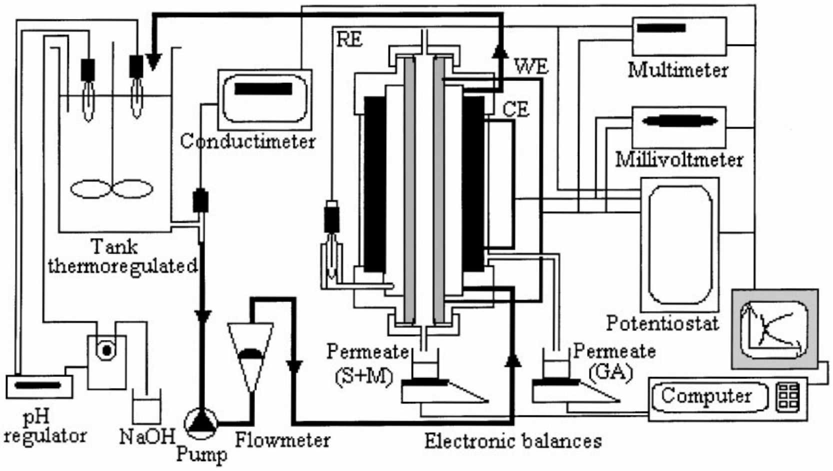

Fig. 1. Experimental set-up (inner support = cathode, outer support = anode, S = sorbitol, M = mannitol, GA = gluconic acid, WE = working electrode, RE = reference electrode, CE = counter-electrode).

the electroreduction products are in the same reaction mixture. The membrane reactor developed in this work offers the possibilities on one hand to operate at ambient temperature and atmospheric pressure and on the other hand to separate simultaneously the oxidation product from the reduction product. The effects of operating parameters such as the pH of the electrolyte and the working electrode potential, were studied. The effects of the electrode material and structure (porosity) and the effect of catalyst were also investigated.

2. Experimental

Experiments were carried out with the equipment described in Fig. 1 which consists of a pulse potentiostat (PIT 20-2-X from Tacussel) in order to perform electrolysis at controlled potential. The potential imposed at the working electrode (WE) and the current intensity between the working electrode and the counter-electrode (CE) were measured simultaneously by a multimeter type Fluke 45 equipped with RS232 output and interfaced card IEEE-488. A millivoltmeter–pH-meter (PHIN 81) was used to measure the difference of potential between WE and CE. The electrolyte conductivity was obtained from a Philips cell type PW9554/00 placed at the feed tank outlet and connected to the conductimeter CDIT-SI-N2 from Tacussel. In order to avoid signal interferences, the analogical output of the multimeter and conductimeter were insulated by an Analog Device card type 3B01 before their connection to the acquisition card PC-MES 2. The electrolyte volumetric flow rate was measured by Sho-Rate Brooks flowmeter. Its pH was controlled using a pH meter (pH-stat) driving a peristaltic pump above which was a reservoir containing a solution of NaOH 0.05 M. All the equipments — conductimeter, multimeter, millivoltmeter and electronic balances — were connected to a microcomputer type 286C-100 COPAM. The electrolyte cell was the membrane reactor which is described below.

2.1. Reactor description

The electrochemical membrane reactor was made with two porous tubular and coaxial electrodes. Each tube was formed with conducting particles and can be used as anode or cathode. Owobi et al. [6] in a previous study have shown that the configuration for this reactor is to use the internal tube as the cathode and the external tube as the anode. The electrolyte which is an aqueous solution of fructose was flowing in the annular compartment of the reactor. Schematic view of the reactor is presented in Fig. 2. Anolyte and catholyte (permeates) were collected in a reservoir placed on an electronic balance PM 6000 from Mettler, interfaced to a computer to collect and record time and mass data. The retentate stream is recycled back

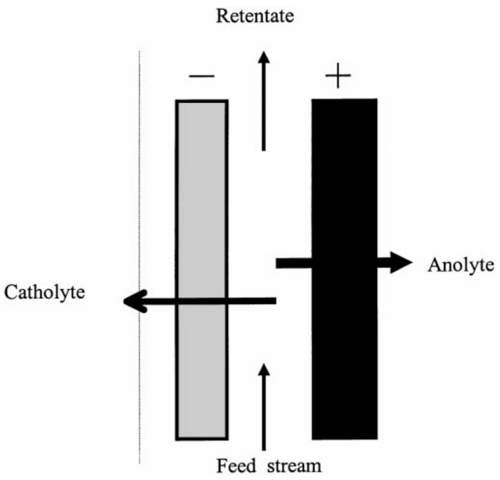

Fig. 2. Schematic view of the reactor.

to the feed reservoir. Mixing in the feed reservoir was provided by magnetic stirring bars.

