Formation of sorbitol by cathodic reduction of glucose

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The steady-state formation of sorbitol by cathodic reduction of glucose was studied in a parallel-plate reactor of 200 cm^2 electrode area. Earlier work was extended to explore the effect of flow rate, pH and current density. The effect of temperature between 20° and 47° C and the use of amalgamated lead as compared with chemical lead and other metals is discussed. It is shown that addition of Zn^{2+} ions accelerates the reaction and the reasons for this are discussed. The implications for industrial application are considered.

1. Introduction

The reduction of glucose at a lead cathode to form sorbitol, a compound with many uses in the foodstuff and related industries, will be known to some [1] as an electro-organic chemical process formerly carried out on an industrial scale. Since the war, it has been totally replaced by the catalytic hydrogenation route which was believed to be more cost-effective. That route was still electrochemical in many cases, in as much as the hydrogen was electrolytically manufactured. Such a plant was involved in a most serious explosion some years ago [2], and indeed the casualties could have been far more serious. All of which has prompted the present authors to re-examine the reaction and to obtain parametric information under controlled conditions, partly in order to better understand the reaction and partly to assess the extent to which application of modern electrochemical reaction technology might once more return the competitive edge to the electrochemical route.

There is a fair body of literature concerning the electroreduction of glucose. This has been reviewed by Fedoronko [3]. He divided his review into the polarographic work and that done on solid electrodes. The polarographic studies form a coherent picture, in which the experimentally observed data, which take the form of a plateau, not diffusion controlled, are explained in terms of a rate-determining step of mutarotation from the cyclic (inactive) form of the sugar to the linear (electroactive) form. The process is known to be both acid and base catalyzed, and has been reviewed by Capon [4]. It is generally assumed that no hydrogen evolution takes place in the polarographic plateau region.

In contrast, when the cathodic reduction is attempted at solid electrodes, hydrogen evolution forms the predominant reaction. Fedoronko [3] reviews this too, but makes little attempt either to interpret the data or in any way to link together polarographic and solid electrode studies, which are, quite wrongly in our view, too often treated as separate and unrelatable disciplines.

We shall not here cover again the work of Fedoronko [3] except to say firstly that there are virtually no published data relating to current–potential measurements at solid electrodes, and secondly that there has been no attempt at elucidation of a mechanism. Rather, the literature on cathodic reduction of mono-saccharides is, almost without exception, concerned with the relationship between current density and product efficiency, and with the effect of temperature, electrolyte composition and electrode materials. Virtually absent are measurements of cathode

potential and its relationship to current density. Stirring or other forms of forced convection are also largely ignored. Thus Creighton [5] mentions that at a cathode potential of -1.53 to -1.71 V (versus an unspecified reference) the current density was 0.5–1 A dm^{-2} at $\sim 20°$ C. The effect of stirring has been referred to by several workers in a qualitative manner. Belenkaya [6] showed that stirring improves the yield by $\sim 16\%$. On the other hand the co-evolution of hydrogen, which is known to take place and, indeed, forms the major Faradaic reaction, has itself a stirring action [7].

In terms of the electrolyte used, there is again a mass of qualitative data which states that alkaline electrolytes yield the highest current efficiencies. However, a homogeneous side reaction can take place in the bulk electrolyte, an isomerization of glucose to form mannose and fructose, and for this reason, such electrolytes have not been used. The use of sodium sulphate solutions solves this problem in that although they are themselves nearly neutral in pH, hydrogen evolution in the near-electrode layer causes a marked increase in alkalinity there. This creates an environment suitable for the reduction of the glucose. This was described by Creighton in a patent [8].

Turning finally to the effect of the cathode material, most work relates to either lead or amalgamated lead. These two metals are of course well known in electro-organic chemistry for their very high overpotential for the hydrogen evolution reaction, which allows a potential 'window' in which other reductions of organic species may occur. However, higher yields have been found on zinc cathodes, while there is also a patent which advises the addition of zinc salts to solution. These must be electro-deposited on the cathode, where they will provide a fresh and therefore active cathode with a high surface area. Nickel has also been studied.

