JOURNAL OF APPLIED ELECTROCHEMISTRY 19 (1989) 877–881

Studies of bipolarity in fluidized bed electrodes

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Received 17 October 1988; revised 13 February 1989

Measurements have been made of the anodic reaction products due to the anodic over-potential resulting from the bipolarity of particles in a nominally cathodic fluidized bed electrode reactor. Investigations of the lead particle–basic carbonate solution system show that charge transfer occurs by a bipolar as well as a monopolar mechanism in a nominally monopolar fluidized bed electrode. The bipolar intensity was found to increase with decreasing superficial current density and also with increasing bed voidage.

1. Introduction

A conducting particle fluidized bed electrode has such advantages over a conventional electrode as high space-time yields, low inventory of materials, and low operating costs. It is also expected to have uses in metal recovery from dilute solutions, and in the electrolysis of reactants with high activation energies. Commercial utilization [1] and large scale experiments [2] have been reported.

Several mechanisms for the charge transfer or flow of current through a conducting particle fluidized bed electrode have been proposed. One of the first postulated mechanisms was the so-called 'collisional mechanism' which described the passage of current in terms of the transfer of discrete packages of charge from feeder to particle and particle to particle by a charge sharing process following collision [3, 4]. Simple calculations based on the capacitance of a single particle, however, indicated that for this mechanism to account for observed currents, collision frequencies with the feeder of the order of 10^5–$10^6\,s^{-1}\,cm^{-2}$ would be necessary. Such a frequency seems unrealistically high, and indeed by employing measured values for the relevant parameters Beenackers *et al.* [5] concluded that charge transfer based upon single particle collisions was unable to account for the observed behaviour of fluidized beds. This led them to postulate a mechanism based on the collision of aggregates of particles. Based on measurements of bed effective resistivities as a function of the frequency of an imposed alternating current, Sabacky and Evans [6] have proposed a 'conductive mechanism'. In this mechanism, chains of particles are assumed to be in contact with the current feeder, and the current is passed through these continuous chains. However, these two monopolar mechanisms may not be appropriate for explaining the phenomenon of a non-cathodically protected zone (or anodic zone) appearing in the bed when the overpotential distributions are measured [7–9] in a nominally cathodic fluidized bed. At low current densities and high bed voidages, moreover, the current efficiencies are negative [9, 10]. Fluidized systems are, however, dynamic and when conditions in the bed are examined as a function of time it is observed that local overpotentials in a nominally monopolar bed are characterized by rapid fluctuations, both anodic and cathodic, and that the peak values attained on either side of the rest potential are comparable [11–13]. Based on this observation Plimley and Wright [11] recently proposed the 'bipolar mechanism'.

In the bipolar mechanism, it is proposed that particle aggregates formed in a nominally monopolar fluidized bed electrode, (albeit of irregular size depending on the degree of fluidization), are made partly bipolar when they are isolated from the current feeder. On the other hand, aggregates in contact with the feeder take on the same polarity as the feeder. Plimley and Wright [11] observed time-varying potential distributions and time-averaged potential distributions, and compared them with those predicted by their model which was based on the bipolar mechanism for charge transfer. Good agreement was obtained. Based solely on these results, however, it cannot be assured that the charge transfer will occur by the bipolar mechanism.

Anodic and cathodic polarities on each side of an

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aggregate isolated from the feeder give rise to appropriate anodic and cathodic reactions in the coulombic sense. In this paper, a series of experiments was performed to measure the anodic reaction products due to the anodic overpotential when the fluidized particle aggregates reveal bipolarity in the nominally cathodic fluidized bed electrode. The principle of this investigation can be illustrated by considering silver particles fluidizing in an acidic chloride solution above a cathodic feeder plate. If silver particle aggregates exhibit bipolarity, then Ag^+ ions will be produced on the anodic side of the bipolar aggregates, and would be immediately precipitated by the Cl^- ions. The appearance of AgCl would thus confirm bipolarity in a nominally monopolar cathodic fluidized bed electrode.

2. Experimental

2.1. *Electric cell*

The cell used in this investigation is shown in Fig. 1. It is divided into anode and cathode compartments to avoid the dissolution of oxygen generated from the anodic reaction. Both compartments are made of acrylic resin and are cylindrical in shape with an internal diameter of 2.75 cm. The anode compartment is placed vertically 2 cm above the surface of the fluidized bed. The anode is a platinum coated titanium mesh held above a sintered glass diaphragm of porosity 3. The cathode current feeder is placed just above the porous PVC distributor (Atlas Mineral and Chemical Co.). The static height of the bed is 2 cm. Solution and current flow axially. The catholyte enters the column through a calming section and recirculates successively through a reservoir, while the anolyte remains stationary.

