CURRENT PATHS AND ELECTROLYSIS EFFICIENCY IN BIPOLAR PACKED-BED ELECTRODES

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The characteristics of bipolar packed-bed electrodes were studied by using copper deposition reaction from a copper sulfate solution. Ferrite pellets were used as a particulate phase and were packed in three kinds of mode. The Faradaic current in the particulate phase, the by-pass current in the electrolyte phase and the short-circuiting current were measured separately.

The minimum bipolar cell voltage was a function of decomposition voltage, distance between two plate electrodes, pellet diameter, and solid holdup. For regularly packed bipolar electrodes, the interaction between Faradaic and by-pass current was small, and a simplified parallel current model is proposed. For randomly packed bipolar electrodes, the interaction was not negligible at higher cell voltages.

The minimum value of energy consumption was observed at a particular cell voltage which was a function of pellet size and packing mode. Because of increase in the short-circuiting current due to copper deposition, the energy consumption in the randomly packed bed increased with increase in electrolysis time. The regularly packed bed where the direction of current was parallel to the plain faces of the pellets was found to be the most efficient under the present experimental conditions.

Introduction

In recent years, considerable attention has been paid to particulate electrodes, including packed-bed, trickle-bed, and fluidized-bed types.

Bipolar packed-bed electrodes consist of electrically conductive particles packed between two plate electrodes. By imposing a sufficiently steep potential drop across the bed, one side of each particle becomes cathodic and the other side becomes anodic. To achieve this situation, particles have to be isolated from each other by dilution with non-conducting particles or by spacers.

Smith *et al.*[5], Yoshizawa *et al.*[7], and Yoshimura *et al.*[6] discussed the applicability of bipolar packed-bed electrodes to waste water treatment. Fleischmann *et al.*[1] used packed-bed electrodes of a mixture of glass and graphite-coated glass particles for the electrochemical production of hypobromite and propylene oxide. Motozawa[3] used sintered ferrite pellets as the particulate phase and found that these pellets provided high contact resistance between adjacent pellets and enough chemical stability for industrial use. However, the characteristics of bipolar packed-bed electrodes are not as yet clear. The fraction of Faradaic current in the total cell current still remains obscure.

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In the present work the characteristics of bipolar packed-bed electrodes were investigated by using the electrowinning of copper from copper sulfate solution. The Faradaic current in the particulate phase, the by-pass current in the electrolyte phase and the short-circuiting current between adjacent pellets were measured separately. Based on these results, a simplified model of bipolar packed-bed electrodes is proposed. The effects of pellet size and cell voltage on electrolysis efficiency are also discussed.

1. Experimental Apparatus and Procedure

1. 1 Experimental apparatus

The electrolysis cell, shown schematically in **Fig. 1**, was made of transparent polyvinyl chloride resin. The cell was rectangular in cross section, 0.04 m in width and 0.05 m in height. The distance between two platinum plate electrodes was 0.08 m. These electrodes were 0.04 m in width and 0.02 m in height. The

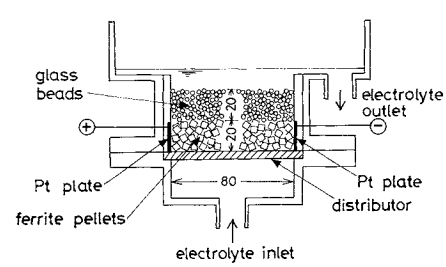


Fig. 1 Cross section of rectangular elcetrolysis cell

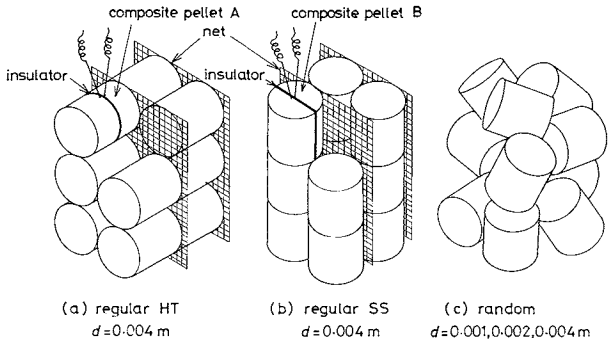


Fig. 2 Packing modes of ferrite pellets

liquid distributor was a sintered plate of polyethylene resin 0.004 m thick.