Smirnova and Kovachenko [9] divide the cathode materials into three categories. The first of these is the high overvoltage metals (Pb, Hg, Zn–Hg, Pb–Cu, Sn–Hg, Sn, In, Te, Ga, Bi). The second category comprises Cu, Ag, Ge, C, Tl, Cu–Sn and Ce–Pb. The metals in the third group are Pt, Ni, Al and Co. Quoted current efficiencies are 40–70% for the first category, 15–35% for the second and 3–7% for the third.

What follows is therefore an attempt to co-ordinate some of these factors on a more systematic basis, and to establish a body of data which can be used both to give more insight into the mechanism and also to enable those qualified to do so, to estimate the potential of the reaction for scale-up.

2. Experimental

Results were obtained by using a parallel-plate cell with 200 cm^2 electrode area. Both anode and cathode were 'chemical grade' lead (99.9% minimum) and the cell was divided with an ion-exchange membrane (Nafion, type XR 475). Anolyte and catholyte were circulated with Iwaki magnetically coupled, PTFE rotored, glandless pumps. Catholyte was held in a reservoir of 2 dm^3 capacity. Also in the circulation loops were glass coils placed in water baths, which served to remove the heat generated during electrolysis. The pH of the catholyte was controlled using a 'pH-stat' based on a pH meter driving an electrically operated valve, above which was a reservoir of concentrated sulphuric acid. This flowed under gravity when the valve was opened and catholyte pH could be maintained at ± 0.3 pH unit or better. Power was supplied from a 'Westalite' cinema arc rectifier capable of delivering up to 70 A d.c. and incorporating its own ammeter.

The current efficiencies quoted in Section 3 and the partial current data derived from them,
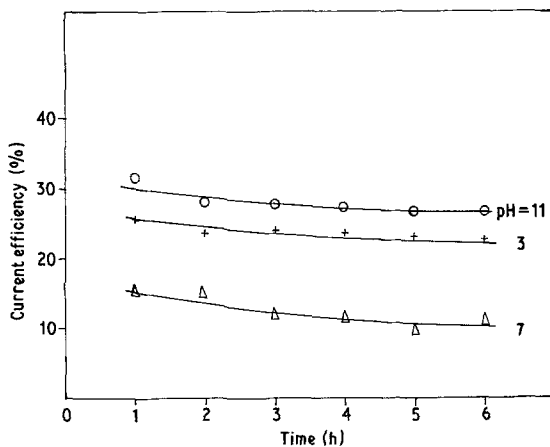

Fig. 1. Current efficiency as a function of time and pH. Lead cathode, D-glucose = 0.39 M, current density = 2 A cm^{-1}, temperature = 20° C.

were obtained by chemical analysis. Samples of the catholyte were withdrawn at regular intervals and were derivatized using a standard silyation technique. These derivatives were then injected on to a GLC machine. By calibration of the peaks using standard solutions, it was found that glucose and sorbitol, the major components, could be determined to within ± 3%. Other species, not present in significant amounts, gave smaller peaks. However, their quantitative estimation was not considered important in the context of the work. All chemicals used were 'CP' or 'GP' grade and the water was singly distilled. Further details of the experimental apparatus and procedure can be found in [10].

3. Results

The first and qualitative result of the work was that sorbitol appeared to be the predominant product in the sodium sulphate media. In the literature it is reported as being present in much the same proportions as mannitol, which is a less desirable product. It was realized that the reason for this apparent discrepancy was that the duration of runs in the present work, usually 4 hours, was much less than those reported in earlier literature, which lasted over one day. While only traces of mannose and fructose were found, after longer times their concentration becomes substantial, especially at higher temperatures, and mannitol is the resulting product (from mannose). There is thus no dichotomy, but the observations point to the advantages of the higher throughput

rates achieved in a forced-flow reactor.

