The use of a porous hydrogen diffusion anode in the electrochemical reduction of glucose to sorbitol

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For the electrochemical reduction of glucose to sorbitol at a lead cathode the effect of varying the secondary electrode is examined. A porous hydrogen diffusion anode was used and the results compared with those using a lead anode. Reaction conditions involved change of pH from 3.5 to 9.5, temperature from 30 to 45° C and concentration of glucose from 0.5 to 2.5 M. Using the gas diffusion anode, efficient operation was possible without a diaphragm and the cell voltage decreased by about 50% with no change to the efficiency of the cathodic reduction compared with the conventional divided cell with lead electrodes. Thus the power usage can be reduced greatly, which may influence competition between electrochemical and pressure hydrogenation routes.

1. Introduction

The electrochemical reduction of glucose to sorbitol was commercially viable prior to 1950 [1] since when it has been more economic to use catalytic hydrogenation. Given improvements in electrochemical technology new approaches to the electrochemical reduction of glucose may now be worthwhile.

The literature concerning the electrochemical reduction of glucose can be conveniently subdivided. Firstly that concerned with cathode materials [2, 3, 4], then that concerned with working conditions [1, 3, 6, 7] such as temperature, pH, current density, electrolyte composition and stirring, and, finally, research concerned with mechanism [5, 8, 9]. In each case variations in cathode and catholyte conditions were involved and little effort was devoted either to anodic conditions or to the relationship between cell voltage and current density.

In this work, the electrolytic cell as a whole has been studied. Cathodic conditions have not been further explored as these have previously been much studied. The work described here concentrates on the anode and in particular the use of a porous hydrogen diffusion anode in place of the traditional lead one.

2. Electrochemical parameters

The cost of electrical energy and capital investment in the cell are major parts of the cost of an electrochemical process. Key relationships between electrochemical parameters and power usage are given by Equations 1 to 4.

$$R = R_m + R_s + R_o \tag{1}$$

$$V = |V_a - V_c| + I(R_m + R_s + R_o)$$
$$= |V_a - V_c| + IR \tag{2}$$

$$I_e = I\mu \text{ or } I = I_e/\mu \tag{3}$$

$$P = VIt = VI_e t/\mu = (I_e t)V/\mu \tag{4}$$

The symbols used are: I, total current of the cell; I_e, effective current for glucose reduction; P, electrical energy consumed (power usage); V, cell voltage; V_a, anode potential; V_c, cathode potential; R, cell resistance; R_m, membrane resistance; R_o, other resistance; R_s, solution resistance; t, time of electrolysis; μ, current efficiency.

Equation 4 indicates that the power usage can be decreased only by decreasing cell voltage V or increasing current efficiency μ. The factor $I_e t$, which is proportional to the production of sorbitol, has probably already been optimised. Much previous work on the electrochemical reduction of glucose or other monosaccharides has been concerned with the current efficiency, but there have been few attempts at decreasing the cell voltage.

From Equation 4 it can be seen that in order to halve the energy consumed either the cell voltage can be halved or the current efficiency doubled. In the absence of further possibilities for increasing the current efficiency it is likely to be more profitable to halve the cell voltage. Furthermore, hydrogen
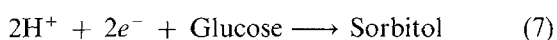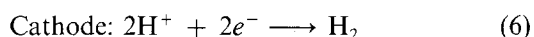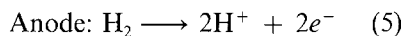
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evolution is a major competing reaction in cathodic reduction of glucose at solid electrodes, but no use is made of the hydrogen. Part of our work is an attempt to decrease cell voltage by using the hydrogen evolved in the anode reaction, i.e. the relatively low potential oxidation to protons.

According to Equation 2, there are four ways of reducing V: (a) decreasing I; (b) increasing V_c (i.e. less cathodic); (c) decreasing V_a, and (d) decreasing $[R_m + R_s + R_o]$. As mentioned above, (a) is counterproductive, and (b) is impractical because the reducing ability of the cathode would decrease.

The solution resistance, R_s, can be decreased by decreasing the electrode separation, but this has hitherto been limited by the need for a diaphragm. Typically this is porous ceramic, as used 40 years ago, or, more recently, an ion-exchange membrane. Removal of the divider not only gives $R_m = 0$, but also allows close separation of the electrodes. In previous cells, the main purpose of the diaphragm was to prevent the anodic oxidation of both glucose and sorbitol [5]. The diaphragm can therefore only be discarded when the anode potential is sufficiently low that oxidation of the glucose and sorbitol is precluded. The porous hydrogen diffusion anode operates at a potential which meets this requirement. In addition, the hydrogen generated at the cathode can be recycled to the anode.

