EQUIVALENT RESISTANCES FOR CURRENT PATHWAYS IN A BIPOLAR PACKED-BED ELECTRODE CELL

KATSUKI KUSAKABE, SHIGEHARU MOROOKA AND YASUO KATO
Department of Applied Chemistry, Kyushu University, Fukuoka 812

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The electric currents flowing through the pathways existing in a bipolar packed-bed cell (BPBE cell) were calculated by use of an equivalent resistance model which was a modification of the King-Wright model for the bipolar rod cell. The bypass, Faradaic, and total currents were shown as functions of the resistance coefficient, the specific conductivity of electrolytic solution, the number of bipolar layers, and the decomposition voltage.

In the BPBE cell, graphite pellets of 4.74 mm diameter and 5 mm length were packed in layers which were separated by plastic nets. Methoxylation of furan was studied, where bromine was used as mediator.

The resistance coefficient for the bypass current was evaluated from experimental results and the Bruggeman equation. The resistance of the total current flowing in the open space of the insulation net was affected by the cell configuration, such as the arrangement of the insulation nets. In the reactor under discussion, the reaction resistance was negligible, and the respective currents through the pathways could be represented by the model proposed. The overall current efficiency based on the total current and the energy consumption were also evaluated. The intrinsic current efficiency based on the Faradaic current of the reaction was more than 0.9.

Introduction

The bipolar packed-bed electrode cell (BPBE cell, hereafter) is composed of a number of electroconductive particles packed between two feeder electrodes, and each particle works as a bipolar electrode when the terminal voltage of the packed cell is high enough. It is thought that the overall current efficiency based on the total current is related to the cell geometry, the electrical conductivities of both electrolyte and solid particles, and the current density or the reaction rate, though details have not been clarified as yet.^{6,7,9,12)}

Furan is an important intermediate for industrial chemicals.¹⁰⁾ The electrochemical methoxylation of furan to 2,5-dimethoxy-2,5-dihydrofuran (DMDHF) can be carried out with either an undivided disk-stack cell³⁾ or a pump cell,⁴⁾ so that the BPBE cell must also be a candidate.

This paper deals with the analysis of the current pathways in the BPBE cell for methoxylation of furan. The current efficiency and the energy consumption for the reaction are also discussed.

1. Experimental Apparatus and Procedure

The BPBE cell used in this work consisted of three compartments: top, center and bottom; it was made of a glass cylinder of 7.5 cm diameter. The length of the center compartment was 6 cm, and the total length was 16 cm. The top and bottom compart-

ments were equipped with respective feeder electrodes, as shown in Fig. 1. The distance between the feeder electrodes was the same as the length of the center compartment. Each electrode was composed of a perforated graphite plate, 5 mm thick and having 168 holes of 3-mm diameter in a triangular arrangement of 5-mm pitch. The open area of the perforated plates was about 27%.

Graphite pellets of 4.74 mm diameter and 5.0 mm length were packed between the two feeders. These packings were made of the same material as that of the feeder electrodes (EG 38 supplied by Nippon Carbon Co.). Polyethylene net of 1 mm thickness was used as the insulating spacer. The fiber diameter of the net was 0.6 mm and the openings were 2.07 mm square. The packed column was divided into n layers by inserting the plastic nets. Packings were also separated from the feeder electrode by the same nets. The actual distance between adjacent pellet layers was around 1.5 mm. About 172 pellets were packed at random in each layer.

Methanol solution of furan containing NaBr and NaNO₃ was used as the electrolytic solution. The furan concentration in the make-up solution was kept constant at 82.7 or 165 mol·m⁻³. On the other hand, the concentrations of NaBr and NaNO₃ were varied in the ranges of 0.97–39 and 0–10.6 mol·m⁻³, respectively. The operating temperature was 293 K in most cases. The solution conductivity was measured with a conventional Kohlrausch bridge at 1 kHz. The solution was stored in a 1-liter reservoir at constant

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Fig. 1. Schematic diagram of bipolar packed-bed electrode cell.

temperature and usually pumped to the cell at a superficial velocity of $21 \text{ cm} \cdot \text{s}^{-1}$. The electrolyzer and the reservoir were sealed to avoid leakage of bromine generated.

Electrolysis was conducted at constant voltage. The amount of electricity passed was measured with a coulometer. The concentrations of furan and the product in the electrolyte were determined by gas chromatography with a separation column of PEG 20M at a specified time interval. The current efficiency was measured every 500–1000 C with the exception of prolonged electrolysis.

The electric current passing through a pellet (Faradaic current) was evaluated by using monitor electrodes* embedded at three positions in the column.

