ENERGY CONSUMPTION IN A NOVEL ELECTROLYZER HAVING A VERTICAL STACK OF PERFORATED GRAPHITE PLATES AS BIPOLAR ELECTRODES

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A novel electrochemical reactor having a vertical stack of perforated graphite plates as bipolar electrodes was investigated by using the electrolysis of sodium bromide. The ratio of Faradaic current to reactor current was explained by an equivalent circuit model which consisted of bypass, sandwiched solution and Faradaic resistances.

Energy consumption for bromine production was influenced by liquid flow regime such as continuous flow or trickle flow and by introducing inert gas countercurrently. Effects of flow regimes of liquid and gas on energy consumption were clarified by the changes of Faradaic current efficiency and the ratio of Faradaic current to total reactor current with the electrode potential difference between the two sides of a bipolar plate.

Introduction

To design an effective electrochemical reactor having bipolar electrodes, considerable efforts are needed for increasing Faradaic current and decreasing short-circuit and bypass currents. Bipolar packed-bed electrodes were experimentally studied by Yoshizawa *et al.*^{17,18)} for waste water treatment and by Kusakabe *et al.*¹⁴⁾ regarding current paths and electrolysis efficiency. A bipolar rod flow cell was designed and studied by King *et al.*^{11,12)} on the ratio of Faradaic current to reactor current, and applied by Goodridge *et al.*^{1,10)} to electrochemical production of propylene oxide. A bipolar trickle bed consisting of carbon Raschig rings or perforated plates was examined by Jansson *et al.* for organic synthesis,^{2,7,8,9)} pollution control of cyanide-containing effluent^{5,6)} and recovery of metal.⁴⁾

Recently, Kusakabe *et al.*¹³⁾ reported the effect of solution electroconductivity on the overall current efficiency in bipolar packed-bed electrodes. Sasaki *et al.*¹⁶⁾ discussed the bypass resistance of bipolar disk electrodes with a network model.

The purpose of this study is to clarify the characteristics and the energy consumption of a novel electrochemical reactor having a vertical stack of perforated graphite plates as bipolar electrodes. Experimental studies were made with electrolysis of aqueous solution of sodium bromide in this reactor.

1. Experimental Apparatus and Procedures

The bipolar electrochemical reactor, schematically

shown in Fig. 1, was a cylindrical column made of transparent polyacrylate resin. The dimensions were 5 cm in inner diameter and 50 cm in height. Ten perforated plates of graphite, 5 cm in diameter and 1 cm thick, were used as bipolar electrodes. Figure 2 shows schematic diagrams of two kinds of graphite plates. The A type plate had 13 holes of 8 mm diameter and with right triangular pitch, and the B type plate had 12 holes of the same diameter and with square pitch. Five plates of A type and five of B type were arranged by setting A type and B type alternately. The distance H between two plates was 5 mm for most experiments. For the experiments shown in Fig. 9, however, the distance was 2 mm or 1 cm. The top and bottom plates were used as feeder electrodes and connected with a stabilized D.C. power source (NISTAC, NC-12010M). The fifth plate from the bottom was sliced into two equivalent plates, and an insulating plate of polyvinyl chloride resin was inserted between them as shown in Fig. 1. The two separated plates were electrically connected with platinum wire of 0.5 mm diameter by using electroconductive adhesive of graphite powder and epoxy resin, and the Faradaic current I_f through this wire was measured by the galvanometer shown in Fig. 1. Spaces above and below the stack of perforated plates were packed with glass spheres of 1 cm diameter. An electrolyte was dispersed uniformly on the glass sphere packings with the liquid distributor. The experiments were carried out in continuous-flow and trickle-flow regimes. For continuous-flow operation, nitrogen gas was introduced from the column bottom and flowed countercurrently to liquid flow. For trickle-flow operation, no gas was fed to the reactor.

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Fig. 1. Schematic diagram of apparatus.

Fig. 2. Detail of perforated graphite plates (A type, 5 cm in diameter; 8 mm ϕ $\times$ 13 holes; $\phi = 0.333$. B type, 5 cm in diameter; 8 mm ϕ $\times$ 12 holes; $\phi = 0.307$).

The electrolyte was a 0.1 mol $\cdot$ dm $^{-3}$ aqueous solution of sodium bromide and its temperature was 291–293 K. The electroconductivity of the electrolyte was adjusted with sodium sulfate and measured by a conductivity cell (Toa, CM-30ET). Total resistance of the electrolyte sandwiched between bipolar plates was obtained by measuring A.C. resistance between feeder electrodes at 1 kHz. The electrolyte was sampled from the outlet of the reactor, and the concentration of bromine in the electrolyte was determined by iodometric titration in aqueous sulfuric acid.