In the proposed new cell, the electrode reactions are those given in Equations 5 to 7.

$$\text{Anode: } H_2 \longrightarrow 2H^+ + 2e^- \quad (5)$$

$$\text{Cathode: } 2H^+ + 2e^- \longrightarrow H_2 \quad (6)$$

$$2H^+ + 2e^- + \text{Glucose} \longrightarrow \text{Sorbitol} \quad (7)$$

3. The porous electrodes

3.1. Principles of gas-diffusion electrode preparation

Polytetrafluorethylene (PTFE)-bonded gas diffusion electrodes have been studied for several years as part of the development of hydrogen-oxygen fuel cells [11, 12]. With their porous, hydrophobic and special conducting characteristics, these electrodes minimize the required quantity of expensive electrocatalysts,

such as platinum, by greatly enhancing the area of the three-phase interface between the gas, catalysts and electrolyte. Despite their well-known use in fuel cells, the gas diffusion electrodes have not been extensively used as the counter electrode in electrochemical reactors.

In this work, the hydrogen diffusion electrodes were made up of three layers: (a) a metal current collector screen; (b) a hydrophobic gas-porous layer; and (c) a catalytic layer. The three layers were first prepared separately, and then pressed together to form the anode, as shown in Fig. 1.

A well designed hydrophobic gas-porous layer should ideally: let hydrogen gas pass through; be sufficiently hydrophobic to prevent corrosion of the metal current collector; and be highly conducting. The layer is first made of acetylene black, PTFE and an inorganic salt or organic material. The inorganic salt is leached out in boiling water or the organic material is extracted using organic solvents. The layer is porous to hydrogen. The PTFE confers hydrophobicity and acetylene carbon blacks confer conductivity. In this application they are better electrical conductors than channel blacks [13].

In addition to being porous to hydrogen, and highly conducting, the catalytic layer should provide as large as possible surface area of catalytic metal. In addition it should permit electrolyte to penetrate, but without clogging the structure and so providing the largest area for reaction at the three-phase interface. The catalytic layer is composed of platinum deposited on channel blacks, with more porous material and less PTFE than for the hydrophobic layers.

The pressure used to compress such layers is critical. Too low a pressure may not give good contact between the three layers which causes high resistance or a separation of the metal current collector from the other layers. Too high a pressure may damage the porous structure of the catalytic layer which decreases the reacting area for the three-phase interface.

3.2. Electrode preparation

3.2.1. Preparation of metal current collectors. The metals used were platinum, silver, and nickel, as wire netting or as gauzes. The netting was handmade from
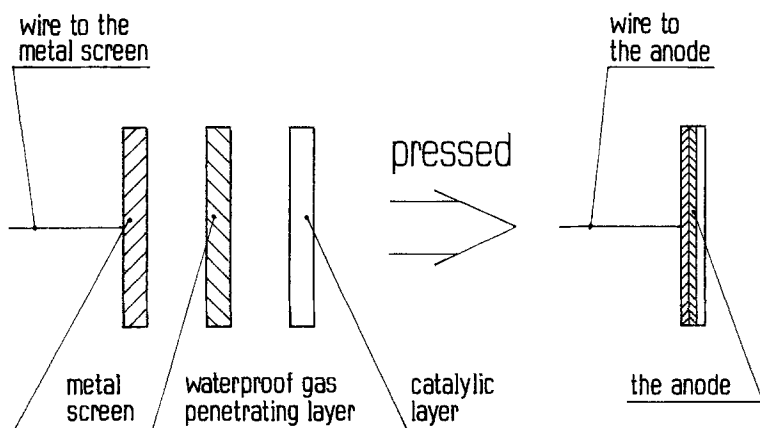

. Fig. 1. The anode subassembly.

0.1 mm wire and woven to give a mesh of hole size *ca.* 1.5 mm × 1.5 mm. The gauzes were 36 mesh (BS, 40 × 40 holes per square inch). The nickel collectors were polished with fine emery paper and then washed with distilled water before being connected to the other layers by compression. The platinum collectors were cleaned with dilute hydrochloric acid for 30 min and then washed with distilled water.

