

# ***Current efficiencies and regeneration of poisoned Raney nickel in the electrohydrogenation of glucose to sorbitol***

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Poisoning of the Raney nickel cathode during the paired syntheses of sorbitol and gluconic acid has been studied. Sorbitol poisons the Raney nickel powder cathode and sorbitol current efficiencies decrease from 100% to < 50%. Current losses of the poisoned Raney nickel were due to hydrogen evolution. Electrocatalytic activity was restored by washing the Raney nickel in a 17 wt % NaOH solution at 60°. This procedure, when performed *in situ* for the undivided packed bed flow reactor, increased sorbitol current efficiencies from 35-45% to 70-100%. The effects of glucose concentration and applied current on sorbitol and gluconic acid current efficiencies have also been examined. High sorbitol current efficiencies were obtained with fresh Raney nickel when glucose concentrations were high and the current low. The high gluconic acid current efficiencies were independent of current and glucose concentration. To maintain high sorbitol current efficiencies as glucose was consumed, a systematic procedure for lowering the applied current was developed in which the current was decreased from 500 mA per 10 g of Raney nickel at 1.6 M glucose to < 100 mA per 10 g at 0.2 M glucose.

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## **1. Introduction**

We have recently reported on the paired electro-oxidation and electro-reduction of glucose in an undivided packed bed flow-through reactor [1]. In this paired synthesis, glucose is electrohydrogenated to sorbitol at a Raney nickel powder cathode and glucose is indirectly oxidized to gluconic acid via electrogenerated HOBr. When the solution pH is maintained at or below 7, the only side reaction is hydrogen evolution at the Raney nickel cathode. Sorbitol current efficiencies of 80-100%, gluconic acid current efficiencies of 100% and high product yields were obtained.

In this paper the effects of long-term flow reactor operation on sorbitol and gluconic acid current efficiencies and yields are examined. Specifically, sorbitol current efficiencies of poisoned Raney nickel, methods to regenerate its activity and the effects of glucose depletion on

gluconate and sorbitol current efficiencies and yields have been studied.

## **2. Experimental details**

Electrolysis experiments of glucose oxidation-reduction were carried out in a standard glass H-cell containing a medium porosity glass frit. Paired syntheses flow reactor electrolyses were performed using a glass flow-through packed bed reactor operated in a batch recycle mode. Detailed descriptions of the H-cell, flow reactor apparatus, associated equipment and instrumentation have been presented elsewhere [1].

All chemicals were of analytical reagent grade and the water was deionized and doubly distilled. Preparation of Raney nickel powder catalyst, with an activity comparable to that of W-2 [2], has been described previously [1].

Current efficiencies and product yields were determined by HPLC analysis of glucose and the

reaction products [3]. Calibration of peak areas with standard solutions indicated that sorbitol concentrations could be determined to within  $\pm 5\%$ , while glucose and gluconate concentrations were within  $\pm 10\%$ .

### 3. Results and discussion

#### 3.1. Raney nickel poisoning experiments

A long-term paired syntheses experiment was carried out using the undivided flow reactor with a freshly prepared Raney nickel powder cathode. The electrolysis was performed to determine whether high current efficiencies and yields could be maintained beyond  $0.2 \text{ F mol}^{-1}$ . The electrolysis conditions were: 1.6 M glucose and 0.4 M  $\text{CaBr}_2$  initial electrolyte,  $T = 60^\circ \text{C}$ ,  $\text{pH} = 6-7$ , volumetric flow rate of  $100 \text{ ml min}^{-1}$ , and a constant applied current of 200 mA per 10 g Raney nickel powder.

Sorbitol current efficiencies are shown in Fig. 1. The 100% sorbitol current efficiency at  $0.2 \text{ F mol}^{-1}$  agrees with previously obtained results [1]. Between 0.2 and  $0.4 \text{ F mol}^{-1}$ , however, the current efficiency decreased to  $\sim 75\%$  and in the interval 0.4 to  $0.5 \text{ F mol}^{-1}$  only one-half of the applied cathodic current was being used to produce sorbitol. Although not shown in Fig. 1, the oxidation current efficiencies through  $0.5 \text{ F mol}^{-1}$  were  $\sim 100\%$ . HPLC analysis of electrolysis samples indicated that no organic by-products were formed at the cathode and current efficiency losses were attributed to hydrogen evolution. To determine if the decreasing sorbitol current efficiencies were due to the decreasing bulk solution concentration of glucose, glucose was added to the electrolyte solution (at  $0.5 \text{ F mol}^{-1}$ , point A) to increase its concentration to 1.6 M. After an additional  $0.2 \text{ F mol}^{-1}$  of charge was passed, the sorbitol current efficiency improved slightly to  $\sim 60\%$  (cf. Fig. 1). Thus, it does not appear that the decrease in the sorbitol current efficiencies with time of reactor operation is due to depletion of reactant.