2. Equivalent Circuit Model

The equivalent circuit shown in Fig. 3 consists of the bypass resistance r_b , the Faradaic resistance r_f of a bipolar plate and the sandwiched solution resistance r_s between two electrodes. Similar network models for bipolar particles were reported by Robertson *et al.*¹⁵⁾ and King *et al.*¹²⁾

Total sandwiched solution resistance R_s is given as follows.

$$R_s = (N_B + 1)r_s \quad (1)$$

where N_B is the number of bipolar plates. Reactor resistance R_t is defined by the ratio of voltage and current between feeder electrodes, and is given as

Fig. 3. Equivalent circuit model.

follows.

$$R_t \equiv E/I_t = (N_B + 1)r_s + r_f' + \{N_B r_b r_f / (r_b + r_f)\} \quad (2)$$

The Faradaic resistance r_f' of feeder electrode in Eq. (2) can be ignored because r_f' is much smaller than $(N_B + 1)r_s$ or $N_B r_f$. At low voltage before bipolarity begins, r_f is larger than r_b . Then the total resistance R_b is given by the following equation on the basis of Eq. (2).

$$R_b \equiv (E/I_t)_o = (N_B + 1)r_s + N_B r_b \quad (3)$$

From Eqs. (1)–(3), r_s , r_b and r_f are obtained as follows, respectively.

$$r_s = R_s / (N_B + 1) \quad (4)$$

$$r_b = (R_b - R_s) / N_B \quad (5)$$

$$r_f = (R_t - R_s)(R_b - R_s) / \{N_B(R_b - R_t)\} \quad (6)$$

Then the ratio of the Faradaic current I_f to the reactor current I_t is given by the following equation.

$$I_f/I_t = r_b / (r_b + r_f) = (R_b - R_t) / (R_b - R_s) \quad (7)$$

When the voltage E is applied between feeder electrodes, the difference of electrode potential between the two sides of a bipolar plate, E_B , is given by using Eq. (2) as follows.

$$E_B = I_t r_b r_f / (r_b + r_f) = (E - I_t R_s) / N_B \quad (8)$$

E , I_t , I_f and R_s are measured experimentally. R_t and R_b , respectively, are calculated from Eqs. (2) and (3) with the measured values of E and I_t . E_B is calculated from Eq. (8) with the measured values of E , I_t and R_s .

3. Faradaic Current Efficiency and Energy Consumption

Electrode reactions at both sides of a bipolar electrode are given below.

Anodic reactions:

Cathodic reaction:

The Faradaic current efficiency of bromine generation, $C_{e,f}$, is defined by the ratio of experimental bromine production to the theoretical value. The latter is given by $(N_B I_f / nF)$, if the reactions at feeder electrodes are ignored and only the reaction of Eq. (9) is assumed to occur at the bipolar electrodes.

$$C_{e,f} = Q_L C / (N_B I_f / nF) \quad (12)$$

where C is the bromine concentration at the outlet of the reactor and Q_L is the liquid flow rate.

The energy consumption per mole of bromine produced, E_C , is obtained as follows.

$$E_C = I_t E / (Q_L C) \quad (13)$$

With Eqs. (12) and (13), E_C is arranged to the following equation.

$$E_C = n F E I_t / (I_f N_B C_{e,f}) \quad (14)$$

Equation (14) indicates that the following conditions are necessary for decreasing energy consumption.

- (i) Bipolarity begins at low voltage E .
- (ii) $C_{e,f}$ has high value for slightly higher value of E_B than bipolarity beginning voltage.
- (iii) The ratio of I_f/I_t is increased by reduction of bypass current.

4. Results and Discussion

4.1 Faradaic current

Figure 4 shows reactor currents and Faradaic currents at different reactor voltages. Bipolarity of the plates between feeder electrodes began at about 20 V of reactor voltage. Then Faradaic current began to be observed. The broken lines in Fig. 4 are the Faradaic currents calculated from Eq. (7) with the experimental values of I_t , R_b , R_t and R_s . The calculated values of I_f agree well with the experimental values in the trickle-flow regime. In the continuous-flow regime, however, the deviations between calculated and observed values are large at high voltage, where oxygen and hydrogen gases are vigorously evolved by electrolysis of water and the total bypass resistance R_b is larger than the value measured from A.C. resistance. Reactor current and Faradaic current for continuous flow are larger than those for trickle flow. This is because the effective surface area of the electrode is reduced for trickle flow.