2.2. Description of electrodes

The inner electrode or cathode was made with a support of membrane in graphite or a support and its membrane in graphite type M5 from Orelis (ex Tech-Sep). Its characteristics were: 6 mm of inner diameter, 4 mm of thickness, 0.2 μm of pore average diameter and a porosity of 0.32. A support of membrane in graphite (type M2 from Orelis) with 3 μm of pore average diameter and porosity of 0.16 was also used. The counter-electrode (external tube) was a support in graphite from Union Carbide. Its characteristics were — internal diameter: 22 mm, thickness: 1.2 mm, porosity: 0.26 and average pore diameter: 4 μm. The saturated calomel electrode (SCE) was used as reference electrode. The electrode length was 150 mm. All the membrane support used are commercially available. A fairly narrow pore size distribution was obtained for membrane support M2 and M5 while for the counter-electrode the pore size distribution was not homogeneous.

2.3. Preparation of the electrolyte and analysis of the reaction products

Electrolyte solutions were prepared from ultrapure water (Alpha-Q from Millipore) and Janssen Chimica D-(-) fructose at 98% purity. The concentration of fructose in the prepared solution was about 0.1 M. The pH was adjusted by NaOH 0.05 M obtained from Prolabo. During experiments samples of catholyte, anolyte and electrolyte in the tank were withdrawn at different times and analyzed. Analysis were carried out with a high performance chromatography (HPLC) system. The column used is Sugar Pak from Waters, thermostatted at 90°C. A diluted solution of EDTA ($0.05\,\mathrm{g\,l^{-1}}$) was used as an eluent. The detection of the chromatographic peaks was carried out with a differential refractometer (type R 401 from Waters Associates) and an integrator (Waters 745 Data Module Millipore).

2.4. Preparation of catalytic electrode

The catalytic activity of WE (cathode) was achieved by first cleaning the electrode with a dilute nitric acid solution (10% per volume). This cleaning created active sites on the carbon surface. After rinsing with distilled water, the electrode was then percolated by an aqueous solution of tin dichloride ($SnCl_2$) and hydrochloric acid (HCl) (10 g of $SnCl_2$ and 40 ml of HCl, in 500 ml of water). This treatment allowed the electrode to become sensitive by chemisorption. Tin (Sn) is a reducing metal which, in contact with a noble metal, will be oxidized and therefore the noble metal will be deposited in the electrode. After a second washing with distilled water, platinum (Pt) and rhodium (Rh) ions were substituted to the tin ions in the electrode by percolating 40 ml of aqueous solution of platinum tetrachloride ($PtCl_4$) and HCl (1 g $PtCl_4$ and 3 ml of HCl, in 1000 ml of water) and 10 ml of rhodium trichloride ($RhCl_3$). After a third washing with water, the electrode was calcinated in order to eliminate the chlorine. About $4\,\mathrm{mg\,cm^{-3}}$ of catalyst was deposited in the pores of the electrode.

3. Results and discussion

The use of an electrocatalytic membrane reactor, as previously mentioned, has the advantage of separating anolyte from catholyte. Therefore it leads to a decrease in by-product formation and higher efficiencies and yields because the product from one electrode cannot be altered and destroyed at the other electrode [3]. In order to study the feasibility of performing paired electroorganic reaction in undivided flow cell, the electrochemical oxidation of fructose to gluconic acid and electrochemical reduction of fructose to sorbitol and mannitol have been combined in the electrocatalytic membrane reactor presented in Fig. 1. Except when it is mentioned experiments were carried out at fixed potential, at temperature of 30°C, at pH = 10 and feed electrolyte flow rate of $2.7\,\mathrm{ml\,s^{-1}}$. Under alkaline conditions and high temperature, fructose isomerizes to glucose which is less reducible than fructose. In this work, only the electroreduction reaction is presented as it may concern by catalyst to be performed. Analysis of the catholyte and the feed electrolyte after the electrolysis showed, as depicted in Fig. 3, that the electrocatalytic reduction of fructose at −1.25 V vs SCE leads to a conversion of 60%. The selectivities in mannitol and sorbitol are 60 and 40%, respectively, and are in agreement with the ones commonly reported in literature. Neither the electroreduction nor the electrooxidation products were detected in the analysis of the retentate. The selectivity is defined as

$$S_{[\mathrm{X}]} = \frac{[\mathrm{X}]}{[\mathrm{fructose}]_{\mathrm{feed\ stream}}\mathrm{conversion}}, \tag{1}$$

where X is mannitol or sorbitol. The conversion is defined as follows:

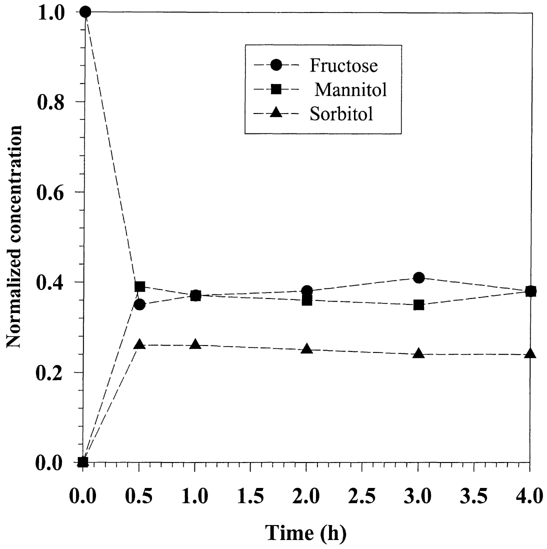

Fig. 3. Evolution of fructose, mannitol and sorbitol in the catholyte at −1.25 V vs SCE.

$$\mathrm{Conversion} = \frac{[\mathrm{fructose}]_{\mathrm{feed\ stream}} - [\mathrm{fructose}]_{\mathrm{catholyte}}}{[\mathrm{fructose}]_{\mathrm{feed\ stream}}}. \tag{2}$$

The conversion and selectivities given were estimated when there was no more deactivation of the catalyst. This deactivation, due to adsorption of some organic compounds on the catalyst surface, occurred for an electrode newly activated and up to four experiments of 4 h (16 h of operation). Experimental results became reproducible. Therefore the steady-state was obtained after 1 h.

Based on this result, experiments were performed to study the effect of catalyst, the influence of the potential imposed at the cathode and to examine the effect of the electrode texture (porosity and pore diameter). Effect of operating parameters such as electrolyte pH and temperature were also investigated. We observed that by increasing the temperature from 30 to 50°C and the pH from 10 to 11, the conversion enhancement was 25% at −1.07 V vs SCE after 4 h of electrolysis. The electroreactivity of fructose is more important in high alkaline medium. However at 50°C and at pH of 11, the isomerization rate of fructose in glucose increased. Under our experimental conditions, 15% of glucose was obtained at 50°C and pH = 10 against 5% of glucose at 30°C and pH = 11 after 4 h of electrolysis. It is clear that temperature and pH must be optimized to limit the isomerization reaction on the one hand, and on the other hand the other probable subsidiary or side reactions.

The effect of the catalyst on the reaction at the cathode is depicted in Fig. 4. It can be seen that the electroreduction transformation of fructose on solid electrode is catalyzed. Without catalyst the conversion is less than 5% at −1.2 V vs SCE. These results indicated that Pt–Rh may be an effective electrocatalyst for the hydrogenation of fructose. The effect of electrode material texture was also investigated. As shown in Fig. 5, the conversion of fructose when using the membrane support M5 as electrode is higher than the conversion obtained when the reaction was conducted on the membrane support M2. In fact this difference in conversion is due to the effect of the specific surface area of the electrode. As it can be observed, the latter support, according to its characteristics previously described, has very low specific surface area. A rough estimation of this specific surface area can be

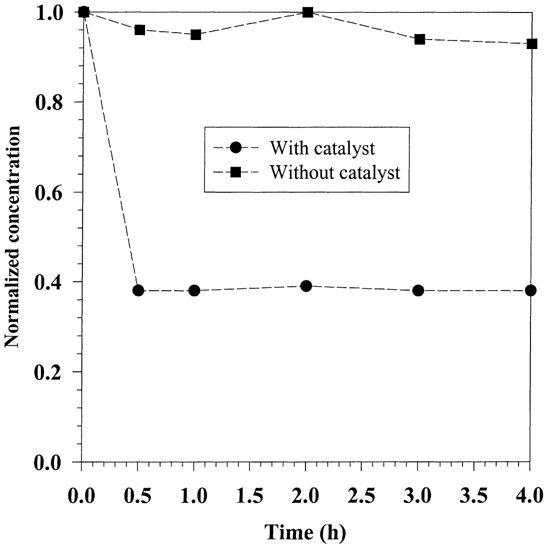

Fig. 4. Effect of catalyst on the electroreduction of fructose at −1.2 V vs SCE.