The flow reactor results suggest that the low sorbitol current efficiencies are due to poisoning of the catalyst. The increased rates of  $\text{H}_2$  evolution during the experiment were accompanied

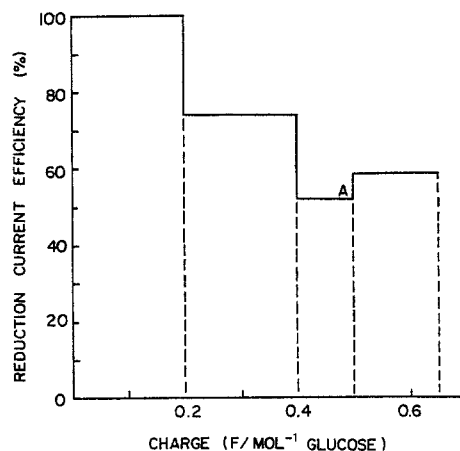


Fig. 1. Relationship between sorbitol current efficiency and charge passage during glucose paired syntheses in a packed bed flow reactor. Cathode, Raney nickel powder (10 g); anode, graphic chips; 1.6 M glucose; 0.4 M  $\text{CaBr}_2$ ; applied current, 250 mA; flow rate,  $100 \text{ ml min}^{-1}$ ;  $\text{pH} 7$ ;  $60^\circ \text{C}$ . Point A, glucose addition to 1.6 M.

by physical changes in the Raney nickel powder; the initially black and finely divided powder appeared to agglomerate into larger size particles and became lighter in colour. In catalytic processes, metal catalyst agglomeration and poisoning are two important and well known deactivation mechanisms [4]. Similar deactivation phenomena may occur when Raney nickel is used as the cathode for electrohydrogenation.

The initial poisoning experiments focused on sorbitol as the deactivating agent. Freshly activated Raney nickel powder (2 g) was soaked in a 0.3 M sorbitol solution at  $60^\circ \text{C}$  for 24 h and then used as the cathode in a constant current H-cell electrolysis of a 1.6 M glucose–0.4 M  $\text{CaBr}_2$  solution. As shown in Table 1, the sorbitol current efficiency at  $0.2 \text{ F mol}^{-1}$  with the 'sorbitol-poisoned' Raney nickel powder was only 17%. In contrast, sorbitol current efficiencies of 70–80% were obtained under similar conditions with freshly activated Raney nickel [1]. HPLC analysis of the catholyte solution showed that no unusual by-products had been formed on the poisoned Raney nickel and the low current efficiency for sorbitol production was attributed to increased hydrogen evolution. This experiment indicated that the sorbitol acts as a Raney nickel catalyst poison in the electrohydrogenation of glucose to sorbitol. Although the activity of the poisoned Raney nickel to electrohydrogenate

Table 1. Regeneration methods for sorbitol-poisoned Raney nickel (divided H-cell electrolysis)

Experiment	Regeneration method	Sorbitol current efficiency at $0.2 \text{ F mol}^{-1}$ (%)
1	No treatment	17
2	Distilled water wash at $60^\circ \text{C}$	14
3	Ethanol wash at $25^\circ \text{C}$	29
4	1.6 M glucose wash at $25^\circ \text{C}$	11
5	0.3 M gluconic acid soak at $60^\circ \text{C}$ for 15 min	50
6	Lactic acid soak at $50^\circ \text{C}$ for 10 min	65
7	17 wt % NaOH soak at $60^\circ \text{C}$ for 90 min	76

Cathode: 2.0 g active Raney nickel, soaked in 0.3 M sorbitol at  $60^\circ \text{C}$  for 24 h. Electrolysis conditions: 1.6 M glucose–0.4 M  $\text{CaBr}_2$  electrolyte, 200 mA applied current,  $\text{pH} = 7$ ,  $T = 60^\circ \text{C}$ .

glucose is significantly lower, it continues to generate molecular hydrogen.

A series of regeneration experiments were performed to reactivate sorbitol-poisoned Raney nickel powder. After carrying out a regeneration procedure on poisoned Raney nickel, the powder was washed with distilled water and then placed back in an H-cell; the electrolysis conditions for all H-cell experiments were: 1.6 M glucose and 0.4 M  $\text{CaBr}_2$ , initial electrolyte composition, 200 mA constant applied current,  $\text{pH} = 7$ , and  $60^\circ \text{C}$ .