4.2 Effects of U_L and U_G on resistances

Figure 5 shows r_s , r_b and r_f calculated at $E_B = 2.5$ V for various flow rates of electrolyte. The gas holdup ε_G in the sandwiched space is estimated by Eq. (15), Bruggemann's equation,³⁾ and is also shown in Fig. 5.

$$\varepsilon_G = 1 - (r_{s0}/r_s)^{2/3} \quad (15)$$

where r_{s0} is the resistance of the sandwiched solution at $\varepsilon_G = 0$. In the trickle-flow regime, r_b , r_s , r_f and ε_G decrease with increasing U_L . Gas holdup in the holes

Fig. 4. Relations of reactor current and Faradaic current to reactor voltage.

Fig. 5. Resistances of equivalent circuit and ε_G at different liquid velocities.

of a perforated plate is supposed to decrease with increasing U_L . r_b and r_s are dependent on gas holdup. Then, the decreases in r_b and r_s with increasing U_L might be due to the decrease in gas holdup. The decrease in r_f with increasing U_L might be caused by the enhancement of liquid-solid mass transfer rate of bromide ion. Since the change of r_f/r_b is small at various U_L , the change of I_f/I_t value calculated from Eq. (7) at various U_L is expected to be small.

Figure 6 shows that, with increasing U_G in the continuous-flow regime, r_b , r_s and ε_G increase but r_f decreases. The increase in r_b and r_s with increasing U_G might be caused by decreased liquid holdup in the holes of the perforated plate and increasing ε_G . Meanwhile, the decrease in r_f might be caused by increasing liquid-solid mass transfer rate with increasing U_G . Then, with increasing U_G , the ratio of r_f/r_b

Fig. 6. Resistances of equivalent circuit and ε_G at different gas velocities.

Fig. 7. Relations between outlet concentration of bromine and reactor voltage at different regimes of liquid flow.

decreases and I_f/I_t calculated from Eq. (7) increases. Therefore, an introduction of gas into the reactor reduces energy consumption in the continuous-flow regime.

Figures 5 and 6 show that ε_G in the trickle-flow regime is much higher than that in the continuous-flow regime. Therefore, the resistances in the trickle-flow regime become much higher than those in the continuous-flow regime.

4.3 Effects of flow regime and electroconductivity on bromine concentration at reactor outlet

Figure 7 shows the relation between the outlet concentration C of bromine and reactor voltage E in different flow regimes. C increases and approaches a saturated value as reactor voltage increases. In trickle flow, C is lower than that in continuous flow at the same reactor voltage. This is because I_f in trickle flow is lower than that in continuous flow, as shown in Fig.

Fig. 8. Relations between energy consumption and reactor voltage at different liquid velocities.

Fig. 9. Relations between energy consumption and reactor voltage at different gas velocities and at different distances between two bipolar perforated plates.

4. In continuous flow with gas introduction, C is higher than that in continuous flow without gas. An introduction of gas increases the liquid-solid mass transfer rate, and then C becomes higher with increasing U_G .

4.4 Effects of flow regime, U_L , U_G and electroconductivity on energy consumption

Figure 8 shows the relation between energy consumption and reactor voltage at different liquid velocities. E_C has its minimum value at a certain value of E . In the trickle-flow regime, the voltage at the minimum value of E_C seems to increase with increasing U_L . At low reactor voltage, I_f/I_t is much smaller than unity. At high reactor voltage, the value approaches unity but $C_{e,f}$ is low because of water electrolysis. The broken straight lines in Figs. 8, 9 and 11 indicate the theoretical value of E_C when $I_f/I_t=1$ and $C_{e,f}=1$.

Energy consumption is reduced by increased gas velocity in the continuous-flow regime, as shown in Fig. 9. In comparison with the results in Fig. 8, E_C shows a steep curve dependent on E , and the minimum value for E_C is larger than that in the electrolyte of low conductivity. The latter phenomenon is also observed in the trickle-flow regime.

The effects of distance H between two plates on E_C is also shown in Fig. 9. The voltage at the minimum value of E_C is lower as the distance becomes shorter. This is because bipolarity begins at lower voltage in the reactor having shorter distance and lower value of R_s .

Figure 10 shows the effects of E_B and the flow regime on $C_{e,f}$ and I_f/I_t . The values of $C_{e,f}$ were calculated from Eq. (12) by using measured values of C and I_f . The Faradaic current efficiency had its maximum value at $E_B \approx 2.7$ V in the trickle-flow and the continuous-flow regimes. Since anodic reactions are two competitive reactions as described in Eqs. (9) and (10), the values of $C_{e,f}$ were calculated from the ratio of net current for water electrolysis to Faradaic current.

