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MACROKINETIC MODEL OF ELECTROCCHEMICAL PARALLEL REACTION

S RAMESH*, S SETHU MADHAVAN* AND C AHMED BASHA

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA
* Students of B.Tech Electrochemical Engineering, Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

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Pair synthesis is the appropriate pragmatic method of energy conservation in electrochemical reactors. In this direction this work is on paired electrosynthesis of sorbital and calcium gluconate from glucose. A sintered nickel matrix is used as cathode and graphite sheet as anode. The feed solution to the reactor contain NaBr, glucose and calcium carbonate. The reaction scheme is modelled. Rate equations are written for each component. Tafel behaviour is assumed. The macrokinetics of the reaction is studied by performing experiment, in a undivided electrochemical parallel plate electrolyzer. The selectivity of sorbital is high below ($2A/dm^2$) and the selectivity of calcium gluconate is high above ($2A/dm^2$)

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INTRODUCTION

Paired synthesis is the appropriate pragmatic method for energy conservation in electrochemical reactors. Essentially in paired sysntesis the wasteful water electrolysis is replaced by a useful electrochemical reaction [1].

The products can be formed directed by electron transfer reaction at the electrode, that is, by a purely electrochemical route as reduction of pthalic acid [2]. The other alternative an intermediate, is formed electrochemically which reacts with the reactants in solutiuon to give the desired product. The formation of sorbital and calcium gluconate take place by the above mechanism.

The applications include electrochemical production receaction in electrowinning of metals. It is also possible to combine electrowinning of zinc and copper from a sulphate electrolyte at cathode with electrochemical production of sodium perchlorate from sodium chlorate at the anode [3].

Principle

The advanced electrocatalytic process for simultaneous electrolytic production of sorbital and calcium gluconate directly from glucose is carried out. A sintered nickel electrode is used as cathode and grahite electrode is used as anode. The feed solution to the reactor contains NaBr, glucose ($C_6H_{12}O_6$) and calcium carbonate. In situ formed bromine at anode reacts with water to form hypobromite (OBr^-) which oxidises glucose to gluconic acid ($C_6H_{12}O_7$). The gluconic acid reacts with $CaCO_3$ resulting in calcium gluconate $Ca(C_6H_{11}O_7)_2$ salt. In-situ generated hydergen at cathode reduces glucose to sorbital [4].

Process modelling in a flow reactor

The sequence of reaction taking place in the system is as follows:

Anode

$$4Br^- \longrightarrow 2Br_2 + 4e \qquad (1)$$

Bulk solution

$$2H_2O + 2Br_2 \longrightarrow 4H^+ + 2OBr^- + 2Br^- \qquad (2)$$

$$2C_6H_{12}O_6 + 2OBr^- \longrightarrow 2C_6H_{12}O_7 + 2Br^- \qquad (3)$$

$$2C_6H_{12}O_7 + CaCO_3 \longrightarrow Ca(C_6H_{11}O_7)_2 + CO_2 + H_2O \qquad (4)$$

Cathode

$$4H^{+} + 4e \longrightarrow 4H \tag{5}$$

$$2C_6H_{12}O_6 + 4H \longrightarrow 2C_6H_{14}O_6 \tag{6}$$

In a parallel plate reactor, assuming plugflow model, the material balance equation for any component A about the whole reactor under steady state is given by:

$$\frac{UdC_A}{dx} = (-r_A) \tag{7}$$

where C_A is the concentration of species A at a distance x along the direction of flow and U is the average superficial velocity. $-r_A$ is the disappearance of species A in the reactor. Expression for each component is as follows

$$\frac{Ud[Br^-]}{dx} = (-4r_2 + 2r_2 + 2r_3) \tag{8}$$

$$\frac{Ud[Br_2]}{dx} = (2r_1 - 2r_2) \tag{9}$$

$$\frac{Ud[OBr^-]}{dx} = (2r_2 - 2r_3) \tag{10}$$

$$\frac{Ud[G]}{dx} = (-2r_3 - 2r_6) \tag{11}$$

$$\frac{Ud[GA]}{dx} = (2r_3 - 2r_4) \tag{12}$$

$$\frac{Ud[CG]}{dx} = (r_4) \tag{13}$$

$$\frac{Ud[S]}{dx} = (2r6) \tag{14}$$

$$\frac{Ud[H^+]}{dx} = (4r_2 - 4r_5) \tag{15}$$

$$\frac{Ud[H]}{dx} = (4r_5 - 4r_6) \tag{16}$$

Where r_j is the rates of individual equation numbered i = 1 to 6. [G], [GA], [CG] and [S] denote concentration of glucose, gluconic acid, calcium gluconic acid and nacent hydrogen, then from equations (9), (10), (12) and (16), the following result are obtained:

