

# The paired electrochemical synthesis of sorbitol and gluconic acid in undivided flow cells. I.

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The strategy of paired electrochemical synthesis for the production of organic chemicals, in which the reactions at both the anode and cathode simultaneously contribute to the formation of the final product(s), could result in as much as a 50% reduction in energy consumption as compared to conventional electro-organic syntheses. In order to evaluate this hypothesis the electrochemical oxidation of glucose to gluconic acid and the reduction of glucose to sorbitol were paired in undivided flow-through parallel plate and packed bed cells.

To date, the optimum electrode materials and operating conditions for the paired synthesis are: an amalgamated zinc cathode, a graphite anode, an initial glucose concentration of  $0.8 \text{ mol dm}^{-3}$ , a  $0.8 \text{ mol dm}^{-3}$  NaBr supporting electrolyte, an electrolyte flow rate of  $0.81 \text{ min}^{-1}$  and an electrolyte pH of 7. Under these conditions the current efficiencies for sorbitol and gluconic acid were 26% and 68%, respectively at  $0.25 \text{ F mole}^{-1}$ . Current losses are believed to be due to hydrogen evolution and the reduction of  $\delta$ -gluconolactone (an intermediate in the formation of gluconic acid) to glucose.

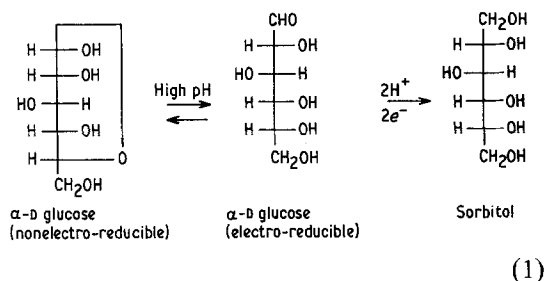
## 1. Introduction

It would appear to be intuitively persuasive that conducting paired reactions in one undivided flow cell, in which reactions at both electrodes contribute to the formation of useful final product(s), should be more energy efficient than using two separate cells to prepare the cathodic product (with accompanying 'sacrificial' anodic reaction) and the anodic product (with accompanying 'sacrificial' cathodic reaction). On the other hand, two synthesis reactions carried out in the same cell without a membrane to separate anolyte from catholyte can lead to an increase in by-product formation and lower current efficiencies and yields because the product from one electrode can be altered or destroyed at the other electrode; if the anodic reaction is an indirect one, the mediator can also have access to the cathode resulting in a loss of current efficiency. A careful choice of experimental conditions and cell design can often minimize these problems.

In order to study the feasibility of performing paired electro-organic reactions in undivided flow

cells, the electro-oxidation of glucose to gluconic acid and the electro-reduction of glucose to sorbitol have been combined into a paired synthesis. Each of these processes has been separately carried out on an industrial scale and much is known about the individual reactions.

The reduction of glucose to sorbitol (Equation 1),



has been the subject of extensive investigation and was commercially produced by the Atlas Powder Co. from 1937 to 1948 [1], when it was replaced by a catalytic hydrogenation route. A comprehensive review of both polarographic data and synthesis studies has been published [2].

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More recent reviews have been published by Kassim [3] and by Chum and Osteryoung [4]. Polarographic studies [5] indicate a small reduction wave ( $-1.6$  V vs NCE) that was not diffusion controlled but dependent on the rate of transformation of the irreducible cyclic hemiacetal form of glucose to the open chain aldehyde form (cf. Equation 1). The height of the wave increased when catholyte pH increased from 6.5 to 8.1 and also when the temperature was increased. Los *et al.* [6, 7] determined the rate and equilibrium constants for the mutarotation of glucose from these kinetic studies.

The conditions for the electrolytic production of sorbitol were initially proposed by Creighton [8]. He used a divided cell with an amalgamated lead cathode, a lead anode and an aqueous catholyte of glucose ( $1.8 \text{ mol dm}^{-3}$ ) and sodium sulphate ( $0.5 \text{ mol dm}^{-3}$ ). The hydroxyl concentration of  $0.5 \text{ mol dm}^{-3}$  was maintained constant during an electrolysis by addition of sulphuric acid. At current densities of  $10 \text{ mA cm}^{-2}$ , current efficiencies of about 55% could be obtained; the remainder of the current being consumed by hydrogen evolution. Under these conditions sorbitol (70% yield) and mannitol (20% yield) were produced. Mannitol is formed by the reduction of mannose, an isomer of glucose. Analysis of commercial samples from the Atlas Powder Co. by Wolfrom *et al.* [9] indicated the presence of a number of by-products: 2-deoxysorbitol from low alkalinity electrolyses (pH 7–10) and 2-deoxysorbitol, 1-deoxymannitol, an allitol, DL-glucitol and a dodecitol from more alkaline catholytes (pH 10–13).

Glucose isomerizes under alkaline conditions to fructose and mannose. Most of the by-products are formed by this route. Many electrode materials for the reduction of glucose have been tested [10, 11] and only high hydrogen overvoltage metals (Pb, Th, Cd, Zn) and their amalgams appear applicable. However, Balenkaya and Belozersky [11] reported that the best cathode for the reduction was an Al–Ni alloy.

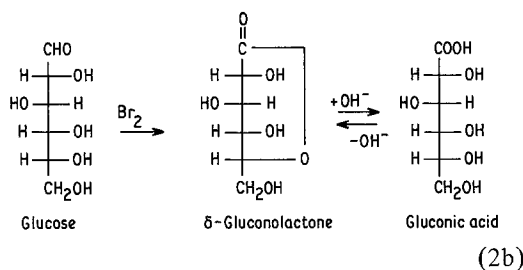
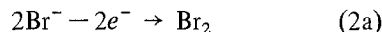
In addition to alkaline solutions, the reduction could also take place in acid catholytes (pH 1.5–7) using sodium sulphate, sulphuric acid and a zinc amalgam cathode as reported by Hales [12].