$$(C_{e,f})_{\text{cal.}} = 1 - I_{f,w}/I_f \quad (16)$$

where $I_{f,w}$ indicates the Faradaic current obtained by water electrolysis in aqueous solution of the same electroconductivity without sodium bromide. The upper part of Fig. 10 shows that the observed values of $C_{e,f}$ agree well with the calculated ones in the range above 2.3 V. In the lower part of Fig. 10, the observed values of I_f/I_t are compared with those calculated from Eq. (7). Agreement is fairly good in the trickle-flow regime. In the continuous-flow regime, there is a large deviation between the values when E_B is higher than 2.5 V. As with the explanation of Fig. 4, this is due to the fact that gas evolving by water electrolysis makes R_b higher than the initial value. I_f/I_t in continuous flow increases with gas velocity, and this is caused by the increase in bypass resistance. I_f/I_t in trickle flow is larger than that in continuous flow, since r_f/r_b in trickle flow is smaller than that in continuous flow. As mentioned above, E_C is influenced by $C_{e,f}$ and I_f/I_t . Then, E_C is assumed to have its minimum value at about 2.7 V of E_B .

Figure 11 shows that E_C values observed agree well with those calculated from Eq. (14) by using $C_{e,f}$ obtained by Eq. (16) and I_f/I_t given by Eq. (7). Therefore, E_C could be predicted fairly well with the equivalent circuit model, if the contribution of water electrolysis to $C_{e,f}$ was taken into consideration.

Both trickle flow and continuous flow with gas introduction reduced energy consumption. The bromine concentration at the reactor outlet for the latter operation is higher than that in the trickle-flow operation, as shown in Fig. 7. Thus energy con-

Fig. 10. Relations of Faradaic current efficiency and the ratio of Faradaic current to reactor current at various electrode potential differences between the two sides of a bipolar electrode.

Fig. 11. Comparison between experimental values of energy consumption and values calculated from the model.

sumption and space time yield for bromine generation might be improved by introducing gas into the liquid continuous flow.

Conclusion

For the continuous-flow regime (countercurrent gas-liquid flow), the energy consumption E_C for bromine production was reduced by increasing gas velocity.

For the trickle-flow regime (no gas flow), E_C was almost constant at liquid velocity up to 0.9 cm s^{-1} and increased with further increase in liquid velocity.

Low electroconductivity favored the reduction of

E_C for the continuous-flow and the trickle-flow regimes. However, the bromine concentration at the reactor outlet was higher for the higher electro-conductivity.

Since water electrolysis was predominant above 2.7 V of E_B , $C_{e,f}$ reached a maximum value and then decreased with increasing E_B . E_C had its minimum value at about 2.7 V of E_B .

The value of I_f/I_t was predicted fairly well with an equivalent circuit model. The value of $C_{e,f}$ was estimated from the experimental results of water electrolysis. The effects of flow regimes of liquid and gas on E_C were clarified by the changes of I_f/I_t and $C_{e,f}$ with the electrode potential difference between the two sides of a bipolar plate.

An introduction of gas into the liquid continuous flow might be effective in improving energy consumption and space time yield of bromine production.

Nomenclature

C	= concentration of bromine produced	[mol·m ⁻³]
$C_{e,f}$	= Faradaic current efficiency	[—]
E	= reactor voltage between two feeder electrodes	[V]
E_B	= electrode potential difference between the two sides of a bipolar plate	[V]
E_C	= energy consumption per mole of bromine produced	[J·mol ⁻¹]
F	= Faraday's constant	[C·mol ⁻¹]
H	= distance between two perforated plates	[m]
I_f	= Faradaic current of a bipolar plate	[A]
$I_{f,w}$	= Faradaic current of a bipolar plate when only water electrolysis occurs	[A]
I_t	= reactor current between feeder electrodes	[A]
N_B	= number of bipolar perforated plates between feeder electrodes	[—]
n	= stoichiometric number of anodic reaction on electrode	[—]
Q_L	= liquid flow rate	[m ³ ·s ⁻¹]
R_b	= total bypass resistance	[Ω]
R_s	= total sandwiched solution resistance	[Ω]
R_t	= reactor resistance	[Ω]
r_b	= bypass resistance	[Ω]
r_f	= Faradaic resistance	[Ω]
r'_f	= Faradaic resistance of feeder electrode	[Ω]
r_s	= sandwiched solution resistance between two bipolar perforated plates	[Ω]

r_{s0}	= r_s for continuous flow when $\varepsilon_G=0$	[Ω]
U_G	= superficial gas velocity	[m·s ⁻¹]
U_L	= superficial liquid velocity	[m·s ⁻¹]
ε_G	= gas holdup in sandwiched solution	[—]
κ	= electrolyte conductivity	[S·m ⁻¹]
ϕ	= proportion of free area of a perforated plate	[—]

<Subscripts>

o	= value at low voltage where bipolarity is not observed
cal.	= calculated value

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