

## THE PAIRED ELECTROCHEMICAL SYNTHESIS OF GLUCONIC ACID AND SORBITOL

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Gluconic acid and sorbitol are obtained simultaneously both with 90% yields by paired electrolysis of glucose, with a Pb sheet cathode and a dimension stable anode (DSA) in a press filtration diaphragm cell. The anolyte is composed from 66.7% glucose and 2% NaBr, and the catholyte from 66.7% glucose and 2.5% Na<sub>2</sub>SO<sub>4</sub>, respectively. The electrolysis was performed at the temperature of 60 °C, at the current density of 50 mA cm<sup>-2</sup>,  $Q_r$  is 110%. At this optimum conditions the current efficiencies for both gluconic acid and sorbitol are higher than 80%.

Gluconic acid and gluconates have a broad variety of applications such as the food additives and in medicine<sup>1-3</sup>. Since they have close relationship to the biological fuel cells and glucose sensors<sup>4-6</sup>, electrooxidation and electroreduction of glucose have attracted attention of many electrochemists. Sorbitol also has many applications, for synthesis of vitamin C, as sucrol, plasticizer and humidity controller<sup>1,20</sup>.

Up to now, the chemical synthesis and fermentation have been the most frequently used methods for synthesis of gluconic acid and sorbitol<sup>6,7</sup>. Although these methods have some advantages, such as mild reaction conditions and no special requirements for equipment the high cost of production, the low quality of the product and negative influence on the environment made them less favourable.

It can be concluded that the electrochemical process has more advantages than chemical and fermentation processes<sup>8-22</sup>.

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The electrooxidation of glucose leads to gluconic acid. Recent studies on the oxidation of glucose have found that the process is affected directly by the electrode material, its surface, electrolyte, its pH value and the temperature<sup>8-18</sup>. The electroreduction of glucose to sorbitol has also been studied. Park et al. assumed that glucose is reduced by direct electrode reaction to sorbitol at cathodes with high hydrogen over-potential and at a high pH value<sup>20</sup> according to Scheme 1.

Recently, the paired electrochemical synthesis of gluconic acid and sorbitol in undivided flow cells has been reported<sup>20</sup>. Our work makes the process more efficient and expandable to the industrial scale.

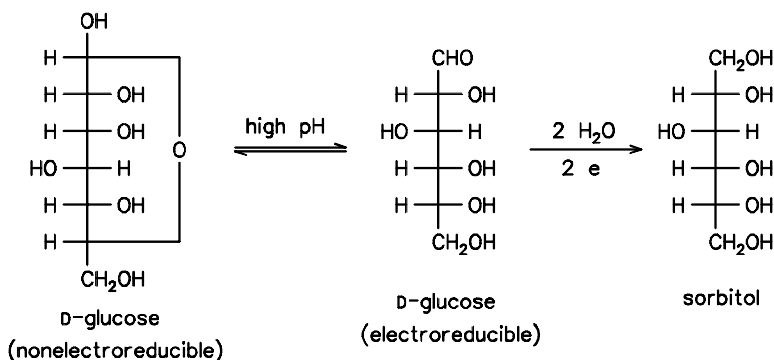
## EXPERIMENTAL

In our work, NaBr is added to the anolyte, and the following mechanism is proposed by Isbell<sup>19</sup>.

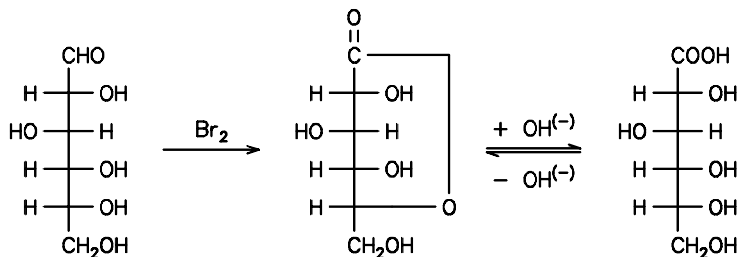
The process is initiated by the electrochemical oxidation of bromide



then  $\text{Br}_2$  oxidizes the glucose to gluconolactone, and further to gluconic acid according to the Scheme 2.