All of the previous work on glucose reduction was essentially carried out in stirred tank reactors.

Recently, Kuhn *et al.* [13, 14] have examined the use of parallel plate flow cells. Using a lead cathode, they obtained better results (current efficiencies of 25–30%) at pH values of 3 and 11 then at 7. They concluded that the mutarotation of glucose is catalysed by acid and base and is at a minimum in neutral solution.

It can be concluded from these studies that the reduction of glucose to sorbitol can be carried out successfully if a high hydrogen overvoltage cathode is used at a fairly low current density ( $1\text{--}2 \text{ mA cm}^{-2}$ ). To obtain optimum yields of sorbitol, moderate temperatures ( $20\text{--}30^\circ \text{C}$ ), to minimize degradative chemical reactions, and catholytes of low alkalinity (pH 8–10) should be used.

The earliest studies of glucose oxidation to gluconic acid were carried out by Isbell *et al.* [15, 16]. Bromide ions were first electrochemically oxidized to hypobromite. Then, the hypobromite chemically oxidized glucose to gluconic acid via a  $\delta$ -gluconolactone intermediate, as shown in Equations 2a and b.



Fink and Summers [17] tested many factors in order to find the optimum conditions for the semi-industrial production of calcium gluconate in an undivided cell. They electrolysed aqueous solutions of glucose ( $0.8 \text{ mol dm}^{-3}$ ) and sodium bromide ( $0.17 \text{ mol dm}^{-3}$ ) until all the glucose was consumed. Calcium carbonate was added to maintain neutral pH and to give calcium gluconate as the product. After removing the precipitated calcium gluconate and recharging with glucose, the solution could be recycled to the cell repeatedly for several months. The yields and current efficiencies were reported to be quantitative under these conditions. Fioshin and Avrutskaya [18] found that even small amounts of anions such as sulphate or chloride should be avoided as they

produce an anodic shift in the oxidation potential of bromine and increase formation of bromate. (Bromate does not take part in the oxidation reaction and its presence lowers the current efficiency of the process.)

## 2. Experimental details

Exploratory electrolyses on each half of the glucose oxidation-reduction 'pair' were carried out in a standard glass H-cell divided by a medium porosity glass frit. Electrode potentials were monitored with a commercially available saturated calomel electrode and mixing was provided by magnetic stirring bars.

The paired synthesis was investigated using parallel plate and packed bed flow cells. The parallel plate cell, shown in Fig. 1, was undivided and designed with a long entry region to ensure that the flow was reasonably well developed before the electrolytic solution reached the electrodes. The flat plate electrodes were each 50 cm<sup>2</sup> in area and were separated by a 3.0 mm gap. Fig. 2 shows one packed bed flow cell in which the current flow is perpendicular to the solution flow. Each packed bed was 9.0 cm long, 3.0 cm wide and 1.5 cm thick. The two beds were electrically insulated from one another using a nylon mesh screen which was covered on each side by filter paper. Located at the entrance and exit were 5 mm glass beads which ensured a uniform upward flow of electrolyte through the packed beds. Reference electrode probes were inserted through the body of the cell and into the cathode compartment at the front face of the bed and 1.3 cm into the bed. A second type of packed bed cell, shown in Fig. 3, had parallel current and solution flow. The anode was located above the cathode and the solution flow was in the upward direction. The packed bed electrodes were cylindrical in shape with a 5.7 cm diameter and a thickness of 1.2 cm. The anode and cathode were separated from one another and from the glass beads (which were present to ensure a uniform flow distribution) by perforated polypropylene discs sandwiched between two sheets of nylon mesh screen. Reference electrode probes were inserted through the body of the cell at the front face of the anode and cathode.

Each flow cell was operated in a batch recycle mode by inserting it into a circulation loop

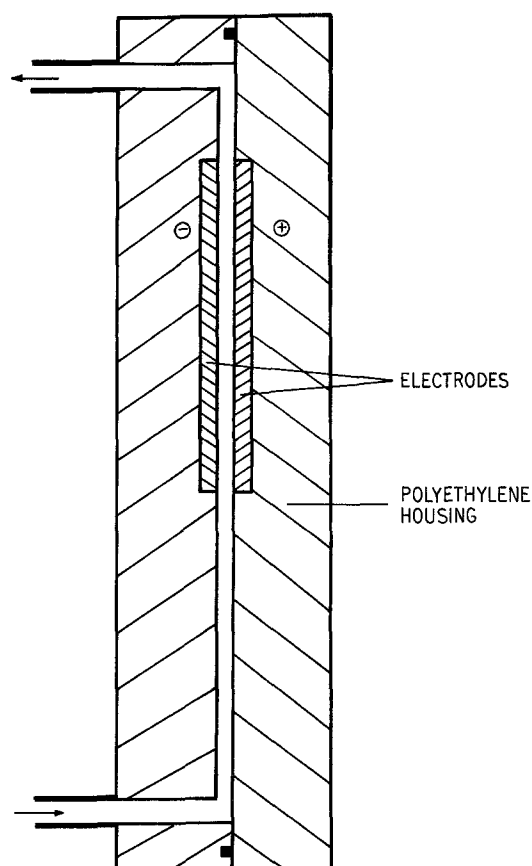


Fig. 1. The parallel plate flow cell.

(Fig. 4) which normally contained a magnetically coupled pump, hydrocyclone gas disengager, throttle valve and a port for sample removal. Power was supplied by either a Wenking ST72 or Bioanalytical Systems SP-2 potentiostat or a DCR 80-60B Sorenson Power Supply. Currents were measured with a Simpson ultra high sensitivity microammeter; potentials were measured with a Keithley 610B Electrometer and a Keithley 168 digital multimeter; and the total charge passed during an electrolysis was measured using a model 541 Koslow Scientific Co. coulometer.