3.2.2. Preparation of the hydrophobic gas-porous layer. Acetylene carbon blacks (5 g), "OP" (a proprietary organic binding material, 2.5 g) and PTFE dispersion (10.25 g, PTFE content 60% by weight, Fluon, GP1, ICI) were mixed with distilled water to form a uniform slurry. The slurry was heated to boiling and the PTFE coagulated to form a carbon dough. This was stretched by rolling to form a thin layer having a thickness less than 1.0 mm. The layer was put into a Soxhlet thimble and the "OP" extracted with acetone (24 h). In an alternative method acetylene carbon blacks (5 g), Vaseline (2.5 g) and PTFE (10.25 g, as before), in dispersion, were mixed with distilled water to form a uniform slurry with distilled water. The slurry was converted into a layer as described above and the Vaseline extracted with chloroform (24 h).

3.2.3. Preparation of the catalytic layer. Charcoal (Aldrich, 10 g) was added to a stirred solution of hydrogen hexachloroplatinate (II) hydrate ($H_2PtCl_6 \cdot xH_2O$ Aldrich, 1 g) and dissolved in distilled water (1 dm^3). A 0.5% solution of $NaBH_4$ (Aldrich, 20 ml) was added dropwise and with stirring. Stirring was continued (24 h) during which platinum precipitated onto the carbon particles. The impregnated carbon was subsequently filtered, washed and dried (100° C).

The impregnated carbon (5 g), "OP" [or Vaseline] (3.2 g), and the usual PTFE dispersion (2.1 g) were mixed as before to form a uniform slurry. After conversion into a layer as described, the organics were removed by the appropriate solvent extraction. The layer so formed contained platinum at about 2 mg cm^{-2}.

Finally the three layers were pressed together for 1 min in a hydraulic press to about 500 kg cm^{-2}. The anode so formed had a thickness of about 1.0 mm.

4. The cell and electrochemical equipment

The cell could be used with either a gas-diffusion anode or with a lead anode; the arrangements are outlined in Fig. 2.

The lead cathode (10 cm^2) was first polished with fine emery paper and then washed with distilled water. Next, the electrode was used as the anode, with another lead electrode as the counter electrode, for electrolysis in a 10% H_2SO_4 solution at a current density of 2 A dm^{-2} for 20 min. The electrode thus prepared was kept in very dilute H_2SO_4 solution before use.

A hydrogen-diffusion anode of 10 cm^2 nominal area was prepared as described; the hydrogen pressure used was about 20 mm H_2O. In control experiments the lead anode was first polished with fine emery paper and then washed with distilled water before use.

A saturated calomel electrode (SCE) was used as reference and catholyte solutions contained glucose at various known concentrations with sodium sulphate at 75 g dm^{-3}. When the lead anode was used an ion-exchange membrane separator was required and the anolyte was aqueous sodium sulphate at 75 g dm^{-3}.

Electrochemical measurements were performed with either a San Ming potentiostat Model HDV-7C or a Hi-Tek Instruments Potentiostat Model DT 2101. Cell voltage and cathode-to-reference potentials were monitored with digital voltmeters. Products were analysed by HPLC; the column used was HPX-87H (BIO-RAD Laboratories Ltd.). The pH of the catholyte was adjusted by addition of aqueous solutions of NaOH or of H_2SO_4.

5. Electrochemical experiments

5.1. *Voltammetric*

These were designed to obtain comprehensive data to ascertain the effect of the systematic variation of temperature, pH, and glucose concentration upon the cell voltage — current density curves. Temperature was varied in 5° C steps between 30 and 45° C; glucose concentrations were 0.5, 1.5, and 2.5 M; and electrolyte pH values were 3.5, 6.5, and 9.5. For a given
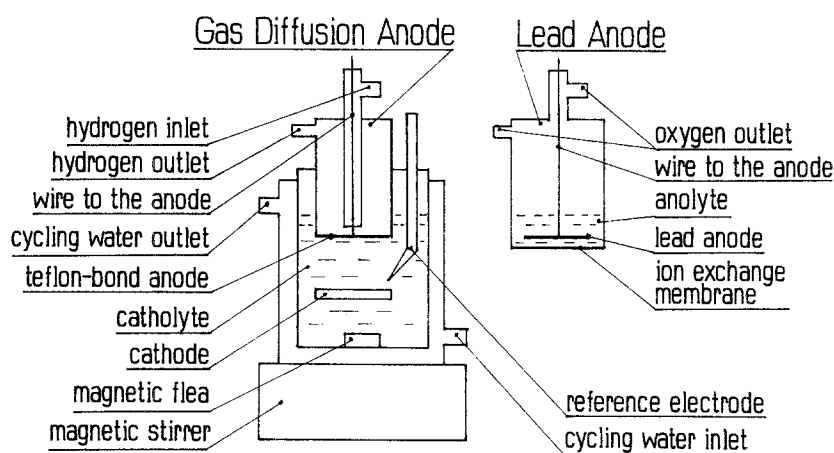

Fig. 2. The cell.

electrolyte/temperature combination amperostatic electrolysis was carried out at 0.5, 1.5, 2.5, 3.5 and 4.5 Adm^{-2}; when steady state conditions were achieved the cell voltage was recorded.