The actual results are shown in Figs. 1 and 2. Fig. 1 shows current efficiency at three pH values as a function of the length of electrolysis. The current efficiencies reflect the fact [4] that the mutarotation is most efficiently catalyzed by base and least effectively in neutral solution: this ranking was observed throughout. Fig. 2 shows the effect of glucose concentration on current efficiency and, while there is a positive trend, it is in no way first-order and indeed shows signs of reaching a limiting value. Such an observation ties in with the observation by Overend and Peacocke [11] that increases in solution viscosity become insignificant above $\sim 1.6\,\mathrm{M}$ and thus lead to a reduction in partial current density.

The literature reports studies in which stirring rate was altered and found to have a slight effect. It was felt that this should be more precisely examined and this is readily done in a forced-convection reactor. Fig. 3 shows, at two pH values, that there is no significant effect.

Further information on the effect of current density and pH is given in Figs. 4a–d. In Figs. 4a and b, it will be seen that increased total current density also leads to increased partial current density for glucose reduction, but the slope is only about 0.3; that is to say, tenfold increase in total current provides only a threefold increase in sorbitol yield. In Figs. 4c and d, it is interesting to note that the effect of pH change is less marked at the higher glucose concentration. The effect of temperature has not been reported in the literature. This is shown in Fig. 5. A 50%
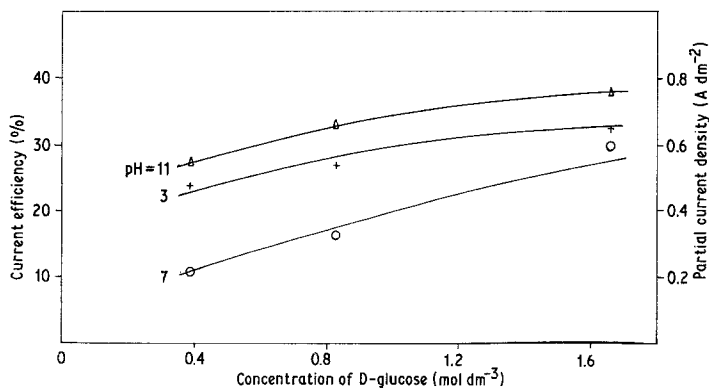

Fig. 2. Current efficiency after 4 hours as a function of initial D-glucose concentration and pH. Lead cathode, current density = $2\,\mathrm{A\,dm^{-2}}$, temperature = 20° C.
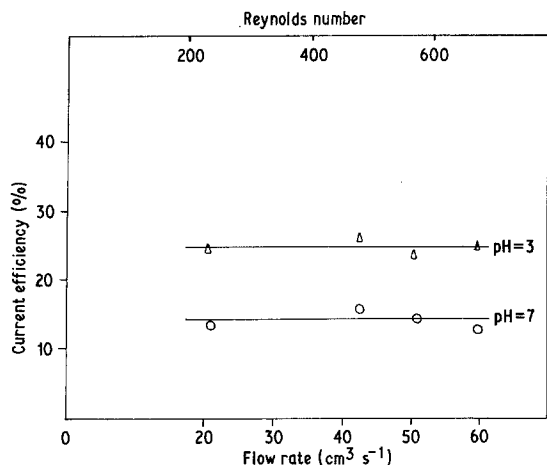
Fig. 3. Current efficiency and partial density after 4 hours as a function of flow rate and pH. Lead cathode, D-glucose = 0.38 M, current density = 2 A dm^{-2}, temperature = 20° C.
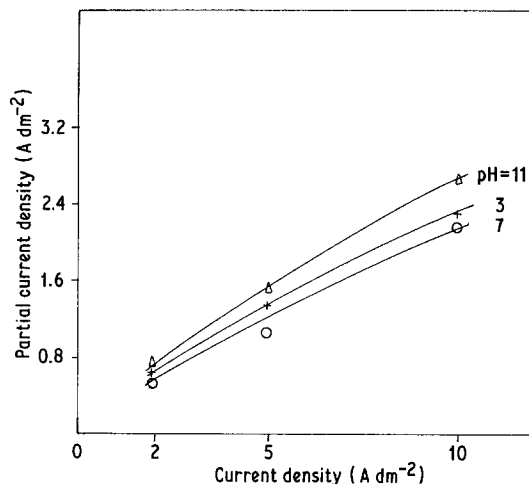
increase in partial current results from a ~ 20° temperature increase. Fig. 6 shows how the addition of Zn^{2+}, advocated in several patents, affects the rate of reduction. This is the first time quantitative data on this have been published and their interpretation is considered below.

