

ELECTROCHEMICAL ACTIVITY OF FLUIDIZED BED ELECTRODES (FBEs) INSERTED ELECTRO-CONDUCTIVE PARTITION PLATES

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Key Words: Fluidized Bed Electrode, Particle Activity, Conductive Partition Plate, Electrolysis, Copper Electrodeposition, Rectangular Cell

Using a rectangular cell with three fluidized-bed electrodes (RTFBEs) separated by two electro-conductive partition plates (ECPs), the electrodeposition of copper from CuSO_4 solution was carried out to examine the electrochemical activity of the respective fluidized beds (FBs).

The particles in each FB were activated as an electrode by the bipolar action of the ECP. Their activity depended on the material of the ECP, the electro-conductivity of the solution and the bed expansion. The current efficiency of copper electrodeposited on fluidized particles using copper or copper-plated Pt plates as ECPs was higher than that using Pt plates. Since the bed thickness in the direction of the electric current could be effectively increased by inserting the ECPs, the electrolytic capacity in this type of cell with FBEs was found to be considerably large compared to that in a cell with a single FBE.

Introduction

In the fluidized-bed electrode (FBE) method, the fluidized particles having electrical conductivity are utilized as an electrode. The FBE has a large electrode surface area and a high electrolytic capacity compared to cells without particles such as the filter press cell.⁴⁾ However, to maintain the activity of particles as an electrode, bed expansion must be controlled in the range of about 10–40%,³⁾ and the bed thickness in the direction of electric current (i.e., the effective bed thickness of the FBE) must be controlled within 0.8–2.0 cm.^{1,2,8–10)} These two limitations are clearly obstacles to increasing the feed rate of electrolyte. For the treatment of a large quantity of industrial wastes within a short time, it is necessary to increase the inlet area of electrolyte, that is, the effective bed thickness. However, only Heiden *et al.*⁷⁾ have reported on an attempt to increase the effective bed thickness.

Insertion of electro-conductive partition plates (ECPs) into the fluidized bed (FB) is expected to increase the bed thickness. In this method, the aim is to activate particles as an electrode by utilizing the bipolar action of the ECP and by the collision of particles with the ECP. In this study, the electrodeposition reaction of copper from CuSO_4 solution was carried out in a rectangular cell with three FBEs (RTFBE). The factors affecting the activity of particles as an electrode in each FB were first in-

vestigated. The electrolytic capacity and the power consumption of rectangular cell were also studied.

1. Activation Mechanism as an Electrode of FB by ECP

In the electrolysis of CuSO_4 solution, the reactions shown in Eqs. (1) and (2) occur at the insoluble cathode and the anode respectively.

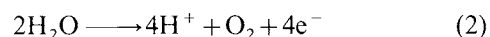
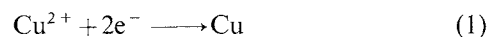


Figure 1 shows a rectangular cell where an insoluble ECP and a diaphragm D_2 are inserted between the diaphragm D_1 and the counter electrode in the FBE and the particles are fluidized between ECP and D_2 . If the ECP acts a bipolar electrode, the reaction of Eq. (2) occurs on plane A of the ECP and the electrons are supplied to the ECP. On the other hand, two processes of electron transfer occur on plane C of the ECP. One is Type A in which copper electrodeposits on plane C by the reaction of Eq. (1). Another is Type B in which electrons transfer to the particles by collision between the ECP and the particles and among the particles, and the electrodeposition of copper occurs at the surface of particles which gained electrons from plane C. If the transfer like Type B occurs, the FB between ECP and D_2 can be regarded as a FBE. Thus, enlargement of the effective thickness of fluidized bed may be also expected by inserting some sets of such a type of FB between feeder

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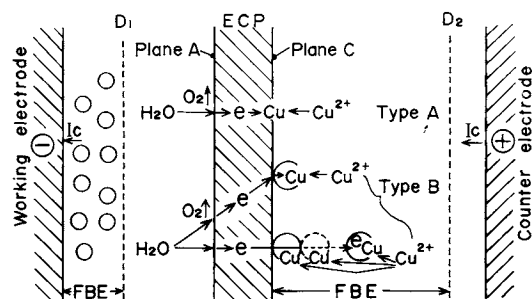


Fig. 1. Electron transfer mechanism at the ECP: D_1 , D_2 , diaphragm; e , electron; I_c , cell current; FBE, fluidized bed electrode; \bigcirc , electro-conductive particle

electrodes.