All chemicals were of analytical reagent grade and the water was doubly distilled. Cathodes were made from chemical grade lead, zinc and cadmium and the anodes were high density graphite (Poco Graphite Inc., TRA-1). The packed bed flow cells used a reagent grade 0.5 cm zinc shot cathode with a void fraction and specific surface area estimated to be 45% and 6.6 cm<sup>2</sup> cm<sup>-3</sup>, respectively. The packed bed anode was composed of cylindrically

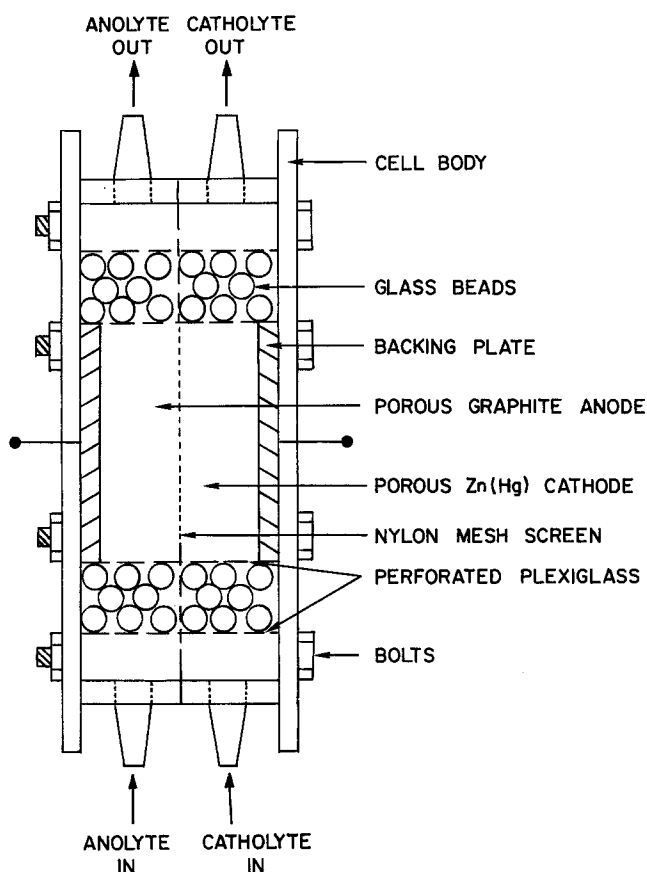


Fig. 2. The packed bed flow cell with perpendicular current and flow.

shaped graphite chips (0.3 cm diameter and 0.3 cm length) with a bed void fraction estimated to be 49% and a surface area/volume ratio of  $8.5 \text{ cm}^2 \text{ cm}^{-3}$ . Cathode amalgamation was achieved by first cleaning the metals with dilute nitric acid, rinsing thoroughly with distilled water, then immersing the electrodes in an aqueous mercurous nitrate solution. After washing with distilled water, metallic mercury was put on the electrode; any excess mercury was wiped off after five minutes.

Current efficiencies and product yields were obtained by analysing for glucose and its products by high performance liquid chromatography (HPLC). For glucose and its reduction products, a cation exchange resin column in its calcium ion form (Bio-Rad Laboratories HPX-87C) was used. The column was thermostatted at  $80^\circ \text{C}$  and the solvent was water. Eluent concentrations were determined using a refractive index detector with sucrose as an internal standard. On this column gluconic acid (sodium gluconate) was eluted as a broad ill-defined peak; consequently a second

cation exchange resin column (hydrogen ion from Bio-Rad Laboratories HPX-87H) with a UV detector (wavelength 216 nm) was used at room temperature to analyse the oxidation products. The solvent for this column was  $0.02 \text{ mol dm}^{-3}$  sulphuric acid. Samples for analysis were obtained by removing a 0.5 ml sample from the flow cell circulation loop and adding to it 0.5 ml of a standard solution of  $0.2 \text{ mol dm}^{-3}$  sucrose. Confirmation of the products was achieved by comparing retention times with those of authentic samples available commercially.

### 3. Results and discussion

#### 3.1. Divided cell experiments

In the development of any paired synthesis it is essential that preliminary experiments be performed in a divided half cell to determine if the product from one electrode will react less rapidly than the starting material at the opposite electrode. If satisfactory results are obtained from