Lastly, we have considered the effect of alternative cathode materials. Figs. 7 and 8 show a selection of metals and the effect of both pH and current density variation. It will be seen in both cases that Ni, the metal with the lowest hydrogen overvoltage, is least effec-
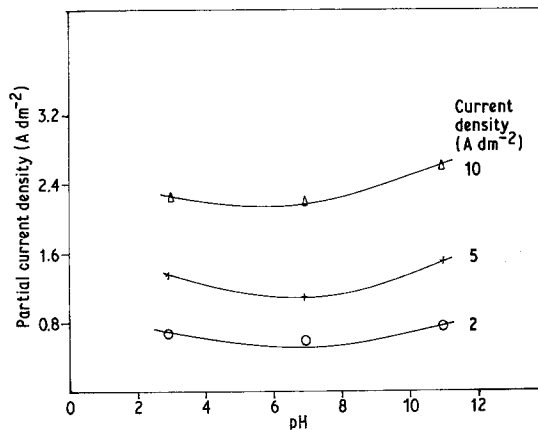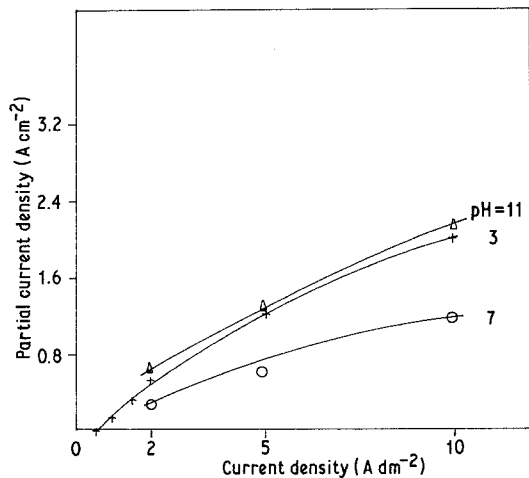

Fig. 4a. Partial current density after 4 hours as a function of current density. Lead cathode, D-glucose = 83 M, temperature = 20° C.

Fig. 4b. As Fig. 4a but D-glucose = 0.38 M,

Fig. 4c. Partial current density after 4 hours as a function of pH. Lead cathode, D-glucose = 1.66 M. temperature = 20° C.
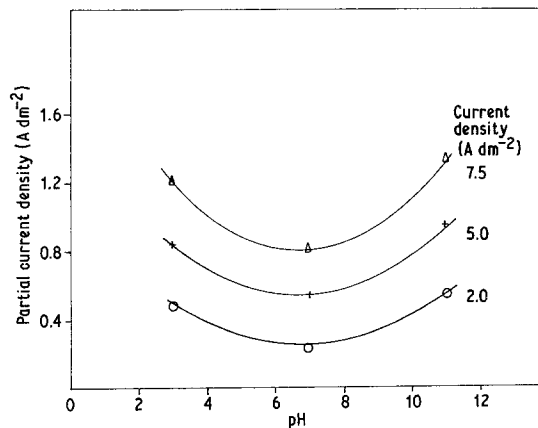

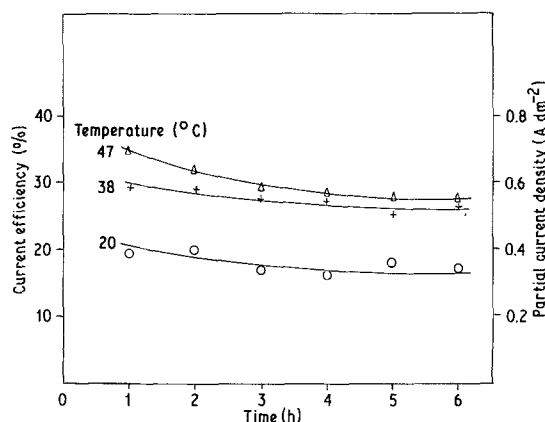Fig. 4d. As Fig. 4c but D-glucose = 0.39 M.