2. Experimental

2.1 Apparatus

A schematic diagram of the RTFBE is shown in Fig. 2. The apparatus comprised three parts made of polyvinyl chloride (PVC): the cell, and the influent and effluent electrolyte vessels. The rectangular cell ($9 \times 4.2 \text{ cm}^2$ in cross-sectional area and 8 cm in height) was divided into three FBs by inserting two ECPs and three sheets of diaphragms. These three FBs are termed respectively bed 1, bed 2 and bed 3 from the one close to the working electrode. The bed thickness of each FB is 1.8 cm, and the width of each anode cell including the anode plate or the ECPs, etc. is 1.2 cm. A cation-exchange membrane was used as the diaphragm and was attached to the PVC plates, in which many holes of 1 mm diameter had been drilled.

2.2 Electrode and ECP

The working and counter electrodes, and the ECP, were all $4.2 \times 8 \text{ cm}^2$ in size. A copper plate or platinum plate was employed as the working electrode. A graphite plate was employed as the counter electrode. Three kinds of ECPs were used: a platinum plate (Pt-ECP), a copper plate (Cu-ECP), and a platinum-copper plate (Pt·Cu-ECP) in which copper was plated on one side of the platinum plate. The thicknesses of the Pt-ECP, the Cu-ECP and Pt·Cu-ECP were 0.5, 1.0 and 1.0 mm respectively. Combinations of materials used respectively as the working and counter electrodes and the ECPs are shown in Table 1.

2.3 Particle

In each FB (obliquely hatched portions in Fig. 2), copper-coated glass particles of 2.62 mm in average diameter were used. The total surface area S_p of particles in each FB was 767.7 cm^2 at a bed expansion of 20% and 657.98 cm^2 at that of 40%. Coating of copper was conducted by the same procedures as those described in the previous paper.¹⁰⁾

2.4 Electrolyte

As a catholyte, aqueous solutions of $0.041\text{--}0.14 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$, $50 \times 10^{-3} \text{ kg} \cdot \text{dm}^{-3} \text{ C}_2\text{H}_5\text{OH}$

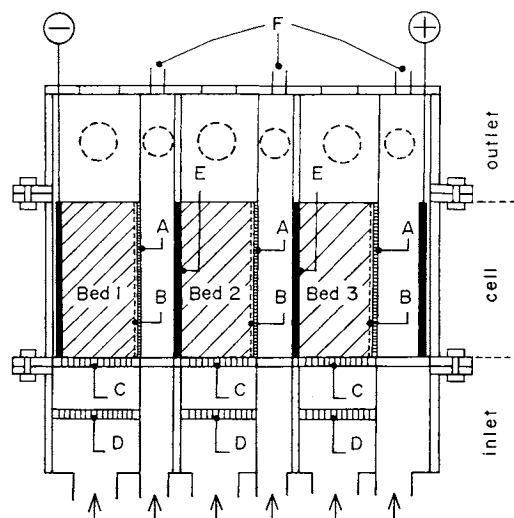


Fig. 2. Schematic diagram of experimental apparatus: A, PVC plate; B, diaphragm; C, D, distributor; E, ECP; F, gas drain; \rightarrow , electrolyte inlet; \bigcirc , electrolyte outlet

Table 1. Combinations of materials used as working and counter electrodes, and ECPs: $E=20\%$; $I_c=1 \text{ A}$; $\kappa_L=2.96 \text{ S} \cdot \text{m}^{-1}$

	WE	ECP ₁	ECP ₂	CE	V_c [V]
Type I	Cu	Pt	Pt	C	11.45
Type II	Cu	Cu	Cu	C	7.12
Type III	Pt	Pt	Pt	C	11.90
Type IV	Cu	Pt·Cu	Pt·Cu	C	10.67

WE, working electrode; CE, counter electrode; V_c , average cell voltage.

and $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ CuSO}_4 \cdot 5\text{H}_2\text{O}$ were employed. An aqueous solution of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ was used as an anolyte. These electrolytes flowed into the cell through the head tanks and circulated back to the reservoirs. The temperature of the electrolyte was kept at 313 K.

2.5 Electrolysis

The electrolysis was carried out under a constant cell current ranging from 1 to 2 A and bed expansions of 20 and 40%. The quantity of electricity was monitored by a coulometer. The electrolytic time was constant at 1 h. That is, the quantity of electricity was 3600 C at 1 A and 7200 C at 2 A. Concentration change of Cu^{2+} in the electrolyte was neglected, since the reduction of Cu^{2+} concentration in the electrolyte was below 1.0% of the initial Cu^{2+} concentration. The amount of electrodeposition of copper was determined from the difference between weights of the particles dried before and after electrolysis.