SCHEME 1



SCHEME 2

At the same time,  $\text{Br}_2$  is reduced to  $\text{Br}^-$ , which is returned back to the reaction. In absence of  $\text{Br}^-$  in anolyte, a conversion of glucose to gluconic acid is not observed. If  $\text{Br}^-$  is added, formation of  $\text{Br}_2$  can be determined in the reaction mixture.

The paired electrolysis system is shown in Fig. 1. The cell we use, shown in Fig. 2, is a press filtration cell with a cation-exchange diaphragm. Pb sheet as a cathode and a dimension stable anode (DSA). Figs 2a, 2b show one cell and assembled system, respectively. It has been proved that the cell can be enlarged directly for the commercial process.

The cell voltage and current were monitored during experiments. All chemicals were of analytic reagent grade and the distilled water was used.

Current efficiencies and product yields were obtained by analysis of glucose and reaction products, according to Park's method<sup>20</sup>.

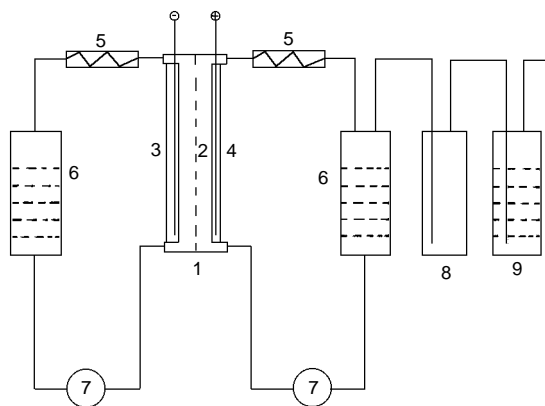


FIG. 1

Paired electrolysis system. 1 Cell, 2 cation-exchange diaphragm, 3 cathode, 4 anode, 5 water mantles, 6 reservoirs, 7 pumps, 8 surge tank, 9 bromine absorption tank

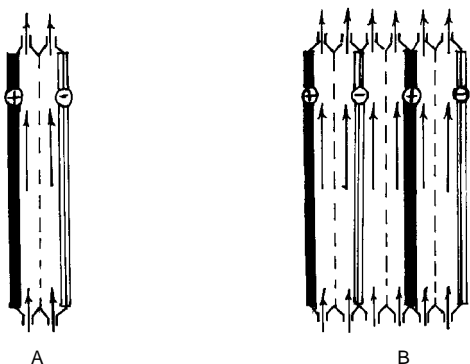


FIG. 2

Structure of the cell. A the cell unit, B assembled electrolyzer

## RESULTS AND DISCUSSION

There are many factors which affect the current efficiency and the yield of gluconic acid and sorbitol. Based on our work, the major factors are the current density  $I$ , the ratio  $Q_r = Q_{\text{pass}}/Q_{\text{theor}}$ , expressed in % (here  $Q_{\text{pass}}$  is the charge passed, while  $Q_{\text{theor}}$  is its value for 100% conversion), temperature, and the concentration of the electrolyte. In our study we first selected the optimum anodic conditions, then determined the cathodic process parameters and made them match. The results are given in Figs 3 – 7.

*The Effect of  $Q_r$  on the Conversion of Glucose*

The results of Figs 3 and 4 show that for  $Q_r > 110\%$ , the content of gluconic acid in anolyte is reaching its lower limit. The content of glucose in catholyte decreases until  $Q_r$  reaches 100%, when the conversion of glucose is near the limit. When  $Q_r$  is lower than 110%, neither the reaction at cathode nor at anode are completed. Both the conversion of glucose  $\Gamma_G$  and the yield of product are low. For  $Q_r > 120\%$ , the yield of by-products increased and the current efficiency decreased. The value of  $Q_r = 110\%$  appeared to be an optimum.