The relationship between the cell voltage and the amperage of a flat-plate graphite electrode was obtained in a separate cell. The working electrode was 2 cm wide and 3 cm high, and the electrode gap was 7 mm. The electrolyte was composed of $97 \text{ mol} \cdot \text{m}^{-3}$ of NaBr and $165 \text{ mol} \cdot \text{m}^{-3}$ of furan in this case, and was agitated with a magnetic stirrer. The ohmic drop between the flat-plate electrodes was measured with a Kohlrausch bridge at 1 kHz.

2. Equivalent Circuit Model

A proposed model for the electrical circuit in the BPBE cell is illustrated in Fig. 2. It is a modification of the King-Wright model for a bipolar rod cell.⁵⁾ The total current, I_t , passing through the open space of the insulation net is represented as follows:

$$I_t = I_p + I_b \quad (1)$$

where I_p is the Faradaic current, and I_b is the bypass current. The bypass resistance for I_b and the sandwich resistance for I_t are reciprocally proportional to the solution conductivity:

* A pellet was cut into halves, and a thin paper was sandwiched between them as an insulator. The lead wires were pasted in the two halves to monitor the electric current. See details in ref. 7.

Fig. 2. Equivalent circuit established in bipolar packed-bed electrode cell.

$$R_b = A_b / \kappa \quad (2)$$

and

$$R_s = A_s / \kappa \quad (3)$$

where A_b and A_s are resistance coefficients which depend on the geometry and the arrangement of packings. Electrolysis may take place when the potential difference between the two sides of a graphite pellet, e , is larger than the decomposition voltage, e_d . Thus the Faradaic current is as follows:

$$I_p = (1/R_p)(e - e_d) \quad (4)$$

where R_p is the equivalent reaction resistance for the electrochemical reactions on the surface of the electrodes. The number of working layers in the column is considered as $(n+1)$ because the feeder electrode is also working. The potential difference between the two sides of a pellet is represented by

$$e = I_b R_b = (I_t - I_p) A_b / \kappa \quad (5)$$

The cell voltage is

$$E = (n+1)(e + I_t R_s) \quad (6)$$

From Eqs. (1)–(6), we have

$$I_t = \frac{\kappa}{(n+1)} \frac{(\kappa R_p + A_b)E - (n+1)A_b e_d}{(A_b + A_s)\kappa R_p + A_b A_s} \quad (7)$$

$$I_b = \frac{\kappa}{(n+1)} \frac{\kappa R_p E - (n+1)A_s e_d}{(A_b + A_s)\kappa R_p + A_b A_s} \quad (8)$$

$$I_p = \frac{\kappa}{(n+1)} \frac{A_b E - (n+1)(A_b + A_s)e_d}{(A_b + A_s)\kappa R_p + A_b A_s} \quad (9)$$

The overall current efficiency based on the total current, C_e , and the energy consumption, E_c , are represented as follows:

$$C_e = z F C_{MF} W / (I_t t) \quad (10)$$

and

$$E_c = z F E / (C_e M_{MF}) \quad (11)$$

where C_{MF} is the molar concentration of DMDHF, W

the electrolyte volume, t the time of electrolysis, and M_{MF} the molecular weight of DMDHF. The number of charge transfer, z , is 2 in this case.

The Faradaic current may flow through the packed layers in series in the BPBE cell. Therefore, Eq. (12) can be obtained from Eq. (10).⁶⁾

$$C_e = (I_p n + I_t) \eta / I_t \quad (12)$$

where η is the intrinsic current efficiency based on I_p . Substituting Eqs. (7)–(9) into Eq. (12), we have

$$C_e = \frac{[\{\kappa R_p + (n+1)A_b\}E - \{(n+1)A_b + nA_s\}(n+1)e_d]\eta}{(\kappa R_p + A_b)E - (n+1)A_b e_d} \quad (13)$$

With an assumption of very small R_p in comparison with both R_b and R_s , Eqs. (14)–(17) are obtained from Eqs. (7)–(9) and (13) as follows:

$$I_t = \kappa \{E - (n+1)e_d\} / \{(n+1)A_s\} \quad (14)$$

$$I_b = \kappa e_d / A_b \quad (15)$$

$$I_p = \kappa \{A_b E - (n+1)(A_b + A_s)e_d\} / \{(n+1)A_b A_s\} \quad (16)$$

and

$$C_e = \frac{[A_b E - \{(n+1)A_b + nA_s\}e_d](n+1)\eta}{\{E - (n+1)e_d\}A_b} \quad (17)$$

On the other hand, when electrolysis occurs only on the feeder electrode, the total current is as follows:

$$I_t = \{\kappa(E - e_d)\} / \{nA_b + (n+1)A_s\} \quad (18)$$

3. Results and Discussion

Furan methoxylation and volt-ampere curves The reaction sequence of the electrochemical methoxylation of furan is shown by Eqs. (19)–(21).¹¹⁾

At the anode:

In the bulk of solution:

At the cathode:

As indicated by Eq. (20), bromine generated at the anode works as a mediator for methoxylation.