2.2. *Procedure and measurements*

The experimental procedure consisted of filling the reservoir with 10 l of catholyte and circulating it continuously through the cell and the reservoir tank by pumping. Nitrogen was sparged into the reservoir to remove the dissolved oxygen in the catholyte. After a half hour, the particles were added to the reactor, the catholyte flow was adjusted for the desired bed expansion, and the current set to the desired level. The electrolysis continued for an hour under the steady state condition. During the experiments, the electrolytes were maintained at 25° C. The fluidized particles were pretreated before each experiment. The lead particles, for example, were cleaned in dilute nitric acid to remove any oxide or hydroxide coatings,

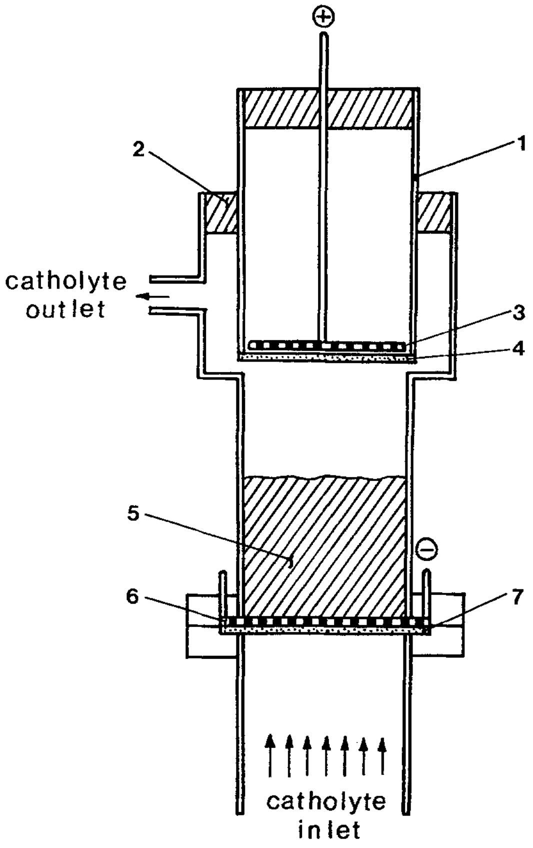

Fig. 1. Schematic diagram of the cell: 1-anolyte chamber, 2-rubber, 3-platinum coated titanium mesh anode, 4-sintered glass diaphragm, 5-fluidized particles, 6-current feeder, 7-porous PVC distributor.

Table 1. Experimental systems

	System 1	*System 2*	*System 3*
Electrolyte	0.5 M NaCl + 1 M HCl	20% NaCl + NaOH (to maintain alkalinity to 5 g l^{-1} Na_2O)	0.5 M CH_3COONa + 0.5% Na_2CO_3
Current feeder	Silver coated titanium mesh electrode	Copper mesh electrode	Stainless steel mesh electrode
Anode	Platinized titanium mesh electrode	Platinized titanium mesh electrode	Platinized titanium mesh electrode
Cross-sectional area of cell (cm^2)	5.94	5.94	5.94
Fluidized particles	Silver coated copper bead (d_p = 1 mm)	Copper bead (d_p = 1 mm)	Lead bead (d_p = 2 mm)
Current density (mA cm^{-2})	56	50	5, 10, 15, 20
Bed voidage	0.52, 0.54, 0.58, 0.61	0.52, 0.54, 0.58, 0.61	0.54, 0.56, 0.58, 0.60, 0.63

rinsed in water, and dried in an oven. Immediately before each experiment they were rinsed in dilute acetic acid and then in distilled water to remove any contamination.

For quantitative (or qualitative) measurements of the anodic reaction products due to the bipolarity in the nominally cathodic fluidized bed electrode, the three systems shown in Table 1 were used. Under the condition of constant superficial current density and bed voidage, anodic overpotentials due to the bipolarity in the bed cause metal dissolution. The dissolved metal ions react with any species in the electrolyte to produce precipitates. These precipitates (anodic reaction products) were qualitatively analysed using X-ray diffraction and an Electron Probe Micro Analyzer (EPMA), and quantitatively determined by a DC Argon plasma spectrometer. In order to examine the activation controlling step, polarization curves were determined for each solution. From the polarization curves, the experimental conditions (shown in Table 1) were chosen.