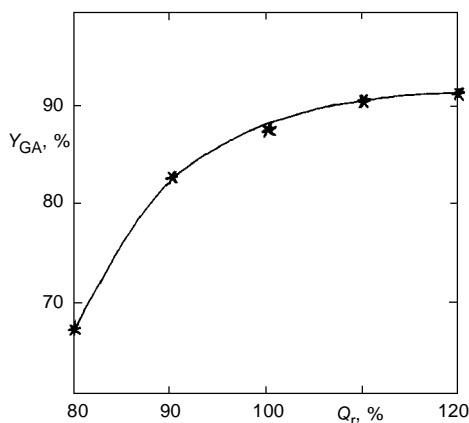


FIG. 3

Effect of  $Q_r$  on the yield of gluconic acid  $Y_{GA}$  in anolyte. Composition of the anolyte: 16.7% glucose, 2% NaBr; composition of the catholyte: 8.3% glucose, 2.5% NaOH, 2.5%  $\text{Na}_2\text{SO}_4$ ;  $I = 50 \text{ mA cm}^{-2}$ , temperature  $54^\circ\text{C}$

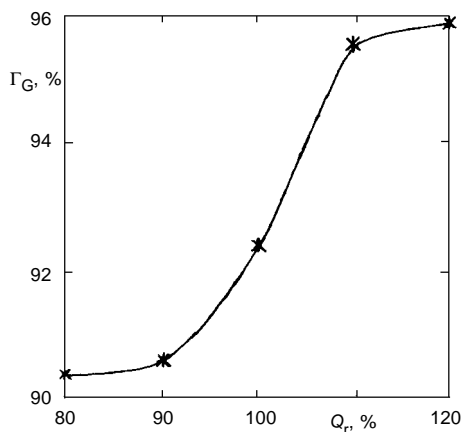


FIG. 4

Effect of  $Q_r$  on the conversion of glucose  $\Gamma_G$  in catholyte. Composition of the anolyte: 16.7% glucose, 2% NaBr; composition of the catholyte: 8.3% glucose, 2.5% NaOH, 2.5%  $\text{Na}_2\text{SO}_4$ ;  $I = 50 \text{ mA cm}^{-2}$ , temperature  $54^\circ\text{C}$

### The Effect of Current Density on Yield of Gluconic Acid

Figure 5 shows that the yield of gluconic acid  $Y_{GA}$  reaches the highest value for the current density  $I = 50 \text{ mA cm}^{-2}$ . As the product can be carried away from the anode very quickly and the concentration ratio of gluconic acid to glucose near the anode is large, it is possible to use high current density in electrolysis. At the higher current density, however, by-product yield increases.

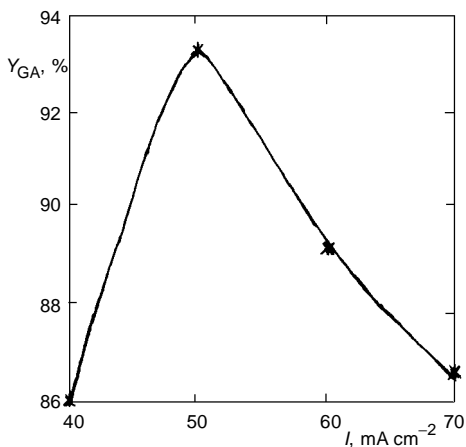


FIG. 5

Effect of the current density  $I$  on the yield of gluconic acid  $Y_{GA}$ . Composition of the anolyte: 14.3% glucose, 2.3% NaBr; composition of the catholyte: 14.3% glucose, 11.7%  $\text{Na}_2\text{SO}_4$ ; temperature  $54^\circ\text{C}$ ,  $Q_r = 100\%$

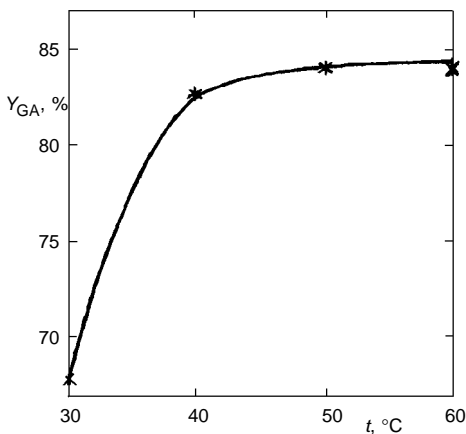


FIG. 6

Effect of temperature  $t$  on the yield of gluconic acid  $Y_{GA}$ . Composition of the anolyte: 14.3% glucose, 2% NaBr; composition of the catholyte: 14.3% glucose, 11.7%  $\text{Na}_2\text{SO}_4$ ;  $I = 50 \text{ mA cm}^{-2}$ ,  $Q_r = 100\%$