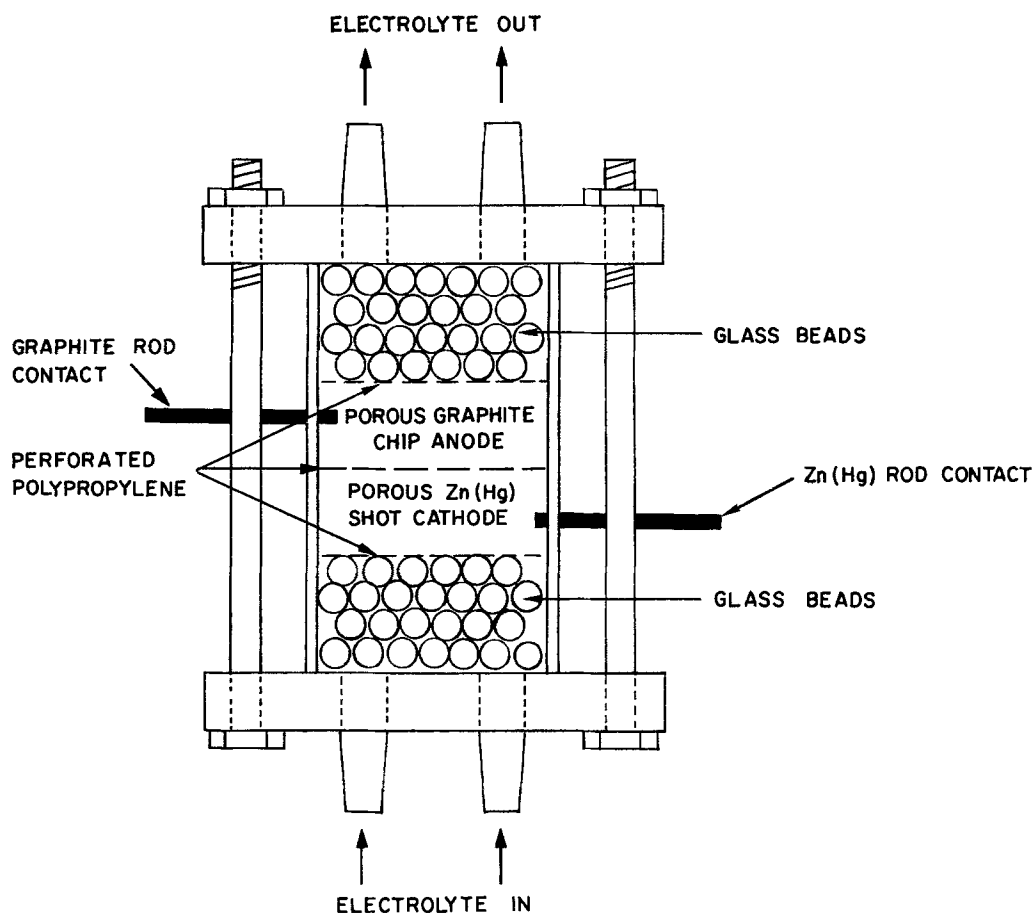


Fig. 3. The packed bed flow cell with parallel current and flow.

these experiments, the investigation can be directed toward finding suitable flow cell configurations and operating conditions which minimize power consumption and maximize current efficiencies and yields. With regard to the paired synthesis of sorbitol and gluconic acid, an aqueous solution of  $0.4 \text{ mol dm}^{-3}$  glucose and  $0.4 \text{ mol dm}^{-3}$  sorbitol containing calcium bromide ( $0.4 \text{ mol dm}^{-3}$ ) as supporting electrolyte was electrolysed in a divided H-cell using a graphite anode. After the passage of sufficient charge to generate enough hypobromite to oxidize theoretically all of the glucose ( $2 \text{ F mole}^{-1}$  of glucose), 86% of the glucose had been consumed and less than 10% of the sorbitol had been oxidized. Thus, the product of glucose reduction is much less easily oxidized than glucose itself. Therefore, in a continuous system in which only partial conversion would occur, it was certain that only glucose would be oxidized. Similarly, a mixture of glucose ( $0.8 \text{ mol dm}^{-3}$ ),

sodium gluconate ( $0.17 \text{ mol dm}^{-3}$ ) and NaBr ( $0.8 \text{ mol dm}^{-3}$ ) was reduced in a divided H-cell with an amalgamated lead cathode. Analysis of the solution after the electrolysis showed that sorbitol was formed and the sodium gluconate remained unreacted.

Based on the work of previous investigators [17, 18] the indirect oxidation of a  $0.8 \text{ mol dm}^{-3}$  glucose solution was carried out in a divided H-cell using a graphite anode and NaBr as supporting electrolyte and source of  $\text{Br}^-$ . A constant potential electrolysis resulted in nearly quantitative current efficiencies and yields; hence the focus of the divided cell experiments was on the glucose reduction reaction. In particular, H-cell experiments were performed to:

1. determine the optimum cathode potential for the glucose reduction reaction
2. determine the effect of supporting electrolyte on the reduction reaction

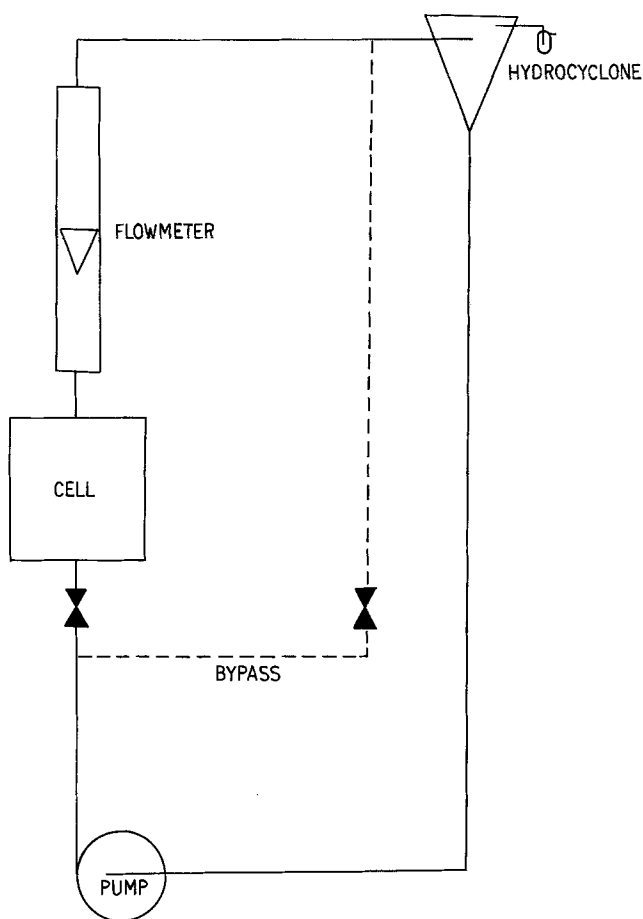


Fig. 4. The batch recycle reaction loop.

3. examine the effect of cathode material on the reduction reaction

4. identify side reactions at the cathode which would consume current and/or starting material and products.