1. 2 Pellets and packing modes

The particulate phase in the bipolar packed bed was sintered ferrite cylindrical pellets ($NiFe_2O_4$). Each pellet diameter, d, was equal to the corresponding pellet length, and was 0.001, 0.002, or 0.004 m. The specific resistance and density of the ferrite were 0.0051 $\Omega \cdot m$ and 5260 $kg \cdot m^{-3}$, respectively.

An inert bed of non-conducting pellets was used to measure the by-pass current flowing through the electrolyte phase. These non-conducting pellets were prepared by spraying the original ferrite pellets of 0.004 m diameter with lacquer.

The pellets were packed up to the plate electrode (0.02 m) in three different ways as shown in **Fig. 2**. For the random packing mode, pellets of d=0.001, 0.002, and 0.004 m were used, and the weight of packed pellets were 0.22 kg. For the regular packing modes, pellets of d=0.004 m were used and polyethylene resin net 0.001 m thick was inserted between rows of pellets in parallel with the plate electrodes. The direction of electric current was vertical to the plain faces of the pellets (regular HT type) or was parallel to them (regular SS type). The number of pellets was 15 in the vertical direction and 57 between the plate electrodes for the regular HT type, and 16 and 50 for the regular SS type, respectively. To reduce stray current, glass beads of 2 mm diameter were packed on the top of the ferrite bed.

The composite pellets shown in Fig. 2 were used to measure the decomposition voltage and the electric current flowing through the pellet (intra-pellet current). The composite pellets were made as follows. A pellet was cut into two parts in two different ways, shown as A and B in Fig. 2. A thin wire lead was attached to each sectioned surface with electroconductive resin. A sheet of paper was sandwiched between the two halves of the pellet as an insulator, and the halves were joined with epoxy resin adhesive to resume their original shape.

1. 3 Procedure

The electrolyte was a 0.01 $mol \cdot dm^{-3}$ solution of copper sulfate. The solution, kept at 298 K in the storage tank, was introduced into the cell through the distributor. The superficial liquid velocity was fixed at 5.2×10^{-3} $m \cdot s^{-1}$, because the total cell current was virtually constant above this velocity. Prior to the start of an electrolysis, nitrogen gas was directed into the storage tank to remove any dissolved oxygen. The electrolysis was carried out potentiostatically by use of a stabilized dc source.

The polarization curves for the cathodic deposition of copper and the anodic formation of oxygen were measured with the circuit shown in **Fig. 3 (a)**. The working electrode was a 0.004-m pellet insulated with epoxy resin except for one plane face. To reduce the mass transfer resistance in the electrolyte phase, the ferrite pellet electrode was set in the inert bed of the regular packing modes. The decomposition voltage was obtained by using a couple of composite electrodes, which were set face to face in the middle of the inert bed of the regular packing modes, as shown in **Fig. 3 (b)**. **Figure 3 (c)** shows the circuit for measurement of the intra-pellet current in the packed bed of active ferrite pellets.

The short-circuiting current in the randomly packed bed was measured as follows. Electrolysis was interrupted at proper time intervals and the electrolyte was drained. After the bed was washed with acetone and dried, the short-circuiting current was measured. Then the bed was filled with electrolyte and electrolysis was started again.

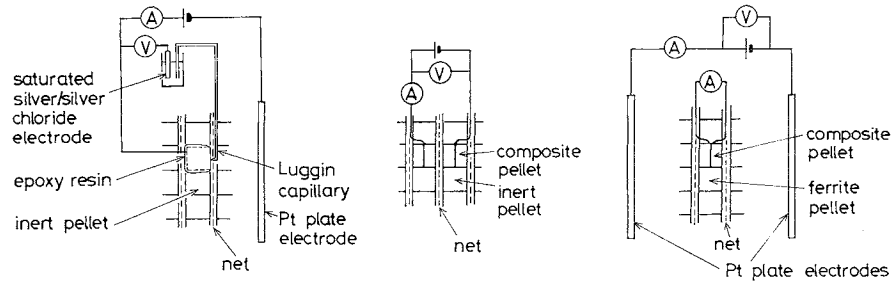
The electrolyte was sampled at regular intervals, and copper ion concentration was analyzed by potentiometry with EDTA. The current efficiency of copper deposition was determined from both the amount of electricity and the decrease in copper ion content.

