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The Behavior of Pellet Packed-bed Electrodes Reactor
−Graphite Pellet Electrode−

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펠레트 충전층 전극 반응기의 특성
−흑연 펠레트 전극−

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Abstract: For describing the bipolar packed-bed electrode cell filled with graphite pellete electrode, the application of the model of equivalent circuit was studied. The ratio between the Faradaic current through bipolar electrodes and the applied current was dependent on the resistance coefficient, specific conductivity of electrolyte, and electrolyte circulation rate. The ratio of the Faradaic current through bipolar electrodes to the applied current increased with the applied current(or cell voltage), but decreased with the increase of electrolytic conductivity and circulation rate of the electrolyte.

요 약: 흑연 펠레트 전극으로 채워진 복극성 고정상 충전층 전극 반응기에 대하여 등가회로 모델을 적용하여 반응기에 가해진 전류에 대한 복극성 전극에 흐른 Faradaic 전류의 비를 전해액의 전도도와 순환속도에 대하여 검토하였다. 전전류에 대한 Faradaic 전류의 비는 인가전류(전압)에 따라 증가하며, 전해액 전도도와 액 순환속도의 증가에 따라 감소하였다.

1. Introduction

The bipolar packed-bed electrode cell (BPBE cell, hereafter) is composed of electroconductive particles or pellets packing between two feeder electrodes, and each particle works as a bipoar electrode when the terminal voltage of the cell is high enough. The distance of each bipolar electrode is almost of 1mm and the effective electrode area per unit cell volume become larger than $10cm^{-1}$. The simple configuration and operation are also attractive features of the BPBE cell. BPBE cells were studied for waste-water treatment by Yoshizawa *et al.* [1, 2] and for regarding current paths and electrolysis efficiency by Kusakabbe *et. al.* [3]. King had been designed the bipolar rod flow cell[4] and compared the ratio of Faradaic current to reactor current. Also Goodridge applied this to electrochemical synthesis of propylene oxide[5]. A bipolar trickle bed consisting of carbon raschig rings or perforated plates were examined by Jansson *et al.* for organic synthesis[6-9], pollution control of cyanide-containing effluent[10], and metal recovery [11].

The applied current to a bipolar electrode system is separated into the Faradaic current passing through the bipolar electrode and the bypass current passing through the electrolyte. Design of an effective electrochemical reactor consisted with bipolar electrodes required the increase of Faradaic current and decrease bypass current and short circuit. The relation between the charateristics of the Faradaic process at the bipolar electrode and the resistance of the bypass current in the electrolyte should be otained to confirm the effectiveness of the BPBE. In those models, the resistance according to the Faradaic current which is referred to as a Faradaic resistance expressed in constant or variable, but the resistanc according to the bypass part which is referred to as a bypass resistance expressed in constant. The former is determined by the charateristics of the Faradaic process and the latter, by the shape(length, cross section, and hold-up) of the bypass part and the specific resistance of the electrolyte.

The purpose of this study is to clarify the characteristics of novel electrochemical reactor having a packed-bed graphite pellets as bipolar electrodes.

2. Experimental apparatus and procedure

The BPBE cell used in this work was consisted of three compartments: top, center and bottom. The center compartment(packed-bed part) was made of a pyrex glass cylinder of 7cm in diameter and 5cm in length. The top and bottom compartments were equipped with respective electrodes of current feeders, as shown in Fig. 1. Each feeder was composed of the perforated graphite plate, 5㎜ thick and had 168 holes of 2㎜ diameter in a triangular arrangement of 3㎜ pitch. The open area of the perforated plates was about 27%. Graphite pellet of 5㎜ in diameter and 5㎜ in length were packed between the two feeders. These pellets were made of the same material as that of the feeder(♯EG 38 graphite, Nippon Carbon Co.). The pellets were packed in nine layers separated by inert mesh spacers, thickness of 1㎜, over the bottom feeder. The plain cutting-faces of the pellet was vertical to the direction of the electrical current flow. Spaces above and below the stack of feeder plates were packed with glass spheres of 5㎜ in diameter in order to the electrolyte was dispersed uniformly. The cross sectional area of the feeder was 32.33㎠. The total projected suface area of the pellets was 40.5㎠ which was roughly equal to the total cathodic area and total anodic area of the bipolar pellets.