Figure 3 shows the volt-ampere curves of a cell equipped with a pair of flat-plate graphite electrodes. The superficial decomposition voltage obtained by projection of a straight line to zero current was ca. 2.5 V. The volt-ampere curve was virtually parallel to the ohmic voltage drop with the exception of the low-current density ranges. This was attributed to a large solution resistance compared to the electrode polariza-

Fig. 3. Volt-ampere curves of a cell equipped with a pair of flat-plate electrodes.

tion. No significant change in solution conductivity was found during electrolysis since the solution contained a sufficient amount of the independent electrolyte.

Resistance coefficient The denominator of Eq. (18) represents the cell constant of the column when the pellets are not polarized. With the Bruggeman equation, we have

$$nA_b + (n+1)A_s = \varepsilon_l^{-1.5} L_T / S_T \quad (22)$$

where ε_l is the volume fraction of the electrolyte phase, L_T the cell length, and S_T the sectional area of the cell. The applicability of the Bruggeman equation was discussed in the previous paper.⁶⁾

The sandwich resistance depends on the arrangement of the insulation nets and the pellets. The relationship between the voltage and the current was measured by changing the number of pellet layers (n) and the number of insulation nets (n_0) in the same solution. As shown in **Fig. 4**, the value of A_s/n_0 increased with decreasing n_0 , and for $n_0=1$ it was estimated to be 0.64 m^{-1} .

Applicability of model **Figure 5** shows that the overall current efficiency increases with increasing number of layers and cell voltage. The solid lines indicate the calculated values from Eq. (17). At high cell voltages, C_e reaches $(n+1)\eta$. The intrinsic current efficiency is close to unity in the range $E \geq 50 \text{ V}$. The broken line in **Fig. 5** indicates C_e at $n=10$ and $n_0=1$, with a spacer thickness of 0.3 mm . No significant variation in current efficiency with the thin spacer was found.

Figure 6 shows that the total current passing through the BPBE cell increases with increasing electrical conductivity of the solution. The experimental results agree well with the solid lines calculated from Eq. (14).

NaBr serves as a current carrier and an anode depolarizer. To evaluate these roles, the NaBr concentration was decreased about one order of magnitude. The electrolyte conductivity was adjusted by adding NaNO_3 as an indifferent salt. **Figure 6** also

Fig. 4. Effect of cell arrangement on resistance coefficient for a sandwich electrolyte.

Fig. 5. Effect of cell arrangement on overall current efficiency.

Fig. 6. Effects of cell voltage and electrolyte conductivity on total current.

shows no significant effect of NaBr concentration on the amperage.

Figure 7 indicates that the Faradaic current obtained by using the monitor electrodes agrees with Eq. (16) in the range $E \geq (n+1)e_d$. Thus the bypass current is in agreement with Eq. (15). In the range $E \leq (n+1)e_d$, the total current follows Eq. (18) with Eq. (22). Experimental results under other conditions also depend on Eqs. (15), (16) and (18), as shown in Fig. 4.

Fig. 7. Breakdown of total current to Faradaic and bypass currents.

Current efficiency The intrinsic current efficiency decreased with increasing NaBr concentration, as shown in Fig. 8. Also, the higher the temperature the larger was the current efficiency. According to Ogumi *et al.*,⁸⁾ Br₂ generated at the anode is consumed by the reaction:

The equilibrium of the reaction shifts to the right-hand side when the NaBr concentration increases. Tribromide ions are reduced to Br⁻ at the cathode, resulting in current inefficiency. Therefore, electrochemical methoxylation must be conducted at high temperatures so that Br₂ dissolved in the solution participates in the chemical reaction quickly, even in concentrated NaBr solutions.

Figure 9 shows the time dependency of the current efficiency at constant cell voltage. Both the overall and the intrinsic current efficiencies decreased gradually with electrolysis time, but the intrinsic current efficiency was still larger than 0.88 even at 90% conversion of furan. Polymerization of furan and the successive reactions of DMDHF might be factors in the gradual decrease in current efficiency.²⁾ Similar results to Fig. 9 were obtained at cell voltages higher than 60 V.