Typical cathodic polarization curves for glucose, obtained at an amalgamated lead cathode, using either  $0.7 \text{ mol dm}^{-3}$  sodium sulphate or  $0.5 \text{ mol dm}^{-3}$  tetraethylammonium bromide as supporting electrolyte are shown in Fig. 5. The optimum electrode potential for glucose reduction with sodium sulphate was found to be *ca.*  $-2.0 \text{ V}$  vs SCE. At this potential the current efficiency for sorbitol production is approximately 70%. It was hoped that the use of a quaternary ammonium salt as supporting electrolyte would cause the onset of hydrogen evolution to shift to a more cathodic potential, thus decreasing the rate of hydrogen evolution and increasing the sorbitol current efficiencies. The results in Fig. 5, however, show that

tetraethylammonium bromide suppressed both hydrogen evolution and glucose reduction; the net effect was a decrease in sorbitol current efficiency (34% at  $-2.1 \text{ V}$  vs SCE). It has been proposed that a hydrophobic region near the cathodic surface, composed of quaternary ammonium cations, is responsible for lowering the rate of hydrogen evolution [19]. Glucose has only a very limited solubility in organic solvents, even alcohol. Thus, if an organic layer were present near the electrode, it would exclude both glucose and water and lower the partial currents for each reaction.

Since bromide ions must be present in the paired synthesis for oxidation to occur (cf. Equations 2a, b), sodium bromide was also tested as a supporting electrolyte. The experimental background (hydrogen evolution) and glucose reduction polarization curves with NaBr were identical to those with sodium sulphate and the optimum cathode potential with NaBr was between  $-2.0 \text{ V}$  and  $-2.1 \text{ V}$  vs SCE.

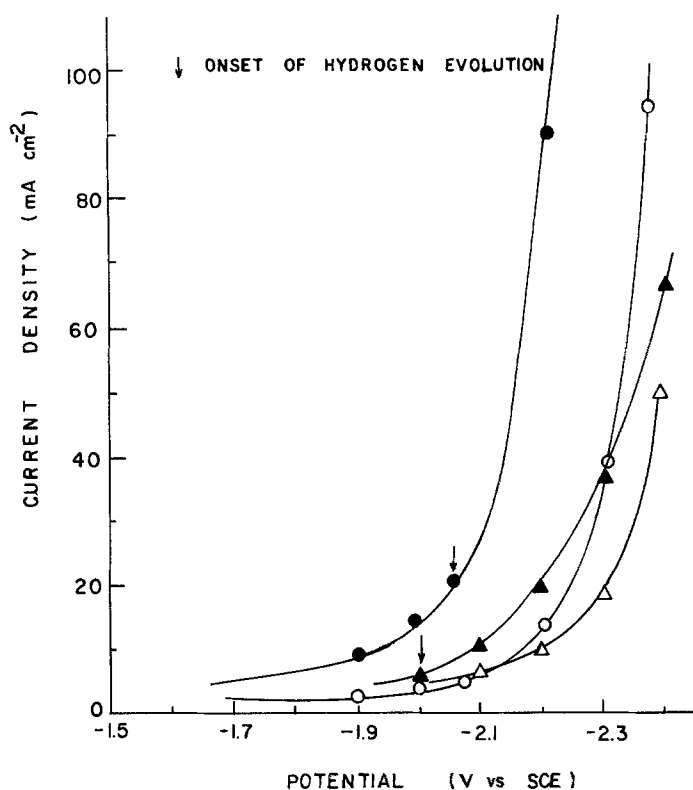


Fig. 5. Effects of sodium sulphate and tetraalkylammonium bromide supporting electrolytes on the cathodic polarization of glucose. [ $\Delta$  tetraethylammonium bromide;  $\circ$  sodium sulphate; open – without glucose; closed – with glucose ( $0.8 \text{ mol dm}^{-3}$ ).]

A number of cathode materials other than amalgamated lead were examined for the reduction of glucose. These were all high hydrogen overvoltage cathodes (amalgamated zinc and cadmium). Mercury was also included for comparison purposes. The results of these half cell experiments are listed in Table 1. The applied potentials were those at which hydrogen was initially observed to evolve from the cathode. The highest current efficiency for sorbitol formation was obtained using a mercury cathode, although for a proper comparison the electrolysis should have been continued for a longer time. Since it is not envisaged that a mercury cathode would be used

in a glucose oxidation–reduction flow cell, it is concluded that among those tested amalgamated zinc is the best cathode.

The sorbitol current efficiency from the constant potential electrolysis with an amalgamated lead cathode, listed in Table 1, is much lower than that predicted by the  $i$ – $V$  polarization curve in Fig. 5. This phenomenon was seen in all constant potential and constant current electrolyses. Excessive hydrogen evolution was not observed during the electrolyses and cannot explain this difference. It was thought that the decrease in glucose concentration during a batch electrolysis was responsible for the low sorbitol current effi-

Table 1. Constant potential electrolyses of glucose at different cathodes in the divided cell, pH 11

Cathode	Potential (V vs SCE)	Supporting electrolyte	Charge passed ( $F \text{ mole}^{-1} \text{ glucose}$ )	Glucose concentration ( $\text{mol dm}^{-3}$ )	Sorbitol current efficiency (%)
Pb/Hg	–2.10	NaBr	0.42	0.8	27
Zn/Hg	–1.95	NaBr	0.37	1.6	35
Hg	–2.2	$\text{Et}_4\text{NBr}$	0.25	0.8	46
Cd/Hg	–2.0	NaBr	0.58	0.8	14

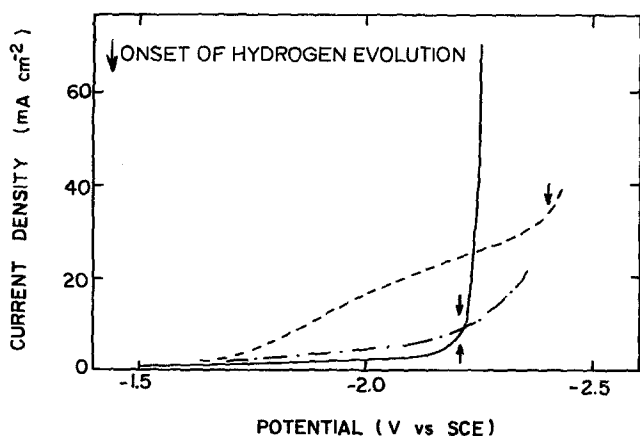


Fig. 6. Polarization curves of glucose electrolysis products and by-products. (— background,  $0.1 \text{ mol dm}^{-3}$  sorbitol,  $0.1 \text{ mol dm}^{-3}$  mannitol; - - -  $0.8 \text{ mol dm}^{-3}$  glucose; - · - ·  $0.1 \text{ mol dm}^{-3}$  fructose.)