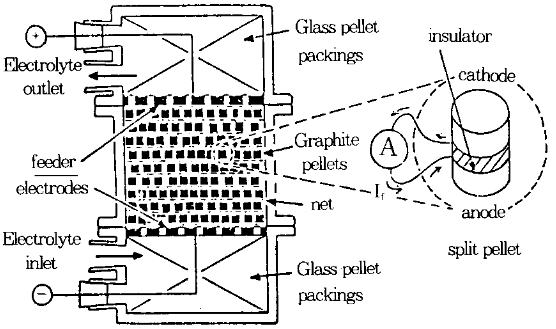

Fig. 1. Schematic view of bipolar packed-bed electrode cell and composite pellet for measuring Faradaic current.

A spacially split pellet electrode as shown in Fig. 1 was substituted for the center of the packed-bed to determine the decomposition voltage and the Faradaic current through the bipolar bed. A graphite pellet was sliced perpendicularly to its axis and an insulator was placed between the two halves of the pellet, which was electrically connected with a short circuit wire, and the halves were joined with epoxy resin adhesive to resume their original shape.

The test electrolyte was methanol and its temperature was 293-303K. The electrolyte was 350mℓ in volume and circulated with a roller pump. The electroconductivity of the electrolyte was adjusted with sodium borofluoride and measured by a conductometer. Total resistance of the electrolyte sandwiched between bipolar pellets was obtained by measuring A. C. resistance between two feeders at 1 kHz.

3. Equivalent circuit model

A proposed model for the electrical circuit in the BPBE cell is illustrated in Fig. 2. It is a modification of similar network models for bipolar particle and rod cell[5], which was reported by Roberston *et al*[12] and King *et al*[4].

The equivalent circuit shown in Fig. 2 consists of the bypass resistance(r_b), the Faradaic resistance (r_f) of a bipolar electrode and sandwiched solution resistance(r_s) between two packed pellets.

Total sandwiched solution resistance R_s and total bypass resistance R_b is given as follow;

$$R_s = (n+1)r_s,\ r_s = A_s/\kappa \qquad (1)$$

$$R_b = (n+1)\ r_s+nr_b,\ r_b = A_b/\kappa \qquad (2)$$

where A_s and A_b are resistance coefficients which depend on the geometry, arrangement of packings, and the solution conductivity κ. n is the number of bipolar electrode layers in the cell.

Reactor resistance R_t is defined by the ratio of voltage, E to the applied current, I_t between feeders. The results is given as follow.

$$R_t = E/I_t = (n+1)r_s+[n\ r_b\ r_f/(r_b+r_f)] \qquad (3)$$

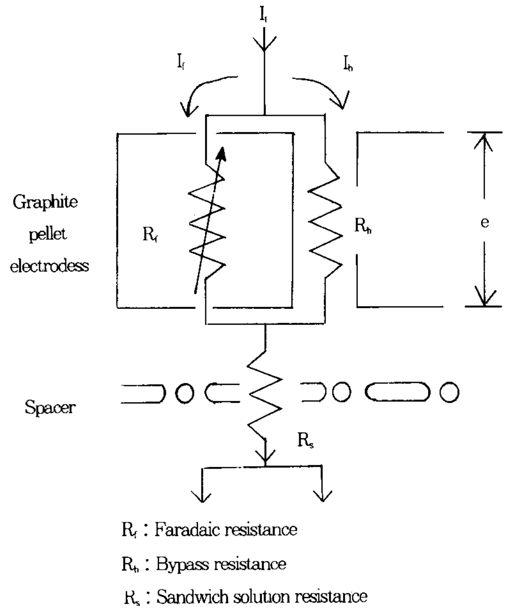

Fig. 2. Equivalent circuit established in bipolar packed-bed electrode cell.