3. Results and discussion

For the silver particle–acidic chloride solution system (Table 1) the silver particles are used as fluidized particles in a nominally cathodic fluidized bed electrode reactor. In this system, silver chloride will precipitate owing to any silver ions dissolved from an anodic surface resulting from any bipolarity of the fluidized particle aggregates. A film of silver chloride formed on the surface of the silver particles during the course of the experiments. This is in agreement with the results of Katan *et al.* [14], who found that under anodic reaction of silver in an acidic chloride solution, an anodic film of silver chloride will form on the surface of the silver continually growing thicker, according to the following mechanism:

$$\mathrm{Ag(s)} \longrightarrow \mathrm{Ag^+} + \mathrm{e^-} \quad \text{(anodic dissolution)} \qquad (1)$$

$$\mathrm{Ag^+} + (n+1)\mathrm{Cl^-} \longrightarrow \mathrm{AgCl}_{n+1}^{n-} \quad \text{(complex formation)} \qquad (2)$$

$$\mathrm{AgCl}_{n+1}^{n-}(\mathrm{a}) \longrightarrow \mathrm{AgCl}_{n+1}^{n-}(\mathrm{b}) \quad \text{(solution transport)} \qquad (3)$$

$$\mathrm{AgCl}_{n+1}^{n-} \longrightarrow \mathrm{AgCl(s)} + n\mathrm{Cl^-} \quad \text{(deposition and growth)} \qquad (4)$$

To confirm the formation of silver chloride film on the surface of the silver particles the film was dissolved in aqueous ammonia, and after the addition of nitric acid solution a white precipitate formed which by X-ray diffraction analysis was shown to be silver chloride. EPMA also detected the silver chloride components on the surface of particles used in the experiment. The results of the X-ray diffraction analysis and the EPMA analysis qualitatively show that the charge transfer occurred by the bipolar mechanism as well as by the monopolar mechanism in the nominally cathodic fluidized bed electrode. Quantitative measurements were difficult because of the formation of a film rather than a precipitate.

Table 2. Rate of the experimental net lead dissolution due to the bipolarity, and calculated bipolar intensities in the lead particle–basic carbonate solution system

Current density *($mA\ cm^{-2}$)*	I_c *(mA)*	ε	W_{diss} *($mg\ h^{-1}$)*	I_b *(mA)*	I_b/I_c
5	29.69	0.54	50.6	13.04	0.44
		0.56	50.2	12.94	0.44
		0.58	52.4	13.50	0.46
		0.60	53.2	13.71	0.46
		0.63	53.4	13.76	0.46
10	59.38	0.54	50.6	13.04	0.22
		0.56	54.8	14.12	0.24
		0.58	56.2	14.48	0.24
		0.60	58.0	14.95	0.25
		0.63	62.6	16.13	0.27
15	89.07	0.54	64.8	16.70	0.19
		0.56	76.6	19.74	0.22
		0.58	71.4	18.40	0.21
		0.60	76.2	19.64	0.22
		0.63	71.0	18.30	0.21
20	118.76	0.54	64.5	16.62	0.14
		0.56	78.6	20.26	0.17
		0.58	77.8	20.05	0.17
		0.60	78.0	20.10	0.17
		0.63	84.8	21.85	0.18

I_c: Total cell current, mA
ε: Bed voidage
W_{diss}: Rate of the experimental net lead dissolution, $mg\ h^{-1}$
I_b: Bipolar current calculated from dissolution rate using Faradaic eq., mA
I_b/I_c: Calculated bipolar intensity (defined as the ratio of the bipolar current to the total cell current)

In the copper particle–basic chloride solution system (Table 1) the copper particles were used as the fluidized bed. When fluidized particle aggregates exhibit bipolarity, copper will dissolve on the anodic surface and then form cuprous oxide precipitates. Again, only a qualitative detection of cuprous oxide precipitate was possible in this system, since copper can be dissolved as +1 or +2 ion by anodic polarity on particles.

Quantitative measurement of anodic reaction products arising from bipolarity was possible by using the lead particle–basic carbonate solution system (Table 1). In this system, if the fluidized particle aggregates possess bipolarity then basic lead carbonate precipitates according to the following reactions:

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad (5)$$

$$Pb^{2+} + 2CH_3COO^- \longrightarrow Pb(C_2H_3O_2)_2 \qquad (6)$$

$$3Pb(C_2H_3O_2)_2 + 2Na_2CO_3 + H_2O \longrightarrow 2H_2C_2H_3O_2 + 4NaC_2H_3O_2 + 2PbCO_3 \cdot Pb(OH)_2\downarrow \qquad (7)$$

The amounts of lead dissolved due to the bipolarity were calculated from the amounts of precipitates produced in the form of the basic lead carbonate. The addition of 20 ml acetic acid to the catholyte dissolved the basic lead carbonate precipitates once the lead particles used as the fluidized bed were removed, and the lead ions were detected by the DC argon plasma spectrometer. The amounts of dissolved lead due to the bipolarity varied with the superficial current density and the bed voidage as shown in Table 2. Since, in this system, there may be chemical dissolution, for example through the presence of dissolved oxygen, corrections have to be applied by noting the amount of dissolution under the same fluidizing conditions at zero current. In Table 2, the net or actual electrochemical dissolution weight under anodic overpotential conditions is reported.