The electroconductivity of the electrolyte was measured with an ac impedance bridge. The specific conductivity of 0.01 $mol \cdot dm^{-3}$ $CuSO_4$ solution was about 0.2 $S \cdot m^{-1}$.

2. Modeling of Bipolar Packed Bed Electrodes

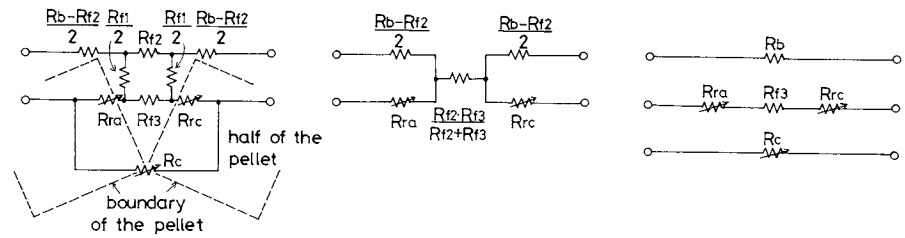
Figure 4 illustrates equivalent resistance networks for the bipolar packed-bed electrodes. Three main paths of electric current are considered. 1) By-pass current in the electrolyte phase: The equivalent resistance is R_b. The resistances of R_{f1}, R_{f2}, and R_{f3} originate from the electrolyte between adjacent pellets. 2) Faradaic current: The equivalent resistances are R_{ra} and R_{rc}, and vary with the anodic and cathodic reaction rate. 3) Short-circuiting current: This is neglected in the case of the regular packing modes. The equivalent resistance is R_c.

By letting $R_c \to \infty$ and $R_{f1} \ll R_{f2}$ and R_{f3}, the general model is reduced to Case 2, which has been proposed by Robertson[4] and King *et al.*[2]. Under the condition



(a) Polarization curves (b) Decomposition voltage (c) Intra-pellet current

Fig. 3 Electrical circuits



Case 1. general model Case 2. Rc→∞, Rf1/2<Rf2 and Rf3, Case 3. Rc>Rf3, Rf1/2>Rf2 and Rf3

Fig. 4 Electrical eqnivalent resistance models

of $R_c \gg R_{f3}$ and $R_{f1} \gg R_{f2}$ and R_{f3}, the general model is reduced to Case 3.

3. Experimental Results

3. 1 Polarization curves

The electrode reactions are written by the following equations.

Anode $H_2O \rightarrow 2H^+ + (1/2)O_2 + 2e$ (1)

Cathode $Cu^{2+} + 2e \rightarrow Cu$ (2)

The electrode current densities of Eqs. (1) and (2) were determined from the polarization curves, and Tafel equation for the overall reaction was obtained as follows.

$$E_0 = 1.215 + 0.205 \ln j_f \quad (3)$$

where E_0 is the cell voltage without ohmic potential drop, and j_f is the Faradaic current density. The broken line in **Fig. 5** is calculated from Eq. (3) and is virtually vertical. This indicates that mass transfer in the diffusion layer was not a controlling step in the present reactions. Figure 5 also shows the voltage-current curves obtained with the composite electrodes. The decomposition voltage was 1.44 V.