Energy consumption The energy consumption for producing DMDHF is shown in Fig. 10. The reaction rate vs. energy consumption curves calculated by Eqs. (10), (11) and (17) with $\eta = 1.0$ are illustrated in Fig. 10. The broken lines represent the energy consumption at constant voltage. The reaction rate increased but the current efficiency decreased with increasing NaBr concentration. The flow rate of electrolyte was a small factor in the current efficiency in the range 2.3–45.2 cm·s⁻¹. However, the electrolytic solution must be circulated to some extent, to eliminate accumulation of hydrogen bubbles in the bed.

Conclusion

The electric current passing through the bipolar packed-bed electrode cell was calculated by using an

Fig. 8. Effects of NaBr concentration and temperature on overall current efficiency.

Fig. 9. Overall current efficiency for prolonged electrolysis.

Fig. 10. Relationship between energy consumption and production rates for a sectional area of pellet layers.

equivalent circuit model which was a modification of the King-Wright model for the bipolar rod cell.⁵⁾ The total, bypass and Faradaic currents can be described by Eqs. (14), (15) and (16), respectively, when the reaction resistance is negligible. The resistance for the sandwich circuit was a function of the arrangement of pellets and spacers. Experimental results of the volt-ampere curve in the bipolar packed bed agreed with calculation.

When the pellets were not polarized, electrolysis occurred only at the feeder electrodes, and the total current was well described by Eq. (18) and (22).

Equation (17) was feasible for calculating the overall current efficiency based on the total current. The

intrinsic current efficiency for the methoxylation of furan was close to unity.

Nomenclature

A_b	= resistance coefficient for bypass current	[m ⁻¹]
A_s	= resistance coefficient for total current passing sandwich electrolyte	[m ⁻¹]
C_e	= overall current efficiency defined by Eq. (10)	[-]
C_{MF}	= molar concentration of 2,5-dimethoxy-2,5-dihydrofuran	[mol·m ⁻³]
E	= cell voltage	[V]
E_c	= energy consumption	[J·kg ⁻¹]
e	= potential difference between ends of pellets	[V]
e_d	= decomposition voltage	[V]
F	= Faraday constant	[C·mol ⁻¹]
I_b	= bypass current	[A]
I_p	= Faradaic current	[A]
I_t	= total current	[A]
j	= current density	[A·m ⁻²]
L_T	= distance between feeder electrodes	[m]
M_{MF}	= molecular weight of 2,5-dimethoxy-2,5-dihydrofuran	[kg·mol ⁻¹]
n	= number of bipolar pellet layers	[-]
n_0	= number of insulating spacers between pellet layers	[-]
R_b	= equivalent bypass resistance	[Ω]
R_p	= equivalent Faradaic resistance	[Ω]
R_s	= equivalent sandwich resistance	[Ω]
S_T	= cross-sectional area of cell	[m ²]
t	= electrolysis time	[s]
W	= volume of electrolyte	[m ³]
z	= number of electrons involved in electrode reaction	[-]
ϵ_1	= volume fraction of electrolyte phase in column	[-]
κ	= electrolyte conductivity	[S·m ⁻¹]
η	= intrinsic current efficiency defined by Eq. (12)	[-]

Literature Cited

- 1) Bruggeman, D. A. G.: *Ann. Physik.*, **24**, 636 (1935).
- 2) Clauson-Kaas, N., F. Limbolg and K. Glens: *Acta Chem. Scand.*, **6**, 531 (1952).
- 3) Jansson, R. E. W. and M. Fleischmann: *AIChE Symp. Ser.*, **75** (185), 2 (1979).
- 4) Jansson, R. E. W. and N. Tomov: *Chem. Ind.*, Feb. 96 (1978).
- 5) King, C. G. H. and A. R. Wright: *Electrochim. Acta*, **22**, 1135 (1977).
- 6) Kusakabe, K., T. Kimura, S. Morooka and Y. Kato: *J. Chem. Eng. Japan*, **17**, 293 (1984).
- 7) Kusakabe, K., S. Morooka and Y. Kato: *J. Chem. Eng. Japan*, **15**, 45 (1982).
- 8) Ogumi, Z., S. Ohhashi and Z. Takehara: *Nippon Kagaku Kaishi*, 1788 (1984).
- 9) Robertson, P. M.: "Engineering Aspect of Electrosynthesis," University of Waterloo, May 30 (1973), cited by Fahidy, T. Z.: *Can. J. Chem. Eng.*, **51**, 512 (1973).
- 10) Taniguchi, M.: *Kagaku Keizai*, June 35 (1981).
- 11) Torii, S.: *Yuuki Gousei Kagaku*, **32**, 161 (1974).
- 12) Yoshimura, S., A. Katagiri and S. Yoshizawa: *Nippon Kagaku Kaishi*, 1144 (1978).