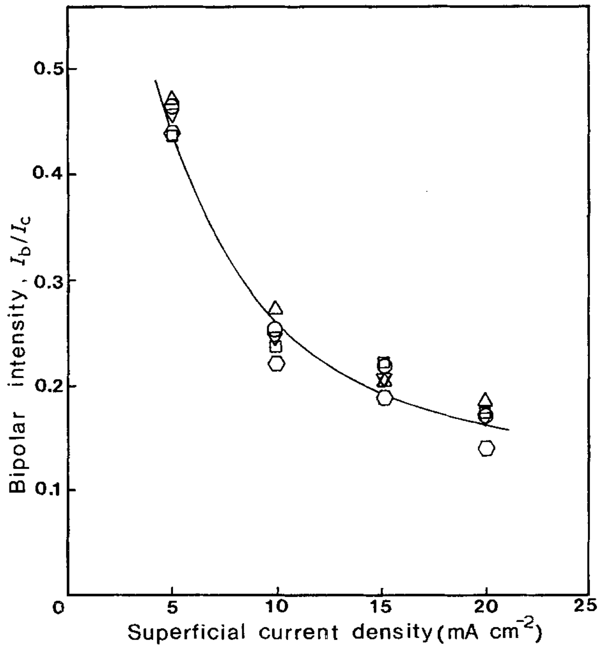

Fig. 2. Bipolar intensity against superficial current density in system 3: bed voidages —○, 0.54; □, 0.56; ▽, 0.58; o, 0.60; △, 0.63.

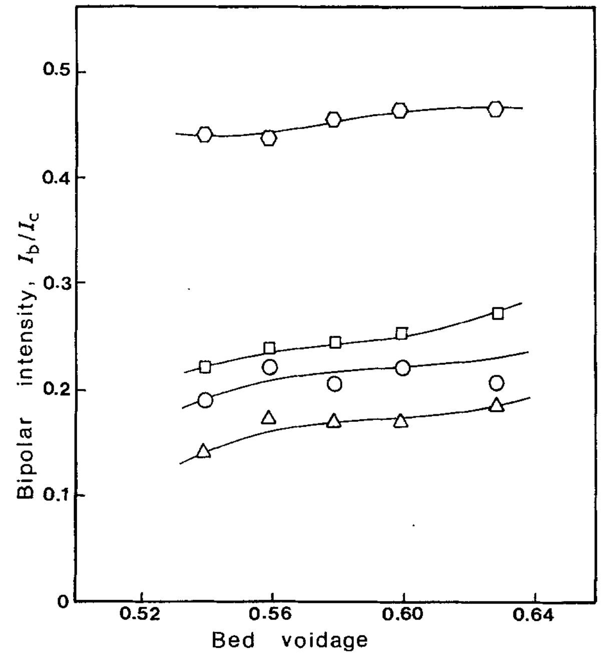

Fig. 3. Bipolar intensity against bed voidage in system 3: ○, 5 mA cm^{-2}; □, 10 mA cm^{-2}; o, 15 mA cm^{-2}; △, 20 mA cm^{-2}.

In order to compare the degree of bipolarity with respect to the superficial current density and the bed voidage in the nominally monopolar fluidized bed electrode the bipolar currents were calculated from the amounts of dissolved lead using Faraday's law. The bipolar intensities (defined as the ratio of the bipolar current and the total cell current) were also obtained. Figures 2 and 3 shown the variations of bipolar intensity with respect to the superficial current density and the bed voidage. As shown, the bipolar intensity increases when the superficial current density is decreased and slightly increases when the bed voidage is increased.

In the nominally cathodic fluidized bed electrode under the kinetically controlling step, the current efficiencies measured at various superficial current densities and bed voidages have been reported to be lower than the theoretical ones. This phenomenon can be clearly explained by the presence of bipolarity. Anodic overpotential due to the bipolarity causes metal dissolution to take place partly in the metal deposition system, and therefore the experimental current efficiencies are lower than the theoretical ones. The current efficiencies are calculated from the amounts of dissolved lead due to the bipolarity in the lead particle basic carbonate solution system. Figures 4 and 5 show the variations of the calculated current efficiency with respect to the superficial current density and the bed voidage. As shown in the figures, the calculated current efficiency increases with the superficial current density and decreases with the bed voidage. This result shows the same trend as those previously reported for not only the copper deposition system but others as well [7, 9, 10].