$$r_1 = r_2 = r_3 = r_4 \tag{17}$$

and

$$r_5 = r_6 \tag{18}$$

That is, the above equations can be written in reaction kinetics notation in more explicit form as

$$-(1/4)d[Br^-]/dt = -(1/2)d[Br_2]/dt = -(1/2)d[BrO^-]/dt$$

$$-(1/2)d[GA]/dt = d[CG]/dt$$

and

$$-(1/4)d[H^+]/dt = -(1/4)d[H]/dt = (1/2)d[H]/dt$$

The total change in the glucose concentration is given by the sum of the changes due to both the reactions, viz (3) and (6). That is -d[G]/dt = (1/4)d[CG]/dt + (1/2)d[S]/dt.

The bromide is discharged at anode to form bromine is given by the following Tafel equation

$$ia/zF = Ka[Br^-]_s \exp(bE) = -r_1 \tag{19}$$

$$ia/zF = 2Ka[Br_2] \exp(bE) = -r_2 \tag{20}$$

Consequently bromine is converted into hypobromite, then

$$ia/zF = 2Ka[OBr^-]_s \exp(bE)$$

$$= 2Ka[G]_s \exp(bE) = -r_3 \tag{21}$$

Further

$$ia/zF = 2Ka[GA] \exp(bE)$$

$$= -Ka[CG] \exp(bE) = -r_4 \qquad (22)$$

It could be easily understood that hypobromite formed at the anode surface is transported to bulk by convection or glucose is transported from bulk to surface for reaction with in-situ formed hypobromite. Hence

$$ia/zF = k_L\, a\, \{[OBr^-]_s - [OBr^-]_b\}$$

$$= k_L\, a\, \{[G]_b - [G]_s\} \qquad (23)$$

Elimination of $[G]_s$ from equations (21) and (23) resulting to the following equation:

$$ia/zF = k_1 [G]_b \qquad (24)$$

where

$$1/k_1 = 1/k_L\, a + 1/[2k\exp(bE)] \qquad (25)$$

This equation is true if the total consumption of glucose is only for the production of calcium gluconate. Otherwise this expression has to be modified. Hydrogen ion discharges at cathode. The rate of discharge is given by Tafel equations (26)

$$ia/zF = k\,[H] \exp(-b'E) = -r_5 \qquad (26)$$

$$ia/zF = k\,[H] \exp(-b'E) = 2k_c\, [G]_s \exp(-b'E)$$

$$= -2k\,[S] \exp(-b'E) = -r_6 \qquad (27)$$

Hydrogen in-situ generated at the cathode is consumed by glucose at the forming sorbital which is transported to bulk and glucose is transported from bulk to electrode surface by convection for further reaction. Similarly glucose is consumed in anodic reactions also for producing calcium gluconate. Hence, the total rate of depletion of glucose for tye reaction (3) and (6) is given by:

$$ia/zF = -Ud[G]/dx = [k_1 + k_2][G] \qquad (28)$$

where

$$1/k = 1/k_L\, a + 1/(2k_a \exp(bE) \qquad (25)$$

$$1/k = 1/k_L\, a + 1/(2k_c \exp(-b'E) \qquad (29)$$

On integration it becomes

$$[G] = [G]_0 \exp[-(k_1 + k_2) L/U] \qquad (30)$$

The fractional yields of calcium gluconate (Y_{ca}) and sorbital (Y_s) are given by the following equations:

$$Y_{CG} = -d[CG]/d[G] = r_4/2(r_4 + r_6) = k_1/2(k_1 + k_2) \qquad (31)$$

$$Y_s = -d[S]/d[G] = 2r_6/2(r_4 + r_6) = k_2/(k_1 + k_2) \qquad (32)$$

and the point selectivity of calcium gluconate with respect to sorbital is given by:

$$S = -d[CG]/d[S] = r_4/2r_6 = k_1/2k_2 \qquad (33)$$

On integration we get

$$[CG] = (k_1/2k_2)\ S \qquad (34)$$

$$\text{as } [CG]_0 = [S]_0 = 0$$

A plot of $-Ud[G]/dx$ vs $[G]_b$ or $\text{In}[G]/[G]_0$ vs L/U gives the slope ($k_1 + k_2$ and a plot of [CG} vs [S] gives the slope $k_1/2k_2$. From these slopes individual k_1 and k_2 can be obtained.

Experimental process

The studies are carried out in a single pass undivided, parallel plate electrolytic reactor of the monopolar type. Graphite anode and nickel cathode are placed alternatively in the cell. The electrolyte of the specified composition are passed through the reactor and the flow rate is fixed. The concentration of sorbital and calcium gluconate is analysed for current density of $2A.dm^{-2}$ for four different flow rates. The effect of flow rate on concentration of sorbital and calcium gluconate is studied. The operational yield and selectivity of the products are compared [5]. Calcium gluconate is analysed by EDTA titration and sorbital is

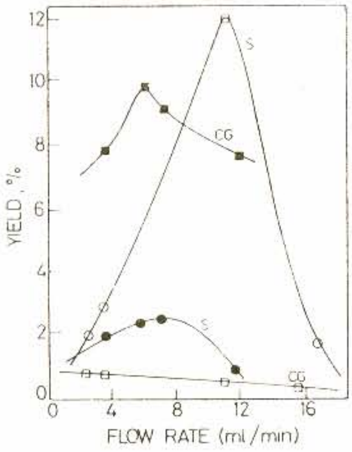

Fig. 1: Variation of yield with flow

C.D.	*1.5 A.dm^{-2}*	*2.0 A.dm^{-2}*
Y_{CG}	□	■
Y_S	○	●

estimated iodometrically. The same sets of experiments were repeated at 1.5/dm^2.

RESULTS AND DISCUSSION

In parallel plate reactor the yield of product is dependent on the flow rate of electrolyte for a fixed current density. The yield of the products is maximum only at an optimum flow rate (Fig. 1) in both the operating current densities. The yield of products are increasing at low flow rates. From same figure it can also be noted that the yield of calcium gluconate is more than sorbital at current density of 2A/dm^2, whereas yield for sorbital is more than calcium gluconate at current density of 1.5 A/dm^2. At low flowrates the yield of the products increase because the residence time for the reactant is high.

CONCLUSION:

As energy conservation being the need of the hour, we propose paired synthesis as a principle idea for use in industries. By modelling of the system it is inferred that the concentration of glucose and its products follows the usual trend of parallel reactions. A plot of -Ud[G]/dx Vs [G] gives the slope $k_1 + k_2$. This can be solved for obtaining k_1 and k_2. In parallel plate reactor the yield of sorbital and calcium gluconate depends on the flow rate and current density. Generally at low flow rates the yield is high and low at high flow rates due to bromine, hydrogen escaping out. It is maximum only at an optimum flow rate. Only at this flow rate, the rate of chemical reaction and rate of electrochemical reaction are equal. The selectivity of sorbital is high at 1.5 amp/dm^2 and selectivity of calcium gluconate is high at 2amp/dm^2.

List of symbols

a	—	specific electrode area
b'	—	Tafel slope for cathodic polarozation
b	—	Tafel slope for anodic polarozation
[CG]	—	Concentration of calcium gluconate
E	—	Electrode potential
F	—	Faraday constant (96485 C/mol)
[G]	—	Concentration of glucose
[GA]	—	Concentration of gluconic acid
i	—	Total current density
k_L	—	Mass transfer coefficient
k_a	—	Hetorogeneous rate constant for anodic process
k_c	—	Hetorogeneous rate constant for cathodic process
k_1	—	See eqn.(25)
k	—	See eqn.
L	—	Length of the reactor
r	—	Rate of reaction
[S]	—	Concentration of Sorbital
S	—	Selectivity of A with respect to B
U	—	Superficial Velocity
x	—	Electrode length
Y	—	Yield
z	—	Number of electron transfer

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