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ELECTROCHEMICALS

PACKED BED REACTOR FOR OXIDATION OF GLUCOSE

C AHMED BASHA and K I VASU
Central Electrochemical Research Institute, Karaikudi-623 006, INDIA
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In order to improve the performance of three dimensional electrodes for synthesis of electroorganic compound, investigations have been carried out in a packed bed reactor of flow-by configuration with batch recirculation system. This paper also deals with some aspects of modelling for such an investigation.

Key words: Packed bed reactor, glucose oxidation, modelling

INTRODUCTION

The heart of any electrochemical process is the cell. As wide range of conditions are required in the cell system, the selection of an optimum cell design is usually difficult. A comprehensive treatment of laboratory cells has been published [1] as well as several reviews on electrolyzers [2-4]. The best cell design is one that meets the following process requirement at minimum cost: (i) the desired productivity, (ii) adequate mass transfer rates for reactant and product, (iii) temperature control, (iv) minimum IR and current efficiency losses, (v) ease of maintenance and (vi) safe operation. The main requirement can be accomplished by raising the current density and/or the active electrode area of cells. Hence the use of three - dimensional electrode has been the recent development for synthesis of electro-organic compounds. The present study is on electro-oxidation of glucose to calcium gluconate in a packed bed reactor. The basic aspects of the indirect oxidation have been studied and reported [4,5]. The oxidation of bromide ion is the potential determining reaction. As the glucose is indirectly oxidized to gluconic acid by the bromine produced insitu on graphite anode, the gluconic acid as formed is fixed up in solution as calcium gluconate by neutralization with calcium carbonate. This paper also deals with some aspects of modelling.

MODELLING

For modelling, the following chemistry based literature is assumed [5-7] :

Anode : $2Br^- \rightarrow Br_2 + 2e$ .. (1)
$2H_2O \longrightarrow O_2 + 4H^+ + 4e$ ..(2)
Cathode : $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ ..(3)
Bulk : $Br_2 + H_2O \longrightarrow HBr + HOBr$ ..(4)
$HOBr + C_6H_{12}O_6 \longrightarrow C_6H_{12}O_7 + HBr$ ..(5)
$2C_6H_{12}O_7 + Ca\,CO_3 \rightarrow (C_6H_{11}O_7)_2Ca + CO_2 + H_2O$ ..(6)

Treating the packed bed electrode unidimensionally, the mass balance equation in the direction of flow along the x- axis, over a small element of length can be written as (mass flow in) — (mass flow out) + reaction = accumulation

$$\text{or} \quad U \frac{dC_A}{dx} = \frac{i_A a}{zF} + kf\,(C_A) \qquad \ldots(7)$$

where $\frac{i_A a}{ZF}$ is the electrochemical reaction rate, $kf(C_A)$ is the chemical reaction rate, C_A is the concentration of species A, i_A is the partial current density for species A, a is the specific surface area of the electrode, U is the superficial electrolyte velocity. Equation 7 can be applied to each of the species of the reaction scheme. At present, the reaction rate will be simply referred to as r_i corresponding to reaction i.

$$\frac{U\,d[Br^-]}{dx} = -2r_1 + r_4 + r_5 \qquad \ldots(8)$$

$$\frac{U\,d[Br_2]}{dx} = r_1 - r_4 \qquad \ldots(9)$$

$$\frac{U\,d[OBr]}{dx} = r_4 - r_5 \qquad \ldots(10)$$

$$\frac{U\,d[G]}{dx} = -r_5 \qquad \ldots(11)$$

$$\frac{U\,d[GA]}{dx} = r_5 - 2r_6 \qquad \ldots(12)$$

$$\frac{U\,d[CG]}{dx} = r_6 \qquad \ldots(13)$$

where G = glucose, GA = gluconic acid and CG = calcium gluconate. In the above mass balance some of the equations relate to active intermediate species Br_2, OBr^- and GA. The concentrations of these intermediates are so small, that there is no significant accumulation of these components in the reactor. Practically the rate of formation of the intermediate is identical to their rate of destruction. In applying this approach to reactor, the active intermediates do not accumulate along the electrode length. Then the equations (9), (10) and (12) reduce to

$$r_1 - r_4 = 0 \qquad \ldots(14)$$

$$r_4 - r_5 = 0 \qquad \ldots(15)$$

$$\text{and } r_5 - 2r_6 = 0 \qquad \ldots(16)$$

The reactant Br^- is transported from the bulk to the electrode surface where it undergoes conversion to Br_2 and transported to bulk by diffusion process.

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$$r_1 = -\frac{d}{dt}[Br^-] = \frac{d}{dt}[Br_2] = \frac{ia}{ZF} \quad ..(17)$$

Assuming Tafel behaviour

$$\frac{i}{ZF} = K_c\, a\, [Br_2]_s \exp(-bE) \quad ...(18)$$

and

$$\frac{i}{ZF} = k_L a\left([Br_2] - [Br_2]_s\right) \quad ...(19)$$

On rearranging, $r_1 = \frac{iA}{ZF} = K_1 [Br_2]$ ...(20)

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k_e e^{-bE}} \quad ...(21)$$

k_e — electrochemical rate constant
k_L — mass transfer coefficient
k_1 — overall rate coefficient
a — specific surface area
$[Br_2]$ — concentration of Br_2 at electrode surface
$[Br_2]$ — concentration of Br_2 at bulk electrolyte

Further $r_4 = K_4 [Br_2]$ ...(22)