The procedure may be generally described as follows. Catholyte (150 ml) was added to the cell shown in Fig. 2 and the catholyte pH was adjusted to the desired value within ±0.1. Temperature was controlled within ±0.5°C by a thermostatted water jacket. The catholyte was stirred magnetically. The distance between the two electrodes was carefully adjusted to 20 mm and electrolysis was carried out at constant current. The cell voltage and cathode-to-reference potentials were recorded when steady state conditions were achieved.

In another series of experiments, the hydrogen-diffusion anode was replaced by a lead one in a compartment with an ion-exchange membrane. The distance between the two electrodes was carefully adjusted to 20 mm and cell voltage and cathode-to-reference potentials recorded under steady-state conditions.

5.2. Preparative

The cell shown in Fig. 2 was used, with a catholyte of 150 ml. After adjustment of pH, temperature, and electrode separation, constant current electrolysis was carried out (4 h). The pH of the catholyte after the electrolysis was recorded and the catholyte analysed for glucose and sorbitol by HPLC.

6. Results and discussion

6.1. Cell voltage — current density curves

These were determined for combinations of values of temperature, pH, and glucose concentration with either a lead anode or a hydrogen-diffusion anode. The cathode *potential* (V/SCE) was also monitored. Using the values for temperature, pH and glucose concentration given in section 4.1, 36 such plots were constructed and these are exemplified in Fig. 3a, b and c. In every case the cathode *potential* varied only slightly as a function of the conditions used; it was always in the range −1.6 to −2.0 V (against SCE). The plots displayed (Fig 3a to c) illustrate the extremes of variations found. The electrochemical parameters proved to be rather insensitive to the conditions used. The major conclusion is that, consistently, the cell voltage for electrolysis using the hydrogen-diffusion anode is *ca.* 2 V less than that using the lead anode under otherwise identical conditions. Nor is the reducing power of the cathode, as indicated by the cathode potential, altered adversely.

6.2. Preparative and analytical results

Constant current electrolysis at longer times, as described in section 4, with subsequent quantitative analysis of the extent of conversion into sorbitol,
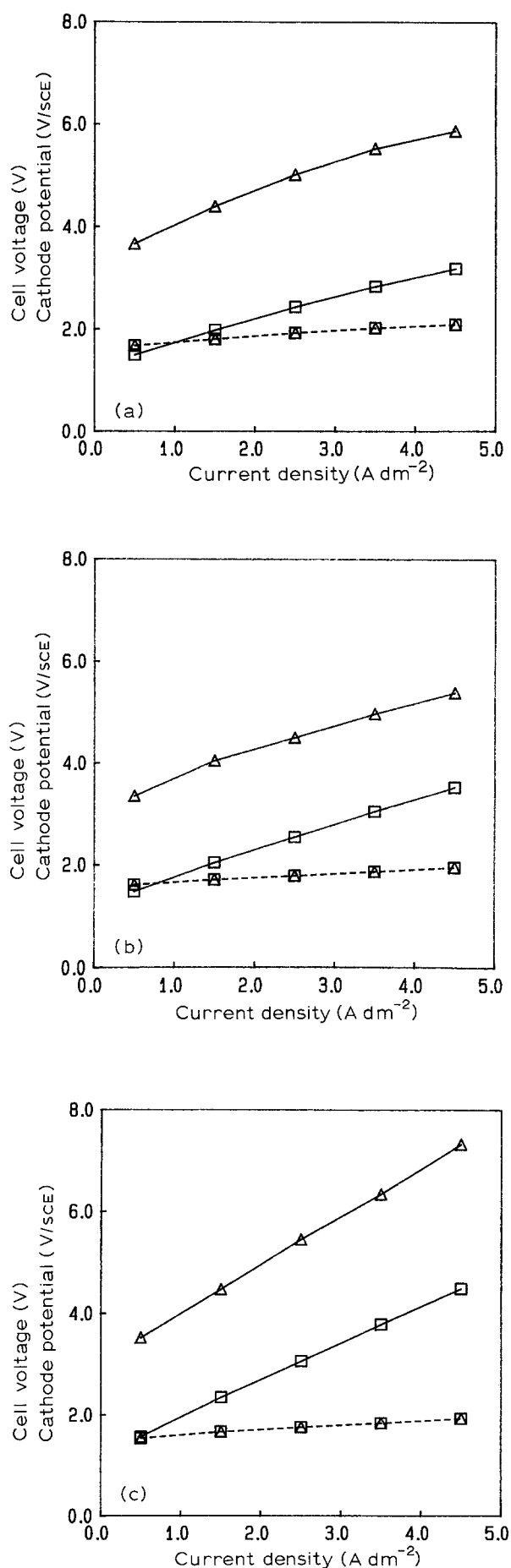