ciencies. However, results similar to those in Table 1 were obtained from an undivided flow cell experiment when the glucose concentration was maintained constant. The effects of glucose reduction products and by-products on the glucose reduction reaction were also investigated. The products and by-products examined were fructose (formed by the base catalysed isomerization of glucose), sorbitol and mannitol. As shown in Fig. 6, both mannitol and sorbitol are nonelectro-reducible and should not be consuming electrons. Fructose, however, is much easier to reduce than glucose. In the literature [9] it is reported that fructose is reduced to sorbitol and mannitol. When fructose was reduced by itself in a divided H-cell it was consumed at about  $4 \text{ F mole}^{-1}$  whereas the formation of mannitol and sorbitol requires only  $2 \text{ F mole}^{-1}$  of fructose. Only 40% of the fructose consumed can be accounted for by the sorbitol and mannitol produced. The HPLC analysis failed to detect any other reduction products. When an aqueous mixture of glucose and fructose was reduced at a constant potential, sorbitol and smaller amounts of mannitol and 2-deoxysorbitol were produced. Although the specific details of the fructose reduction reaction are still unknown it can be concluded that the presence of even small amounts of fructose will lower the sorbitol current efficiency. To minimize current and glucose losses, therefore, the electrolyte should be maintained at a low pH (ca. 7).

The effects of sorbitol, mannitol and, for completeness, sodium gluconate on the reduction of glucose were also studied by performing constant potential electrolyses of solutions containing glu-

cose and one of the product compounds. It has already been established from polarization and constant potential electrolyses that the product compounds are nonelectro-reducible. The results of these new experiments, given in Table 2, show that mannitol and sorbitol did have an inhibitory effect on glucose reduction, for reasons not well understood at this time. These results indicate that the build up of sorbitol and mannitol in the electrolyte should be avoided.

### 3.2. The glucose paired synthesis in the parallel plate flow cell

The paired oxidation and reduction of glucose was studied extensively in the undivided parallel plate flow cell shown in Fig. 1. All electrolyses were run in a batch recycle mode at a constant current. A low flow rate to ensure laminar flow between the

Table 2. Influence of products on the reduction of glucose after passage of  $0.4 \text{ F mole}^{-1}$  (supporting electrolyte  $0.8 \text{ mol dm}^{-3} \text{ NaBr}$ , Zn/Hg cathode at  $-2.2 \text{ V vs SCE}$ ,  $\text{pH} = 11$ )

Electrolyte composition	Sorbitol current efficiency (%)
$0.8 \text{ mol dm}^{-3}$ glucose	54
$0.8 \text{ mol dm}^{-3}$ glucose + $0.1 \text{ mol dm}^{-3}$ sorbitol	42
$0.8 \text{ mol dm}^{-3}$ glucose + $0.1 \text{ mol dm}^{-3}$ mannitol	45
$0.8 \text{ mol dm}^{-3}$ glucose + $0.17 \text{ mol dm}^{-3}$ sodium gluconate	51



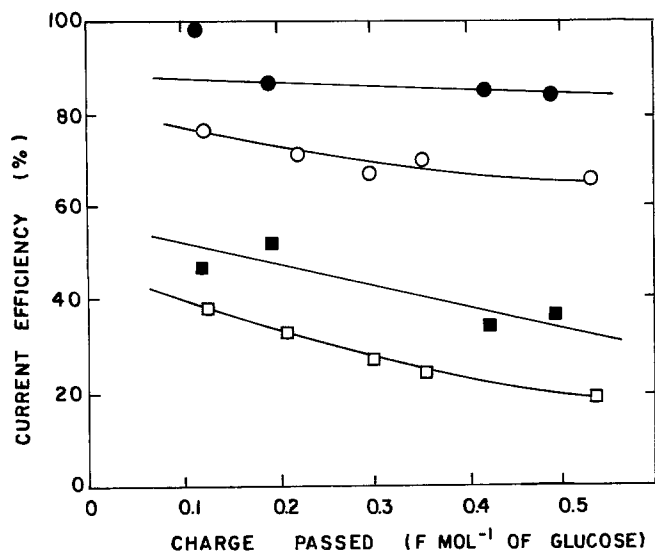


Fig. 7. Comparison of the performance of the paired synthesis using lead and zinc amalgam cathodes. (○ gluconic acid; □ sorbitol; closed – Zn(Hg) cathode, Open – Pb(Hg) cathode.)

electrodes precludes transport of bromine to the cathode where it would be reduced and cause a decrease in current efficiency. During an electrolysis the solution tended to become acidic due to the formation of gluconic acid and therefore sodium carbonate was periodically added to maintain the solution pH at 11. A high solution pH was used in the initial flow cell experiments to minimize hydrogen evolution and maximize the concentration of the electro-active aldehyde form of glucose (cf. Equation 1). Amalgamated lead and amalgamated zinc were used as cathode materials, graphite as the anode and NaBr as supporting electrolyte.