Table 1 lists six different regeneration methods which were investigated. Neither hot water nor room temperature ethanol washes (experiments 2 and 3) reactivated the poisoned Raney nickel. In experiment 4 the poisoned powder was washed with a 1.6 M glucose solution, but this procedure also did not reactivate the electrocatalyst. When poisoned Raney nickel was allowed to soak in a 0.3 M gluconic acid solution at  $60^\circ \text{C}$  for 15 min, a threefold increase in sorbitol current efficiency was obtained although the current efficiency was still below that of fresh Raney nickel powder.

A US patent [5] reports on a regeneration method for Raney nickel involving the use of lactic or other organic acids. This reactivation procedure was applied to the sorbitol poisoned catalyst. Equal weights of sorbitol-poisoned catalyst and lactic acid were mixed in distilled water, heated rapidly to  $50^\circ \text{C}$  and held at that temperature for 10 min. The mixture was then neutralized with NaOH and cooled rapidly to  $0^\circ \text{C}$  by adding ice. After washing with

distilled water, the regenerated Raney nickel cathode attained 65% sorbitol current efficiency (Table 1).

The most effective method tested for the regeneration of sorbitol-poisoned Raney nickel powder involved washing the poisoned catalyst with a 17 wt % NaOH solution at  $60^\circ \text{C}$  for 90 min followed by a thorough distilled water rinse. The NaOH solution concentration was identical to that used to activate the Raney nickel–aluminium alloy powder [1]. The sorbitol current efficiency after reactivation increased to 76%.

After the batch H-cell tests the NaOH regeneration procedure was performed during a paired syntheses experiment in the undivided flow reactor. Initially, the paired syntheses was carried out using freshly prepared Raney nickel powder as the cathode. The operating conditions for the flow reactor are the same as those listed in Fig. 1. The sorbitol current efficiencies are shown in Fig. 2. The initial ( $\sim 0.175 \text{ F mol}^{-1}$ ) sorbitol current efficiency was 100%. To increase the rate of catalyst poisoning, the electrolysis was interrupted at point A and sorbitol (0.2 M) was added to the system. The electrolyte was circulated through the reactor for 2 h before electrolysis was resumed. At  $0.21 \text{ F mol}^{-1}$  (point B) the sorbitol current efficiency decreased to 35%. No sugar by-products were detected by HPLC analysis of solution samples and the current losses were attributed to excessive  $\text{H}_2$  evolution.

The catalyst was reactivated at point B

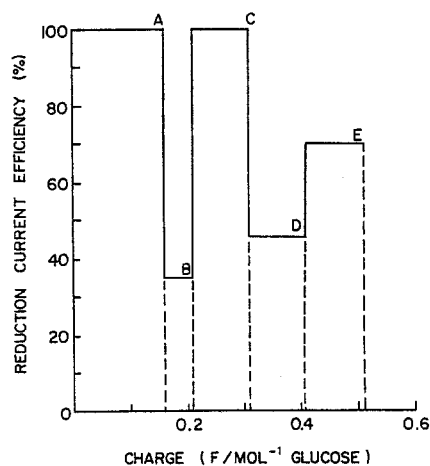


Fig. 2. Sorbitol current efficiencies of sorbitol-poisoned and reactivated Raney nickel powder in a packed bed flow reactor. Reactor characteristics and electrolysis conditions are the same as in Fig. 1. Points A, C: sorbitol addition (0.2M) and 2-h circulation of solution prior to electrolysis. Points B, D: *in situ* regeneration of Raney nickel and addition of fresh solution.

(Fig. 2) by the NaOH wash procedure. First, the electrolyte was drained out of the reactor and the electrode beds were washed with distilled water at 60°C. A 17 wt % NaOH solution at 60°C was then circulated through the reactor for 3 h. After draining the caustic solution from the flow reactor and washing the electrode beds thoroughly with distilled water, electrolysis was resumed using a fresh electrolyte solution containing only 1.6M glucose and 0.4M CaBr<sub>2</sub>. After passing an additional 0.1 F mol<sup>-1</sup> of charge, the sorbitol current efficiency returned to 100% (point C). At 0.31 F mol<sup>-1</sup>, sorbitol (0.2M) was once again added to the system and the electrolyte circulated through the flow reactor for 2 h at open circuit. When the paired syntheses was resumed, the sorbitol current efficiency decreased to 45% (point D).

The current efficiency increased to ~70% after a second *in situ* NaOH regeneration wash, as indicated by point E in Fig. 2. After the second regeneration wash the Raney nickel powder remained agglomerated suggesting that the caustic wash procedure should have been continued for a longer time or more concentrated NaOH solutions should have been used.