3. Result and Discussion

3.1 Activity of FB as an electrode

1) Effect of current density and bed expansion on current efficiency Figure 3 shows the relationship

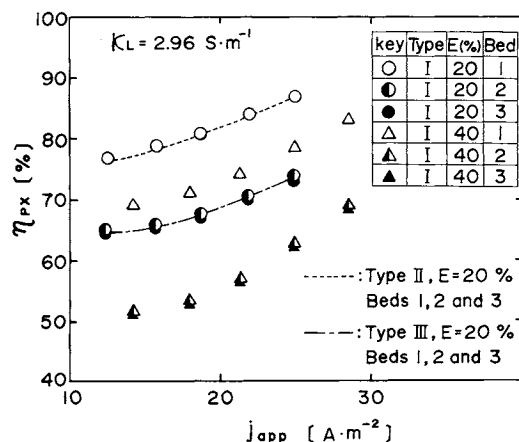


Fig. 3. Relationship between η_{px} and j_{app} for Types I, II and III

between the apparent current density j_{app} and the current efficiency η_{px} in the X-th FB, where the η_{px} value was calculated from Eqs. (3) and (4) with the amount W_{px} of electrodeposition on the surface of particles.

$$\eta_{px} = (W_{px}/m) \times 100 \quad (\%) \quad (3)$$

where m is the calculated amount of electrodeposition of copper when the quantity of electricity is q and is expressed by the following equation.

$$m = 3.293 \times 10^{-7} \times q \quad (4)$$

The bed expansion E and j_{app} were determined from Eqs. (5) and (6) respectively. In the present work, H_f was 8 cm and H_p was changed by the volume of particles.

$$E = \{(H_f - H_p)/H_p\} \times 100 \quad (\%) \quad (5)$$

$$j_{app} = I_c / (S_p + S_c) \quad (6)$$

The η_{px} value tended to increase with increasing j_{app} for all the beds but did not reach 90% at maximum value. The η_{px} value was found to be about 100% when j_{app} was in the range of 1–2 A·dm⁻² for electrolysis with a pair of flat electrodes.¹¹⁾ The j_{app} range of 0.1–0.35 A·dm⁻² in the present experiments was smaller than its optimum range.

In each FB, the values of η_{px} at $E=40\%$ were smaller than those at $E=20\%$. In the FB at $E=40\%$, the number of particles per unit bed volume was smaller than that at $E=20\%$ and the collision frequency between the particles and the working electrode or the ECP and among the particles decreased. Then the quantity of electrons which transfer from the working electrode or the ECP to the particles decreased. On the other hand, an electric current corresponding to the decrease in amount of electrodeposition of copper on the surface of particles was consumed in the electrodeposition of copper on

Table 2. Amount of electrodeposition of copper on working electrode or surface of the ECPs: Type I; $\kappa_L = 2.96 \text{ S} \cdot \text{m}^{-1}$; electrolytic time 3600 s

I_c [A]	$E=20\%$		$E=40\%$	
	WE $\times 10^{-4}$ [kg]	ECP ₁ , ECP ₂ $\times 10^{-4}$ [kg]	WE $\times 10^{-4}$ [kg]	ECP ₁ , ECP ₂ $\times 10^{-4}$ [kg]
1.0	0.474	0.830	1.600	2.371
1.5	0.804	1.067	2.045	3.201
2.0	0.237	1.660	1.185	2.015

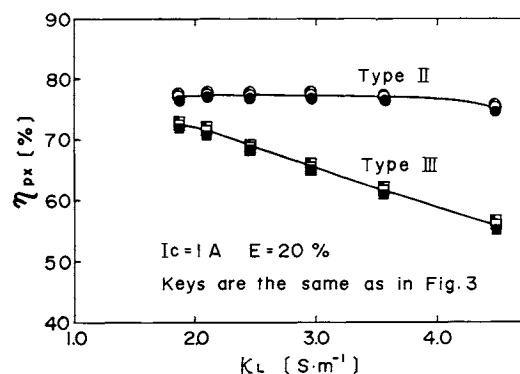


Fig. 4. Effect of κ_L on η_{px}

the working electrode or the surface of the ECP, as shown in Table 2.