$r_5 = K_5 [CG]$ ... (23)

and $r_6 = K_6 [G]$

These expressions may be used in the differential equation (mass balance equation). For knowing the variation of glucose concentration with time, under pseudo steady state condition,

$$\frac{ia}{ZF} = r_1 = r_4 = -r_5 = U\frac{d}{dx}[G] \quad ...(24)$$

$$\text{or} \quad U\frac{d[G]}{dx} = -k_5 [G] \quad ...(25)$$

$$[G]' = [G] \exp\left(-\frac{kaAL}{Q}\right) \quad ...(26)$$

where $U = Q/A\varepsilon$ and $k_5 \simeq ka/\varepsilon$

In a batch recirculation, the reactor volume is small compared with volume of the reservoir, and the mass balance can be written as

$$-V\frac{d}{dt}[G] = Q\left([G] - [G]'\right) \quad ...(27)$$

substituting for $[G]'$ from eq. (26)

$$-V\frac{d}{dt}[G] = Q[G]\left\{1 - \exp\left(\frac{-kaAL}{Q}\right)\right\} \quad (28)$$

Hence $[G] = [G]_0 \exp\left\{\frac{t}{\bar{t}}\left[1 - \exp\left(\frac{-kaAL}{Q}\right)\right]\right\}$ (29)

where $[G]_0$ is the initial concentration of glucose,
V is the volume of the reservoir
$\bar{t} = V/Q$

EXPERIMENTAL

Investigations were carried out for the anodic oxidation of glucose in a single packed bed reactor as shown in figure elsewhere [8]. The cell system consisted of a packed bed anode and a planar graphite electrode as cathode. The packed bed composed of graphite rods of 5mm dia and 12.5 mm length. The graphite rods were stacked such that the circular cross section faced the counter electrode. The complete cell system was fabricated out of a PVC with appropriate provisions for electrical contact and flow. The working electrode had a volume of approximately 70 ml with 40% porosity. Uniform flow of electrolyte through the reactor chamber was achieved using flow distributors. The volume of the reactor was 140 ml and that of the reservoir 2l. The cell belongs to flow by configuration. The electrolyte was recirculated. 20% glucose solution mixed with 2% NaBr was used as the electrolyte. The electrolysis was carried out at constant current. The flow rate was varied from 0.5 Lpm to 2 Lpm. Periodically $CaCO_3$ was added to convert gluconic acid to calcium gluconate, which was analyzed using EDTA.

RESULTS AND DISCUSSION

The results are presented in Tables I and II and Fig. 1 which give the variation of concentration of unreacted glucose with time of electrolysis at different flow rates. At all flow rates, as the reaction proceeds, the concentration of reactant decreases and there is not much difference in the variation of concentration within the range of the flow rates studied. Since the reservoir is a well mix tank, the concentration depletion rate of glucose is exponential as given by eq. (29). The plot of $\ln([G] / [G]_o)$ vs t is also a straight line. The value of rate coefficient was computed from the slope, $\left\{1 - \exp\left(\frac{kaAL}{Q}\right)\right\}/\bar{t}$, of the plot at different values of Q. The data are presented in the Table I. The coefficient increases slightly with flow rate. The current efficiency also improves with flow rate. At higher current density, the temperature of electrolysis is almost doubled in this operating condition, and the coefficient more or less remains constant, but the current efficiency decreases slightly. The temperature effect is not taken while modelling.

In conclusion it can be said that the packed bed can be used for preparation of calcium gluconate, taking advantage of three dimensional electrode.

TABLE-I: Effect of flow rate with the given operating conditions

Volume of electrolyte (reservoir) : 2 litre
Glucose : 485 g; NaBr : 48.5 g
Temperature : 307 - 315K, Duration of electrolysis : 6 hrs.
Current density (apparent) = : 0.6 $kA.m^{-2}$
Current : 2.5A; Cell voltage : 4.3 - 3.8 V

Flow rate (Lpm)	Current efficiency (%)	Overall mass transfer coefficient ($10^{-5}cm.s^{-1}$)
1	69.5	4.98
1.5	70.0	5.00
2	72.5	5.30

TABLE-II: Effect of current density at maximum flow rate

(Duration of electrolysis 1 hr.)

Current density kA.m^{-2}	Current (A)	Cell voltage (V)	Temperature (K)	Current efficiency (%)	Overall mass transfer coefficient (10^{-5}cm.s^{-1})
0.6	2.5	4	313	72	5.3
1.4	11.5	10	353	69	5.6

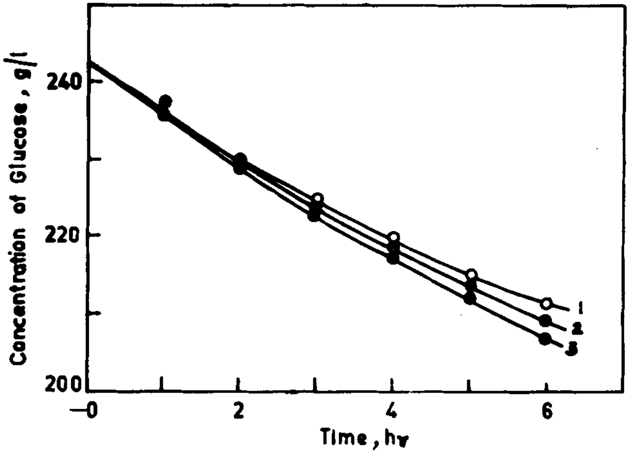

Fig. 1: Variation of concentration of unreacted glucose with time of electrolysis at different flow rate 1 = 1 Lpm; 2 = 1.5 Lpm; 3 = 2.0 Lpm

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