Fig. 5. Current efficiency and partial current density as a function of time and temperature. Lead cathode, D-glucose = 0.83 M, current density = 2 A dm^{-2}, pH = 7.

Fig. 6. Current efficiency and partial current density after 4 hours as a function of $ZnSO_4$ concentration. D-glucose = 0.83 M, current density = 2 A cm^{-2}, pH = 7, temperature = 20° C.

tive. In this, we concur with earlier workers [9], although they found at least a small amount of product due, probably, to the longer duration of their electrolyses.

4. Discussion

We have not found the data, as reported above, easy to interpret. Certain conclusions are clear. Firstly, the reaction is not diffusion controlled, as seen from the effect of flow rate and also from a simple Fick's law calculation, which shows that the limiting current (related to bulk glucose concentration) is 1% or less of that predicted. This is further supported by the effect of temperature. However, the current is not independent of potential, as found in work with the dropping
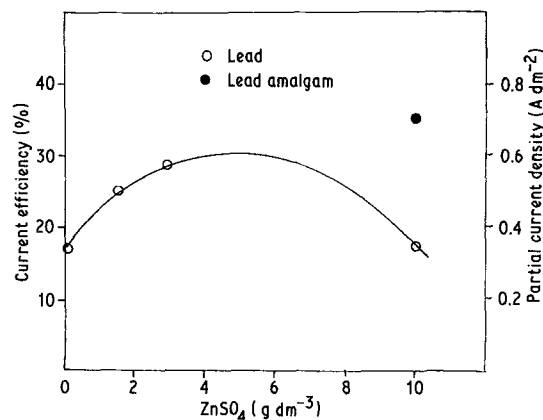
mercury electrode. Attempts to derive electrochemical reaction orders such as

$$\left[\frac{di_{glu}}{d[glu]} \right]_{pH, T, i} \quad or \quad \left[\frac{di_{glu}}{dpH} \right]_{[glu], T, i}$$

led to coefficients of roughly 0.2. This possibly reflects the ill-defined geometry of the zone in which mutarotation is taking place and other effects occurring there.

The effect of Zn^{2+} addition does indeed confirm the claims of the patents. This effect has never been discussed before. Initially, we explained the result in terms of an electrodeposition of Zn as it was observed experimentally that the cathode became grey and rough. In the initial stages of the run, the rate of Zn deposition will form a significant fraction of the total
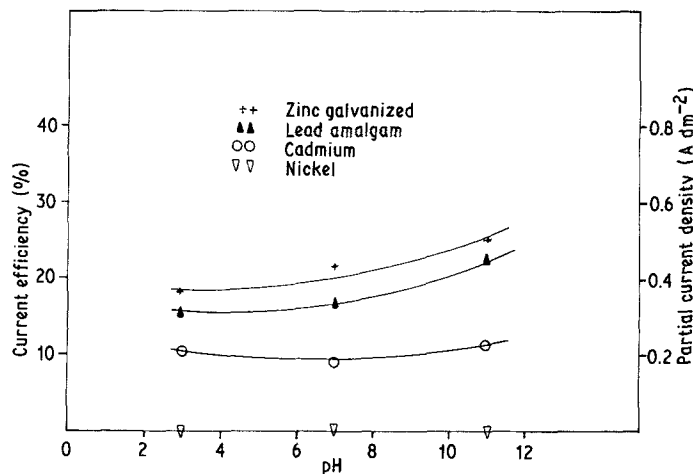
Fig. 7. Current efficiency and partial current density after 4 hours as a function of pH at various cathode materials. D-glucose = 0.83 M, current density = 2 A dm^{-2}, temperature = 20° C.
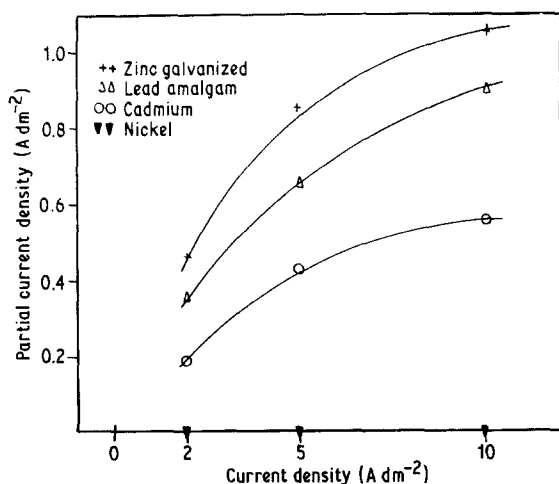
Fig. 8. Partial current density after 4 hours as a function of current density at various cathode materials. D-glucose = 0.83 M, pH = 7, temperature = 20° C.