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

$$r_s = R_s/(n+1) = A_s/\kappa \qquad (4)$$

$$r_b = (R_b-R_s)/n = A_b/\kappa \qquad (5)$$

$$r_f = (R_t-R_s)(R_b-R_s)/n(R_b-R_t) \qquad (6)$$

The total reactor current I_t for r_s, passing through the open space of the insulation net is represented as follows;

$$I_t = I_f+I_b \qquad (7)$$

where I_f is the Faradaic current for r_f, and I_b is the bypass current for r_b.

Electrolysis may take place when the potential difference between the two sides of a graphite pellet, e, is lager than the decomposition voltage, e_d. The Faradaic resistance expressing a decomposition voltage and reaction resistance are represented by a variable resistance at the model, because of the non-linearity of the current-voltage characteristics (polarization curve) of the Faradaic process. Thus the Faradaic current is

$$I_f = (e-e_d)/r_f \qquad (8)$$

When the cell voltage E is applied between the two feeders, the potential difference can be represented by

$$e = I_b\ r_b = (I_t-I_f)\ r_b = I_t\ r_b\ r_f/(r_b+r_f) = (E-I_t\ R_s)/(n+1) \qquad (9)$$

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

$$I_f/I_t = r_b/(r_b+r_f) = (R_b-R_t)/(R_b-R_s) \qquad (10)$$

From Eqs. (1)－(10), I_t, I_b, and I_f are

$$I_t = n(e-e_d)/(R_t-R_s) = n\ E/(n+1)(R_t-R_s) \qquad (11)$$

$$I_b = n(R_t-R_s)(e-e_d)/(R_t-R_s)(R_b-R_s) \qquad (12)$$

$$I_f = n(R_b-R_t)(e-e_d)/(R_t-R_s)(R_b-R_s) \qquad (13)$$

E, I_t, I_f and R_s can be measured experimentally. R_t and R_b, respectively, are calculated from Eqs. (3) and (5) with the measured values of E and I_t. e is calculated from Eq. (9) with the measured values of E, I_t and R_s.

On the other hand, when electrolysis occurs only on the feeder, the applied current is

$$I_t = (E-e_d)/[n\, r_b+(n+1)\, r_s] = (E-e_d)/R_b \quad (14)$$

4. Results and discussion

Fig. 3 shows the curves of cell voltage-applied current and cell voltage-Faradaic current in the BPBE cell. Bipolarity of the pellets between feeder plates began at about 27V of reactor voltage. Then Faradaic current began to be observed. Broken lines are the Faradaic current calculated from Eq. (13) with 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 this study. However, the slight deviations between calculated and observed values at higher voltage was caused from vigorous evolution of oxygen and hydogen gases by electrolysis. It was also found that the total bypass resistance R_b was larger than the value measured from A.C. resistance.

The bypass current density through the electrolyte phase was propotional to the conductivity of the electrolyte, κ, and was given by a modification of Bruggeman's equation[13].

$$I_b/S = \alpha\kappa(1-\varepsilon_l)^{3/2}\, E/L \quad (15)$$

where S is the sectional area of the pellets, α is the cell constant, ε_l is the volume fraction of electrolyte phase in reactor, and L is the distance between two feeder plates.

The values of r_s and r_b could be estimated by Bruggeman's equation.

$$R_b = (1/\alpha\kappa)\,(1-\varepsilon_l)^{-1.5}\, L/S \quad (16)$$

$$\kappa\alpha[n\, r_b+(n+1)\, r_s] = \varepsilon_l^{-1.5}\, L/S \quad (17)$$

$$n\, A_b+(n+1)\, A_s = \varepsilon_l^{-1.5}\, L/S \quad (18)$$

The values of r_s and r_b were calculated to be 5.5Ω and 41.7Ω in this case. Then r_f is 1.1Ω. Also, the values of A_s and A_b are 0.638 and 4.8m^{-1}.