Fig. 7, a plot of gluconic acid and sorbitol current efficiencies as a function of the charge passed during an electrolysis, shows that there is an overall improvement in the cell performance with an amalgamated zinc cathode as compared to amalgamated lead, thus corroborating the divided cell experimental results in Table 1. It is typical of electrolyses in the flow cells that the oxidation takes place at a fairly high current efficiency (*ca.* 80%) while the current efficiency of the reduction is fairly low (10–35%) and is generally more sensitive to electrolysis conditions. The main current loss processes at the cathode are believed to be hydrogen evolution and fructose reduction. Another phenomenon, generally observed during an electrolysis and shown in Fig. 7, is the decrease in current efficiency that occurs in the course of

an experiment, especially for the production of sorbitol. The decrease in sorbitol current efficiency did not appear to be due to degradation of the cathode surface because the shiny amalgamated surfaces of both the lead and zinc electrodes were maintained after an electrolysis. It was not due to glucose depletion either since similar results were obtained when the glucose concentration was maintained constant. This decrease in current efficiency is tentatively ascribed to the build up of sorbitol in the circulation loop and its inhibitory effect on the glucose reduction reaction. Experiments to confirm this hypothesis are to be performed.

The performance of the oxidation and reduction reactions from a number of electrolyses carried out with an amalgamated zinc cathode is shown in Table 3. It would appear that the optimum operating conditions are a current density of  $10 \text{ mA cm}^{-2}$ , an initial glucose concentration of  $0.8 \text{ mol dm}^{-3}$  and a flow rate of  $0.8 \text{ l min}^{-1}$ . For all experimental conditions examined, the gluconic acid current efficiencies and product yields are high and those for sorbitol are low. Since glucose is the substrate for both oxidation and reduction it should theoretically be consumed at a rate of  $1 \text{ F mole}^{-1}$ , although individual reactions require  $2 \text{ F mole}^{-1}$ . Hence the maximum sorbitol or gluconic acid yield is 50%. The results of mass balance calculations on the paired synthesis are also listed in Table 3. The concentration of

Table 3. Performance of the glucose paired reaction in the parallel plate\* flow cell after passage of  $0.4 F \text{ mole}^{-1}$  of glucose

Current density ( $\text{mA cm}^{-2}$ )	Initial glucose concentration ( $\text{mol dm}^{-3}$ )	Flow rate ( $\text{l min}^{-1}$ )	Sorbitol current efficiency (%)	Sorbitol yield (%)	Gluconic acid current efficiency (%)	Acid yield (%)	Total yield (%)	Mass <sup>†</sup> balance (%)
20	0.8	0.8	32	15	76	37	52	84
10	0.8	0.8	39	23	84	50	73	98
5	0.8	0.8	33	14	80	35	49	85
10	1.6	0.8	18	8	78	37	45	84
10	0.8	1.6	36	16	88	40	56	92

\*Amalgamated zinc cathode and graphite anode.

<sup>†</sup>Total concentration of products and unreacted glucose compared to initial concentration of glucose.

unreacted glucose and oxidation and reduction products and by-products determined by HPLC analysis are compared to the initial glucose concentration. In the 10 and 20  $\text{mA cm}^{-2}$  experiments the only by-products indicated by HPLC were fructose and 2-deoxysorbitol. Significant amounts of mannitol were formed only at 5  $\text{mA cm}^{-2}$ . The errors in the mass balance calculations were estimated to be no more than  $\pm 10\%$ . Hence, it appears that, in some experiments, there are one or more unknown by-products which were not detected by HPLC analysis (as the case in the divided cell constant potential electrolysis of fructose).

### 3.3. The glucose paired synthesis in the packed bed flow cells

High surface area electrodes permit the passage of more current per unit time through a given volume of solution than planar electrodes. Thus, reduction in the size of electrochemical cells may be achieved with the use of high surface area (e.g. packed bed) electrodes. Their use is most attractive when the process operates at low current densities, as is the case for the glucose paired synthesis. The paired oxidation and reduction of glucose were examined in the two packed bed flow cells shown in Figs. 2 and 3. All electrolyses were run at a constant cathode potential; the potential difference between the front face of the cathode bed (closest to the anode) and a remote saturated calomel reference electrode was fixed between  $-2.0 \text{ V}$  and  $-2.1 \text{ V}$ . The initial packed bed flow cell experiments were carried out under conditions

similar to those used in the parallel plate cell, i.e.  $0.8 \text{ mol dm}^{-3}$  initial glucose concentration,  $0.8 \text{ mol dm}^{-3}$  NaBr supporting electrolyte, an electrolyte flow rate of  $0.8 \text{ l min}^{-1}$ , pH 10–11, a zinc amalgam cathode and a graphite anode.

A comparison of gluconic acid and sorbitol current efficiencies for the two packed bed flow cell configurations is shown in Fig. 8. The sorbitol current efficiencies in the two packed bed cells are the same as those obtained with the parallel plate flow cell. The gluconic acid current efficiencies in the parallel packed bed cell are comparable to the parallel plate results but are approximately 15%

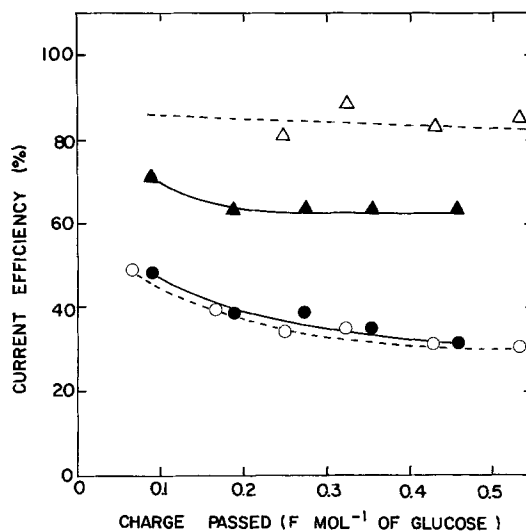


Fig. 8. Comparison of performance of the two packed bed flow cells ( $0.8 \text{ mol dm}^{-3}$  glucose,  $0.8 \text{ mol dm}^{-3}$  NaBr, pH 10, Zn(Hg) cathode and graphite anode). Perpendicular current flow configuration:  $\blacktriangle$  gluconic acid,  $\bullet$  sorbitol; Parallel current-flow configuration:  $\triangle$  gluconic acid,  $\circ$  sorbitol.