current, assuming that this rate is limited only by diffusion control. As the Zn^{2+} is depleted, this deposition current will decay. Meanwhile the electrode will become rougher and of higher surface area, that is to say the true current density will decrease all factors sympathetic to an increase in the partial rate for glucose reduction. However, we later became aware of the work of Neely [12] and Mitzner [13] both of whom studied the effect of metal cations on the rate of mutarotation of aldoses. It is found that these act as effective catalysts for this reaction. Though Zn^{2+} does not appear to have been studied, the range of those that do work in this way, including Ni^{2+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Be^{2+}, Mg^{2+} and Li^+, is so broad as to encourage the belief that the effect of Zn^{2+} addition is a dual one.

The three datum points from Fig. 5 were plotted in Arrhenius fashion. From this plot (not shown), it is clear that the third point at the highest temperature is the 'discrepancy'. From the first two, an activation energy of 21 kJ mol^{-1} is found which is much lower than the polarographic value obtained by Delahay and Strassner [14] of 71 kJ mol^{-1}. We believe a simple explanation for this exists and though the third point may be discrepant, we do not suggest it is erroneous.

The rate of the mutarotation reaction is highly pH dependent and a number of authors [3] point out that during electrolysis, an alkaline zone will be formed at the near-electrode layer, this being the process which catalyzes the mutarotation. Data on pH changes in the near-electrode layer are scant, but some studies exist [15]. One of the findings is that even modest temperature increases are highly effective in repression of such pH changes. Thus Knoedler and Neugebohren [16] show the virtual disappearance of near-electrode pH increase at 50° C at all except the highest current densities, say more than 1 A cm^{-2}. This, we feel, amply explains the effect of temperature on the overall process, as shown in Fig. 5.

The effect of cathode metal is interesting. Zn is seen to be somewhat superior to amalgamated Pb. This may be a surface area effect as the latter material will be of very low specific surface area. That the exchange current density for hydrogen evolution on Zn is slightly higher than on Pb may not outweigh the former effect.

Our parametric analyses point the way, we believe, to a more effective manner of operating the process on a larger scale. Firstly, the reaction should be performed in a reactor with the largest possible surface area to volume ratio, so that the greater efficiencies observed at low current densities are reaped. However, there could be problems in using packed or fluidized-bed reactors: we have observed some very high cathodic overpotentials which indicate that a resistive film of $PbSO_4$ is formed on the cathode surface, quite possibly as a result of the classical sulphation of lead mechanism operating before d.c. power is applied to the reactor [17]. While this effect can be minimized by application of the d.c. voltage before introduction of the electrolyte, small residual interfacial resistances are multiplied in the case of the packed or fluidized-bed reactor so as to render them unattractive. The good results observed on Zn cathodes, where resistive films would not form, point to an alternative solution. Secondly, it is clear that temperature and pH must be optimized to the point where damaging subsidiary homogeneous reactions become insignificant. From this, it follows that the hold-up volume of the reactor system should be minimized, and an operational mode adopted in which a small volume of reactant is rapidly processed and then 'quenched' by neutralization and cooling. The accelerative effect of the metal ions discussed above should be explored. Obviously, preference should be given to cations which do not electrodeposit.

Whether or how the electrochemical process benefitting from these ideas would compete with the pressure hydrogenation route is an excercise we think best left to others. We are confident that sufficient data exist here for at least a preliminary assessment.

Acknowledgement

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