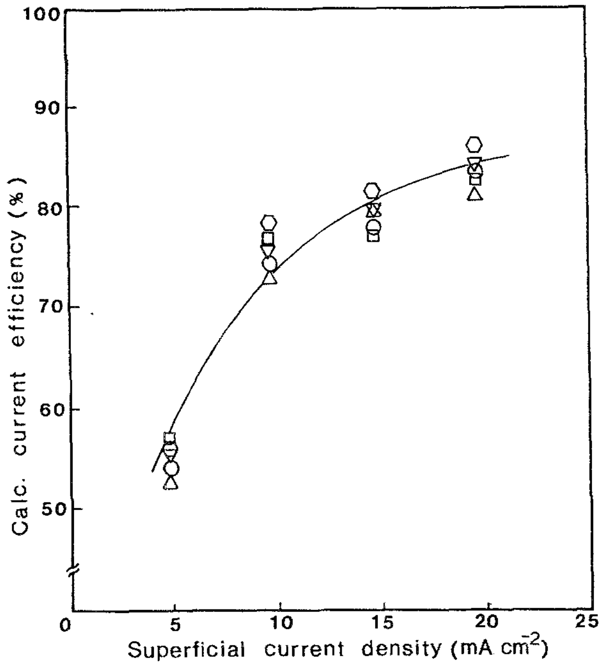

Fig. 4. Calculated current efficiency against superficial current density in system 3: bed voidages—○, 0.54; □, 0.56; ▽, 0.58; ○, 0.60; △, 0.63.

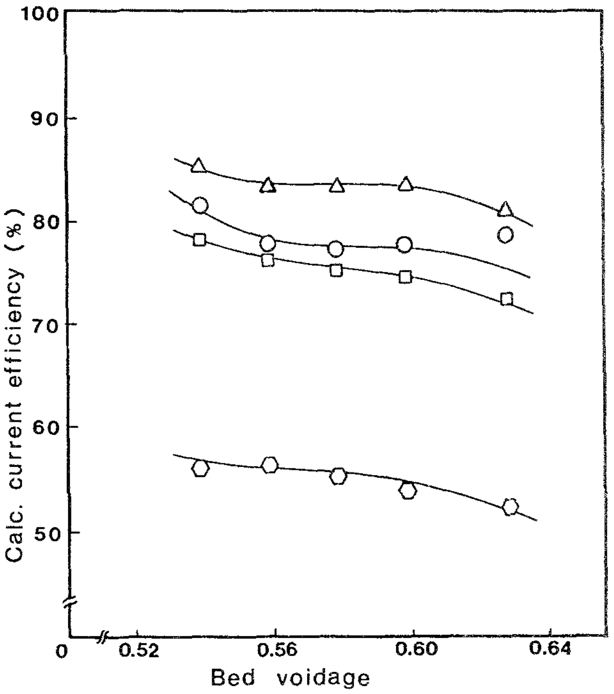

Fig. 5. Calculated current efficiency against bed voidage in system 3: ○, 5 mA cm^{-2}; □, 10 mA cm^{-2}; ○, 15 mA cm^{-2}; △, 20 mA cm^{-2}.

4. Conclusions

A series of experiments to determine the anodic reaction products on fluidized particles have shown the bipolarity in a nominally cathodic fluidized bed electrode reactor. The anodic reaction products were qualitatively measured in the reactor for both the silver particle–acidic chloride solution system and the copper particle–basic chloride solution system, and were quantitatively measured using the lead particle–basic carbonate solution system. From the results, it may be concluded that charge transfer occurs by the bipolar mechanism as well as by the monopolar mechanism in a nominally monopolar fluidized bed electrode.

In the nominally cathodic fluidized bed electrode under the kinetically controlling step, the experimental current efficiencies have been reported to be lower than the theoretical ones. This phenomenon can be clearly explained by the presence of bipolarity in the bed. Anodic overpotential due to the bipolarity causes metal dissolution to take place partly in the metal electrodeposition system, and therefore gives current efficiencies lower than the theoretical ones. It has also been found that the bipolar intensity increased for a decrease in superficial current density and slightly increased for an increase in bed voidage.

Acknowledgements

The first author wishes to acknowledge the financial support of the Korea Science and Engineering Foundation. Acknowledgement of the support of the Natural Sciences and Engineering Research Council of Canada is also made.

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