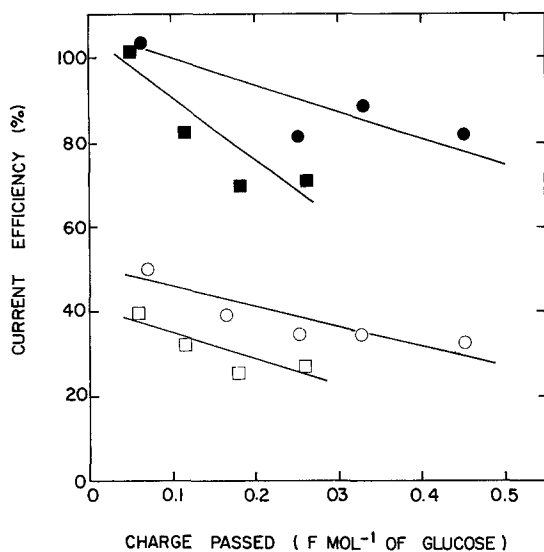


Fig. 9. Effect of pH on the glucose paired reactions ( $0.8 \text{ mol dm}^{-3}$  glucose,  $0.8 \text{ mol dm}^{-3}$  NaBr, parallel configuration packed bed cell, Zn(Hg) cathode, graphite anode). pH 10.5:  $\circ$  sorbitol,  $\bullet$  gluconic acid; pH 7.0:  $\square$  sorbitol,  $\blacksquare$  gluconic acid.

higher than those obtained with the perpendicular packed bed cell. The cause(s) of the poorer performance by the perpendicular packed bed cell is (are) not known at present. The lower gluconic acid current efficiencies obtained for the perpendicular cell compared to the parallel packed bed cell may be due to the diffusion of electro-generated bromine to the cathode and subsequent reduction. It can be concluded from the data that the parallel packed bed flow cell is the optimum configuration.

As in the parallel plate flow cell, the sorbitol yields in both packed bed flow cells were low (*ca.* 20% at  $0.4 \text{ F mole}^{-1}$ ), the gluconic acid yields were higher (*ca.* 30% at  $0.4 \text{ F mole}^{-1}$ ) and mass balance calculations of products, by-products (fructose and 2-deoxysorbitol) and unreacted starting material could account for only 80–85% of the glucose feed. In an effort to improve the product yields, a constant potential electrolysis in the parallel packed bed cell was carried out at pH 7. At this pH value very little fructose should form. The results of the low pH electrolysis are compared with a 'standard' pH 10–11 experiment (with the same packed bed cell) in Fig. 9. Both acid and sorbitol current efficiencies are less at the lower pH but the product yields at pH 7 (34%

sorbitol and 47% gluconic acid at  $0.4 \text{ F mole}^{-1}$ ) are larger than those at pH 10.5 (20% sorbitol and 30% gluconic acid at  $0.4 \text{ F mole}^{-1}$ ). No fructose or 2-deoxysorbitol was obtained in the HPLC analysis and 100% of the glucose feed could be accounted for by a mass balance of starting material and products.

The low current efficiencies are ascribed to hydrogen evolution and the preferential reduction of  $\delta$ -gluconolactone, an intermediate species in the electro-oxidation of glucose (cf. Equation 2b). This intermediate leaves the anode, circulates through the external loop of the experimental apparatus and reenters the cathode compartment. Fedoronko [2] has reported that lactones can be reduced to the corresponding aldoses at a mercury cathode. It has also been shown that the hydrolysis of  $\delta$ -gluconolactone to gluconic acid is acid–base catalysed [20]. In the electrolyses at pH 10.5 the rate of hydrolysis of the lactone is fast compared to the residence time of electrolyte in the circulation loop between the anode and cathode (*ca.* 10 s) and precludes lactone reduction. However, there are current losses due to fructose reduction. At pH 7, the hydrolysis is slow and both the sorbitol and gluconic acid current efficiencies decrease. Methods for converting the lactone to gluconic acid without raising the pH and forming fructose are currently under investigation.

Current losses due to hydrogen evolution may be reduced by using a different supporting electrolyte. With tetraethylammonium bromide as a supporting electrolyte in the divided H-cell, both the evolution of hydrogen and the reduction of glucose were suppressed. A more hydrophilic quaternary ammonium salt, such as an alkyl triethanolammonium bromide, may adequately suppress the evolution of hydrogen without affecting the rate of glucose reduction.

#### 4. Conclusions

The oxidation and reduction reactions of glucose were successfully combined into a paired synthesis using a parallel plate flow cell and two types of porous, packed bed flow cells. To date, the optimum electrode materials and operating conditions for the glucose paired reactions, as determined by product yields and current efficiencies, are an amalgamated zinc cathode, a graphite anode, an

initial glucose concentration of  $0.8 \text{ mol dm}^{-3}$ , a  $0.8 \text{ mol dm}^{-3}$  NaBr supporting electrolyte, an electrolyte flow rate of  $0.8 \text{ l min}^{-1}$ , and an electrolyte pH of 7. The optimum packed bed flow cell configuration has parallel current and solution flow. Under the above conditions the current efficiencies for sorbitol and gluconic acid were found to be low (26% and 68%, respectively at  $0.25 \text{ F mole}^{-1}$ ) but the product yields were high (34% sorbitol and 47% gluconic acid at  $0.4 \text{ F mole}^{-1}$ ; *the maximum theoretical yield for either half of the paired reaction is 50%*). Current losses are ascribed to hydrogen evolution and the reduction of  $\delta$ -gluconolactone to glucose. To minimize hydrogen evolution, a quaternary ammonium salt with some hydrophilic character, such as an alkyl triethanolammonium borate, should be used as supporting electrolyte. To increase the rate of hydrolysis of  $\delta$ -gluconolactone to gluconic acid the electrolyte temperature should be increased and/or pH decreased.

Further work on this paired synthesis is continuing and new results will be presented in a subsequent paper.

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