The Faradaic current through the bipolar electrode was determined using the split electrode at the various applied current. Fig. 4 indicates that the

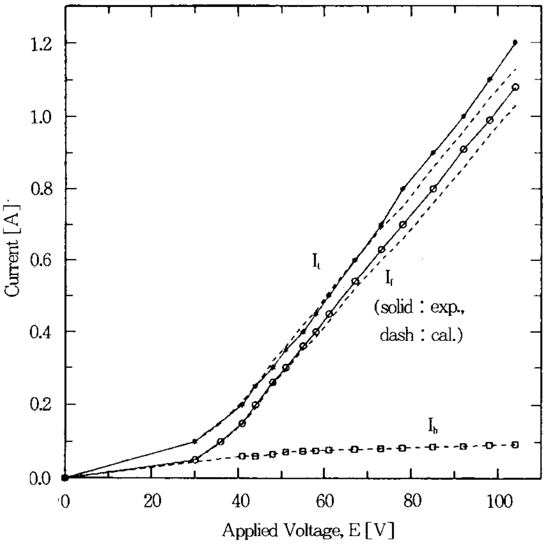

Fig. 3. Breakdown of total current to Faradaic and bypass currents. 0.02M NaBF$_4$; eletrolyte conductivity, 0.116Sm^{-1}; apparent resistance between current feeders, 56 ohm, 298 K. (—) : experimental (…) : theoretical

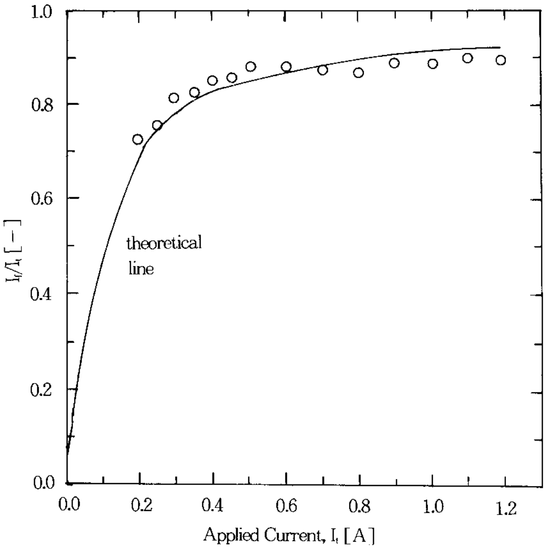

Fig. 4. Plot of I_f/I_t according to various applied current in 0.01M NaBF$_4$. Circulation rate of electrolyte : 840ml/min. (○) : measured (—) : theoretical

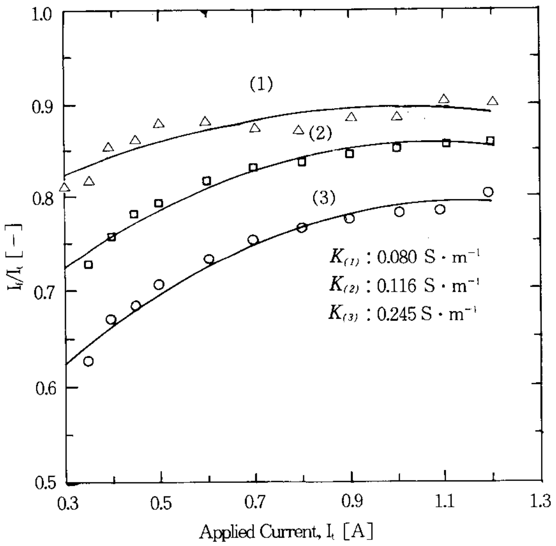

Fig. 5. Plot of I_f/I_t vs. applied current according to the electrolyte condition. Circulation rate of electrolyte: 840ml/min
(1) : 0.01M $NaBF_4$
(2) : 0.02M $NaBF_4$
(3) : 0.04M $NaBF_4$