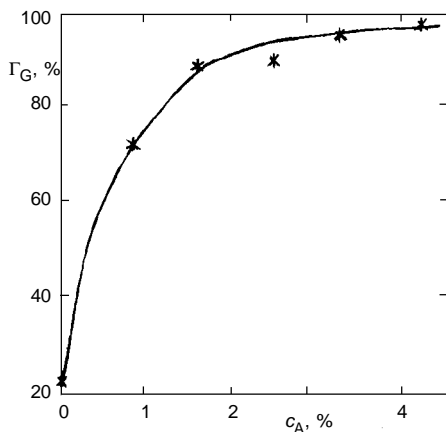


FIG. 7

Effect of concentration of alkali  $c_A$  on the conversion of glucose  $\Gamma_G$  in catholyte. Composition of the anolyte: 16.7% glucose, 2% NaBr; composition of the catholyte: 16.7% glucose;  $I = 50 \text{ mA cm}^{-2}$ ,  $Q_r = 100\%$ , temperature  $50^\circ\text{C}$

### *The Effect of Temperature on Yield of Gluconic Acid*

From Fig. 6 we can infer that with the increase of temperature, the yield of gluconic acid is rising. At 60 °C the yield almost reaches its theoretical value. At lower temperature, the reaction rate is significantly lower. At temperature higher than 60 °C, on the other hand, requirements for high quality equipment and for the process conditions are more strict.

### *The Effect of Glucose Concentration on the Yield of Gluconic Acid and Sorbitol*

Table I indicates that when initial concentration of glucose is increased, the yield is still high. Increasing concentration of glucose can rise the concentration of gluconic acid in anolyte to more than 50%, which is high enough to be utilized for further industrial processing. There is however a concentration limit at about 66% due to the high viscosity of solution and hence growing transportation problem. We have limited the concentration of glucose to 66.7%.

### *The Effect of Electrolyte Composition on Conversion of Glucose at Cathode*

It was found that in basic solution, glucose is easily reduced to sorbitol and mannitol. NaOH is added to the cathodic electrolyte for sufficient basicity and as a supporting electrolyte. At concentration of NaOH higher than 2.5% by-product yield increased. Therefore we have used Na<sub>2</sub>SO<sub>4</sub> as the major supporting electrolyte in order to keep the highest possible conversion of glucose. Figure 7 shows that the conversion of glucose at cathode increases with the increase of concentration of NaOH. The conversion almost reaches 100% when concentration of NaOH is 4.2%. At higher concentration, the structure of glucose molecule is broken, and by-product is produced. We have found the concentration of NaOH in the range 1.7 – 2.5%, and Na<sub>2</sub>SO<sub>4</sub> in the range 2.5 – 3.3% as suitable.

TABLE I  
Effect of initial glucose concentration  $c_i$  on the yields of gluconic acid,  $Y_{GA}$ , and sorbitol,  $Y_S$

$c_i$ , %	Voltage, V	$Y_{GA}$ , %	$Y_S$ , %
16.7	4.1	93.6	64.3
33.3	3.9	88.4	71.7
50.1	4.1	80.6	74.2
66.7	4.1	87.4	82.0

It can be concluded that the optimum conditions for producing gluconic acid and sorbitol were found. Both in the anolyte and in the catholyte the initial concentration of glucose was limited to about 66%.

In anolyte the initial concentration of NaBr was 2%. In catholyte the initial concentration of NaOH was 2.5% and Na<sub>2</sub>SO<sub>4</sub> 2.5%. The electrolyte temperature was 60 °C, current density  $I = 50 \text{ mA cm}^{-2}$ , and  $Q_r = 110\%$ .

The press filtration ion-exchange cell, designed by us, could be used also for synthesis of many other products. It has been used successfully in synthesis of glyoxalic acid with paired electrolysis of glyoxal and oxalic acid, L-cysteine, 3,3'-dichlorobenzidine etc. The cell is designed according to the industrial requirements and can be enlarged directly to the industrial scale.

The yield of products and the conversion of glucose both at anode and cathode reached about 90%, which is higher value than that referred in literature<sup>1,2,21</sup>. The process is simple and easy to operate.

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