### 3.2. The effect of glucose concentration and applied current on sorbitol current efficiencies

Increasing the concentration of glucose in the flow reactor with a poisoned Raney nickel cathode was shown above to have little effect on the low sorbitol current efficiencies. The results of previous flow reactor experiments on the glucose paired syntheses with fresh Raney nickel powder cathode, however, suggest that applied current and glucose concentration affect rates of sorbitol production and hydrogen evolution [1].

The effects of applied current and glucose concentration on sorbitol and gluconic acid current efficiencies were investigated by performing a series of paired syntheses experiments in the undivided packed bed flow reactor. Catalyst poisoning effects were minimized by using fresh Raney nickel catalyst powder (10 g) in each electrolysis run and by limiting in each experiment glucose conversion (to sorbitol) to 0.2 F mol<sup>-1</sup> of initial glucose.

The current efficiency results of the paired syntheses experiments are shown in Table 2. No organic products other than sorbitol and gluconate were detected in electrolysis samples, hence the product yields were very high. The high gluconic acid current efficiencies measured under varying operating conditions were not unexpected. The formation of gluconic acid is a homogeneous bulk phase reaction between glucose and electrogenerated HOBr and is not limited by mass transfer of glucose to the anode surface.

The sorbitol current efficiencies in Table 2 are highest when the glucose concentration is high (e.g. 1.6M) and the applied current is low (e.g. 250 mA or less). Cathodic current losses are attributed to hydrogen evolution. For lower glucose concentrations, 0.4M for example, the sorbitol current efficiency at 250 mA is only 53%. However, 100% sorbitol current efficiencies can be obtained at 0.4M glucose by reducing the applied current to 125 mA. These current efficiency results suggest a preliminary scheme for adjusting the applied current in a series array of electrochemical reactors. For example, if a paired syntheses is to be carried out with complete consumption of glucose (1.6M initial glucose concentration) and

Table 2. The effects of applied current and glucose concentration on current efficiencies of glucose paired reactions (undivided packed bed flow reactor)

I (mA)	Initial glucose concentration (M)	Charge passed (F mol <sup>-1</sup> of glucose)	Current efficiency (%)	
			Sorbitol	Gluconic acid
750	1.6	0.14	75	100
500	1.6	0.30	79 <sup>a</sup>	96 <sup>a</sup>
250	1.6	0.20	100 <sup>a</sup>	100 <sup>a</sup>
	0.8	0.20	75	—
	0.4	0.20	53	—
	0.2	0.46	35	—
200	0.8	0.20	90	100
125	0.4	0.20	100	88
100	0.1	2.0 <sup>b</sup>	17	—

Anode: graphite chips. Cathode: 10 g Raney nickel powder. pH = 5–7; T = 60°C; solution flow rate, 100 ml min<sup>-1</sup>; supporting electrolyte, 0.4 M CaBr<sub>2</sub>.

<sup>a</sup>Data from [1].

<sup>b</sup>After 2.0 F mol<sup>-1</sup>, the glucose concentration was 0.012 M.

oxidation and reduction current efficiencies > 80%, the applied current should be reduced as shown in Table 3. When the glucose concentration reaches ~0.02 M, the electrohydrogenation reaction is essentially controlled by mass transfer of glucose to the Raney nickel surface and ~90% of the cathodic current is consumed by H<sub>2</sub> evolution. Any remaining glucose in solution will react with HOBr to form gluconic acid.

#### 4. Conclusions

Poisoning and reactivation of the Raney nickel cathode during the paired syntheses of gluconic acid and sorbitol from glucose in an undivided flow reactor have been studied. When the reactor was operated continuously for long periods of time, sorbitol current efficiencies decreased from 100% to ~50%. H-cell experiments indi-

Table 3. Relationship between concentration of glucose and applied current for complete consumption of glucose

Glucose concentration (M)	Applied current (mA)
1.6–1.45	500
1.45–1.0	250
1.0–0.6	200
0.6–0.2	100
0.2–0.0	< 100

cated that the decline in the current efficiency was due to poisoning of Raney nickel by sorbitol. An *in situ* catalyst regeneration procedure which consisted of a 17 wt % NaOH solution wash at 60°C for 90 min followed by a thorough distilled water rinse was developed.

The effects of applied current and glucose concentration on the sorbitol and gluconic acid current efficiencies were examined in a series of undivided paired syntheses flow reactor experiments. Sorbitol current efficiencies were high when glucose concentration was high and the applied current low. Gluconic acid current efficiencies were 88–100% for all conditions examined. To maintain high sorbitol current efficiencies as the glucose feed is consumed, the applied current should be decreased in a systematic manner from 500 mA per 10 g of Raney nickel at 1.6 M glucose to < 100 mA per 10 g at 0.2 M glucose.

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