Fig. 3. Cell voltage against current density curves: (a) conc. 2.5 M, temp. 40°C, pH 9.5; (b) conc. 1.5 M, temp. 35°C, pH 6.5; (c) conc. 0.5 M, temp. 30°C, pH 3.5. Key: (△) with lead anode; (□) with gas anode; (– – –) cathode potential (V vs. SCE); (——) cell voltage.

Table 1. Preparative-scale amperostatic electrolysis*

Temperature ($^{\circ}C$)	Current density ($A\,dm^{-2}$)	Current efficiency ($\%$)[†]	pH[‡]
30	2.5	35	9.5
38	3.5	32	3.5

* Hydrogen-diffusion anode, Pb cathode, aqueous Na_2SO_4 ($75\,g\,dm^{-3}$); glucose concentration 2.5 M.
[†] Based on amount of sorbitol formed, assumes a 2 Faraday mol^{-1} process.
[‡] The pH values did not vary during electrolysis.

allowed calculation of current efficiencies. Results from such experiments are given in Table 1.

6.3. Key observations

When the current density is less than $1.5\,A\,dm^{-2}$, use of the hydrogen-diffusion anode results in cell voltages decreasing by 50% or more, *vis à vis* the lead anode. When the current density increases to $4.5\,A\,dm^{-2}$, the cell voltages decrease to the extent of about 30–40%. Noting that the diaphragms used in earlier commercial processes were ceramic ones, which have a higher resistance than the expensive ion exchange membranes now in use, it is likely that a cell based on the principles described here can save more than half of the power consumption when operated at a current density of 1 to $2\,A\,dm^{-2}$. These are the values considered suitable for industrial operation [1].

Cell voltages increase with increasing glucose concentration and decrease with increasing temperature for both hydrogen-diffusion and lead anodes, but the difference in favour of the hydrogen anode is maintained. Furthermore, the cathode potential, and therefore its ability to reduce glucose, is not significantly a function of the anode composition. The lowering of the cell voltage arises entirely from a decreased anode potential and reduced cell resistance. The results of the preparative-scale experiments are in line with this and the current efficiency for reduction to sorbitol is similar to that previously reported [7, 8].

The hydrogen diffusion anode has a potential about 2 V lower than that of the lead ones. It has previously been shown [5] that sorbitol is not oxidised at such an anode, a necessary pre-requisite for the omission of a separator. Electrolysis without a diaphragm was carried out with an amalgamated lead cathode and a graphite anode [5] and sorbitol was not oxidised. The similarity of efficiency of reduction found here (Table 1) to that previously found using lead cathodes and anodes is further evidence of the soundness of this conclusion.

In hydrogen-oxygen fuel cells which use gas-diffusion electrodes the quantity of platinum is about $10\,mg\,cm^{-2}$ or more, and the hydrophobic gas porous layer has a thickness of about 0.5 mm or less. In contrast, the gas-diffusion anode used in this work is much cheaper and easier to make. The anodes were used for several

months and they remained in good condition, so under laboratory conditions they appear to have a good lifetime.

There are no changes in the values of pH before and after the electrolysis (Table 1). This is because protons are generated at the anode *pro rata* to their consumption in the cathodic hydrogenation. In contrast there is an in-built tendency for the catholyte to become alkaline during electrolysis using a lead anode.

7. Conclusions

For the electrochemical reduction of glucose to sorbitol in aqueous solution the use of a porous hydrogen-diffusion anode in place of the usual lead one results in a substantial decrease in cell voltage. The absolute decrease is about 2 V which is *ca.* 40–50% in relative terms. The current efficiency for sorbitol production is not adversely affected and thus the power usage for this conversion is significantly lowered.

The lower oxidizing power of the hydrogen anode avoids the complication of product oxidation and removes the need for a divided cell. This not only lowers the power usage but also reduces capital costs. In the electrochemical cell design used in this study, the pH value of the catholyte is effectively constant during the electrolysis, which assists the high selectivity of reduction and removes the need for ancillary equipment.

8. Acknowledgement

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