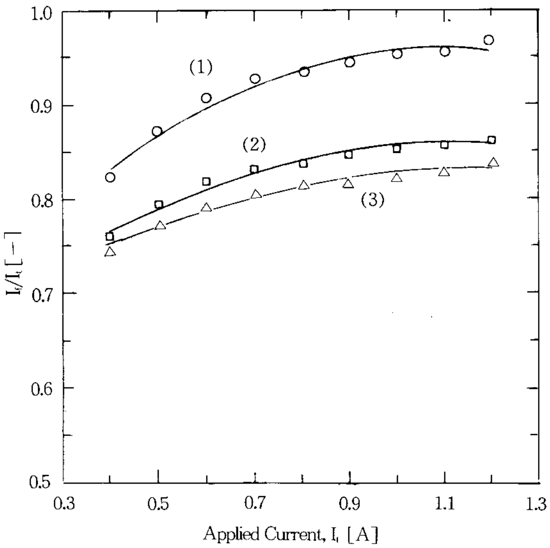

Fig. 6. The ratio of I_f/I_t on the circulation rate in 0.02M $NaBF_4$.
(1) : 130 ml/min
(2) : 840 ml/min
(3) : 1560 ml/min

ratio of I_f/I_t had average value of 0.85 when I_t exceeds 0.4~1.2 A and measured values well agreed with calculated value(Eq. 10) by the use of the equivalent circuit model. The bipolar electrode system could be expressed in terms of a bypass resistance.

The effect of the elecrolyte conductivity on the ratio of I_f to I_t is shown in Fig. 5. An excessive addition of $NaBF_4$ increases the electrolyte conductivity and consequently decreases the potential gradient in the cell under the condition of constant current. This causes a loss of the effective anode area.

Fig. 6 shows that the ratio of Faradaic current to total current passing through the pellets increases with decreasing circulation rate of the electrolyte. This is due to the fact that gas evolving by electrolysis makes the bypass resistance R_b or r_b higher than the initial value. The lower flow rate means the higher gas hold-up. I_f/I_t increases with gas hold-up (decreasing flow rate), and this is caused by the increase in the bypass resistance.

4. Conclusion

A method for measuring the Faradaic current through the bipolar electrode has been developed by the use of a modified split electrode in the compactly packed cell.

It has been shown that the simple equivalent circuit model of the bipolar electrode system must be modified considering the effects of a variable resistance to the bypass part. The ratio of Faradaic current through bipolar electrodes to the applied current of the reactor increases with the applied current(or cell voltage), whereas it decreases with electrolytic conductivity and circulation rate of the electrolyte.

Acknowledgement

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Nomenclature

A_b : resistance coefficient for bypass current $[\mathrm{m}^{-1}]$
A_s : resistance coefficient for total current passing sandwich electrolyte $[\mathrm{m}^{-1}]$
E : cell voltage [V]
e : potential difference between each side of pellet [V]
e_d : decomposition voltage [V]
I_b : bypass current [A]
I_f : Faradaic current [A]
I_t : total current [A]
L : distance between feeder plates [m]
n : number of bipolar pellet layers [−]
r_b : equivalent bypass resistance $[\Omega]$
r_f : equivalent Faradaic resistance $[\Omega]$
r_s : equivalent sandwiched solution resistance between two bipolar pellet layer $[\Omega]$
R_b : total bypass resistance $[\Omega]$
R_s : total sandwiched solution resistance $[\Omega]$
R_t : total reactor resistance $[\Omega]$
S : cross-sectional area of cell [m]
α : reactor constant $[\mathrm{m}^{-1}]$
ε_l : volume fraction of electrolyte phase in reactor [−]
κ : electrolyte conductivity $[\mathrm{S} \cdot \mathrm{m}^{-1}]$

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