done from the following relationship which is valid for cylindrical pore:

$$a_s = \frac{4\varepsilon}{d_p}, \tag{3}$$

where ϵ is the electrode porosity and d_p the pore diameter. More accurate value of the specific surface area can be obtained by BET techniques. The main textural parameter which needs to be taken into account in the electrode design is the ratio porosity/pore mean diameter. Further informations on the effect of potential imposed at the cathode are given in Figs. 6 and 7. Fig. 6 shows the influence of the potential imposed on the reaction transformation while in Fig. 7 is depicted

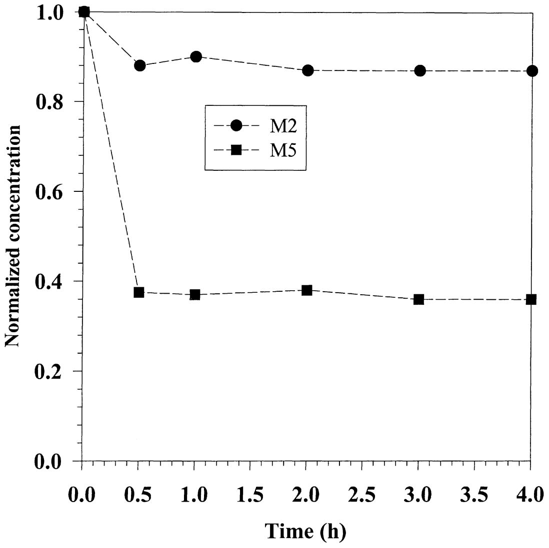

Fig. 5. Effect of electrode texture on fructose concentration in catholyte.

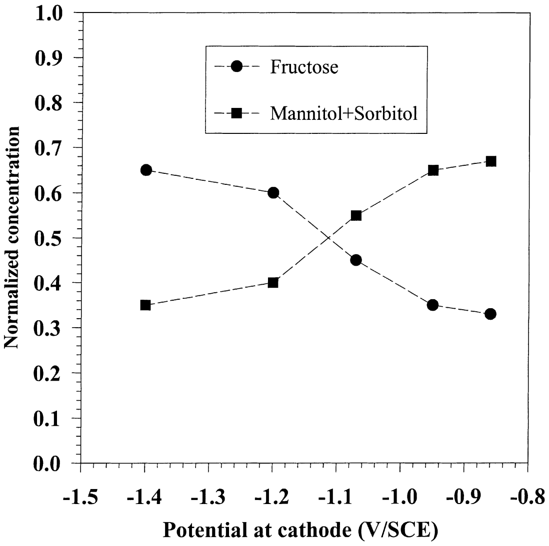

Fig. 6. Effect of potential imposed at the cathode (WE) on the concentrations of fructose and products in catholyte.

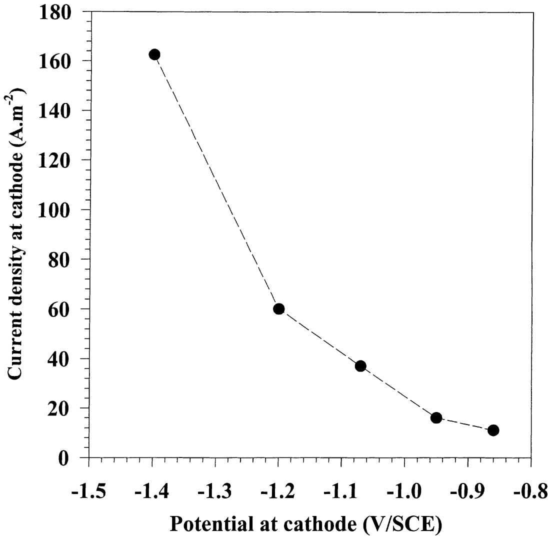

Fig. 7. Effect of potential imposed at the cathode (WE) on the current density at the cathode.

the effect of potential imposed on the current density at the cathode. It can be concluded that the electrocatalytic reduction of fructose to sorbitol and mannitol can be carried out successfully if a fairly low current density is used at the cathode.

4. Conclusion

The oxidation and reduction of fructose were successfully combined in a paired synthesis using an electrocatalytic membrane reactor with graphite anode and cathode. The selectivities obtained are in favor of the mannitol which is commercially less interesting. A possible solution to improve the selectivity to sorbitol is, as mentioned in the literature, to add sodium sulphate as support electrolyte to the fructose solution [5]. A careful choice of operating conditions and cell design are necessary.

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