2) Current efficiency in each FB The current efficiency η_{px} in three FBs of Type I was examined. As shown in Fig. 3, the values of η_{px} in beds 2 and 3 were almost equal but were smaller than those in bed 1. On the other hand, although copper electrodeposited on the surface of the Pt-ECP had a tendency to come off, the amount of electrodeposition of copper on the Pt-ECP corresponding to the cathode of beds 2 and 3 was larger than that on the Cu-working electrode, as is clear from Table 2. Then the quantity of transfer of electrons from the Pt-ECP to the particles was less than that from the Cu-working electrode in bed 1.

The values of η_{px} when identical materials are used as the working electrode and the ECPs are then shown in Fig. 3. In both Types II and III, the values of η_{px} in the respective beds were almost equal. But the η_{px} value in Type II was larger than that in Type III, and the ratio of η_{px} in Type III to Type II was in the range of 0.85–0.90.

3) Effect of electrical resistance of electrolyte on η_{px} The effect of the electrical conductivity κ_L ($=\rho_L^{-1}$) of the electrolyte on the activity of particles are shown in Fig. 4. The κ_L value was changed by the concentration of H_2SO_4 . In Type II, there was no significant effect of κ_L on η_{px} . On the other hand, η_{px} in Type III tended to decrease with κ_L . As for comparison of η_{px} between Types II and III, the difference was considerably small at small κ_L . It was found that the activity of each FB could be sufficiently elevated by increasing ρ_L in the case where the Pt-ECP

was used. When ρ_L increases, the reaction of Type A shown in Fig. 1 becomes small and the reaction of Type B becomes large. Then a high activity of each FB was obtained at the increased ρ_L .

4) Resistances of electron transfer at ECP Based on the results discussed so far, the following resistances are regarded as related to electron transfer at the ECP. They are: 1) the contact specific resistance ρ_c concerning electron transfer between the ECP and the particles, 2) the specific resistance ρ_s including ρ_L and a resistance concerning the cathodic reaction, and 3) the specific resistance ρ_R including ρ_L and a resistance concerning the anodic reaction. The assumed mechanism of electron transfer in terms of these resistances is shown in Fig. 5. To activate the particles, the transfer of electrons from the ECP to the particles must occur more easily. That is, the condition of $\rho_L \gg \rho_c$ is required. However, since increasing ρ_L contributes to increasing the power consumption, it is desirable to select the material of the ECP so as to lessen ρ_c as much as possible, from a practical point of view.

3.2 Reduction of ρ_c

Since the ECP is used over a long period, the ECP must be insoluble. Copper dissolved at the surface of one side of the Cu-ECP working as the anode electrode. This implies that the Cu-ECP, despite its advantage of small ρ_c , is undesirable as the insoluble ECP. As one of the attempts to reduce ρ_c , the Pt-Cu-ECP, in which the plating of copper was carried out on one side of the platinum plate, was employed. This ECP is not completely insoluble, but it is more insoluble than the Cu-ECP because the copper-plated side is used as the cathode. The results for Types IV-1 (active surface) and IV-2 (oxidized surface) are shown in Fig. 6. In both Types IV-1 and IV-2, η_{px} was larger than that for the Pt-plate. η_{px} for Type IV-1 was almost equal to that for Type II but η_{px} in Type IV-2 was smaller than that for Type II. The existence of oxide film in Type IV-2 contributed to the increase in ρ_c . To reduce ρ_c , cleaning to remove stains such as oxide film and oil, etc., on the surface is especially important. The present method is an effective one for reducing ρ_c and elevating the activity of each FB in the rectangular cell.

3.3 Electrolytic capacity and power consumption in rectangular cell with three FBEs

The electrolytic capacity E_c and the power consumption P_w in the present rectangular cell with three FBEs (RTFBE) were compared with those in the rectangular cell with a single FBE (RSFBE). The RSFBE was $3 \times 4.2 \text{ cm}^2$ in cross-sectional area and 8 cm in height, and the bed thickness of the FB was 1.8 cm. E_c and P_w were calculated from Eqs. (7) and (8) respectively.

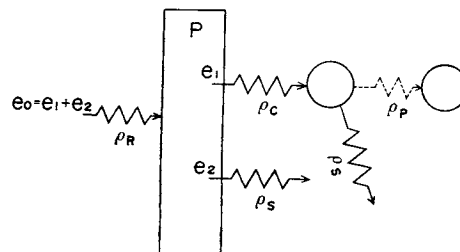


Fig. 5. Resistances related to electron transfer at ECP: e_1, e_2 , electron; O, electro-conductive particle

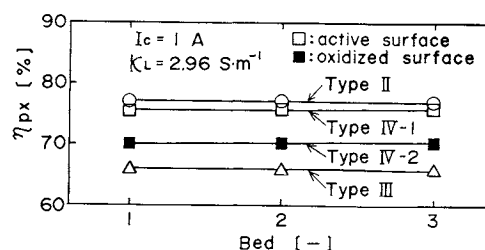


Fig. 6. Comparison of η_{px} in each bed when Types II, III and IV were used

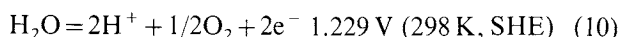
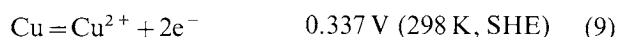
Table 3. Comparison of E_c and P_w in RTFBE with those in RSFBE: $E = 20\%$; $I_c = 1 \text{ A}$; $\kappa_L = 2.96 \text{ S} \cdot \text{m}^{-1}$

	V_c [V]	η_{px} [%]	$E_c \times 10^6$ [(kg-Cu) · C ⁻¹]	$P_w \times 10^{-6}$ [J · (kg-Cu) ⁻¹]
RSFBE	3.57	77.5	0.255	13.97
RTFBE				
Type IV-1	10.67	76.0	0.751	14.22
Type IV-2	10.87	70.3	0.694	15.66
Type III	11.90	65.8	0.650	18.32
Type II	7.12	77.5	0.766	9.29

$$E_c = \Sigma W_{px} / (I_c \cdot H) \quad (7)$$

$$P_w = V_c / E_c \quad (8)$$

where the cell voltage V_c is the mean value during the electrolysis and P_w does not involve the power consumed by the pump. The results of E_c and P_w are summarized in Table 3. E_c of Types II and IV was found to be about three times that in the RSFBE. It is well known that in cases where many conventional cells without particles are arranged in the direction of the electric current, in a bipolar cell, for example, P_w increases compared to that in a single cell.^{5,6)} In the present work, however, the values of P_w of Types IV-1 and II were 1.02 and 0.66 times respectively that in the RSFBE. The cause for a smaller P_w in Type II (Cu-ECPs) was the lower standard oxidation-reduction potential compared to that of anodic reaction in Type III, as can be seen from Eqs. (9) and (10).



The method using the ECPs was effective for scaling up the FBE, since P_w hardly increases with elevating E_c .

Conclusion

To enlarge the thickness of a fluidized bed (FB) having particles activated as an electrode in the direction of the electric current, electro-conductive partition plates (ECPs) were inserted into the FB. The activity of each FB was investigated for copper electrodeposition, and the following results were obtained:

1) The particles contacted the ECP and were activated as an electrode.

2) The materials of the ECP should be selected so that ρ_c becomes sufficiently small compared to ρ_L . Also, it is necessary to remove the oxide film and stains on the ECP surface.

3) E_c could be elevated almost without increasing P_w . Thus, inserting the ECPs into the FB was effective for scaling up the FBE.

Acknowledgment

The authors wish to thank Prof. M. Fujii of Niigata Univ. for his kind suggestions regarding this study. Thanks are also given to Asahi Chemical Industry Co., Ltd. for offering cation-exchange membrane.

Nomenclature

E	= bed expansion	[%]
E_c	= electrolytic capacity	[kg-Cu · C ⁻¹]
H	= electrolytic time	[s]
H_f	= fluidized bed height	[m]
H_p	= settled bed height	[m]
I_c	= cell current	[A]
J_{app}	= $I_c/(S_c + S_p)$, apparent current density	[A · m ⁻²]
m	= calculated amount of electrodeposition of copper	[kg]
P_w	= power consumption	[J · (kg-Cu) ⁻¹]

q	= quantity of electricity	[C]
S_c	= surface area of working electrode or of ECP	[m ²]
S_p	= surface area of total particles in each FB	[m ²]
W_{px}	= amount of copper electrodeposited on the surface of particles in X-th FB from working electrode	[kg]
η_{px}	= current efficiency defined by Eq. (3)	[%]
κ_L	= electric conductivity	[S · m ⁻¹]
ρ_c	= contact specific resistance between particles and ECP	[Ω · m]
ρ_L	= electric specific resistance of electrolyte	[Ω · m]
ρ_p	= contact specific resistance between particles	[Ω · m]
ρ_R	= specific resistance related to both ρ_L and anodic reaction	[Ω · m]
ρ_s	= specific resistance related to both ρ_L and cathodic reaction	[Ω · m]

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