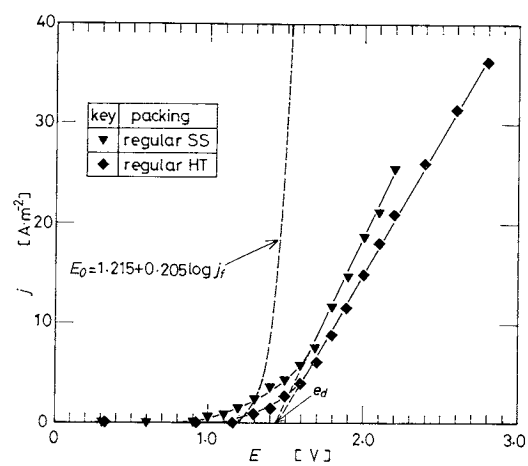


Fig. 5 Polarization curves and decomposition voltages

3. 2 Current paths and minimum bipolar cell voltage

1) Regularly packed bed **Figures 6** and **7** show the current densities via different paths for the regular packing modes, where no short-circuiting occurred. In this case, Faradaic current density, j_f, was calculated from the following equation.

$$j_f = I_p n_c / A \quad (4)$$

where I_p is the intra-pellet current, n_c is the number of pellets between two net separators and A is the area of

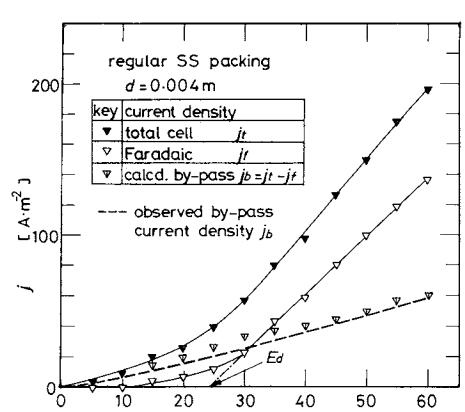


Fig. 6 Current densities via different paths in regular SS-type packed bed

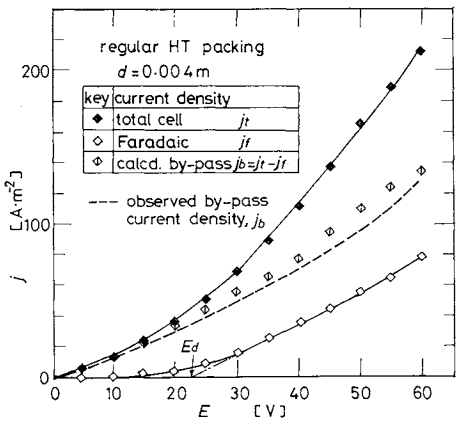


Fig. 7 Current densities via different paths in regular HT-type packed bed

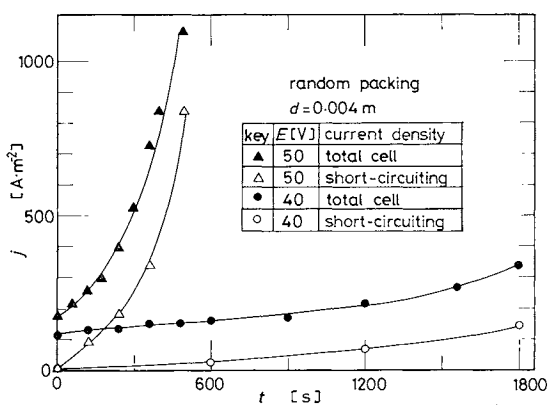


Fig. 8 Effect of electrolysis time on total cell current density and short-circuiting current density in randomly packed bed of 0.004 m pellets

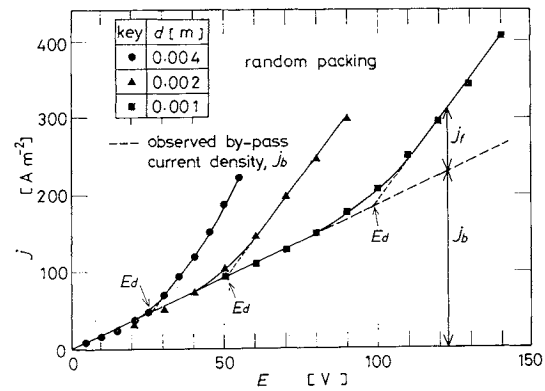


Fig. 9 Effect of cell voltage on cell current density and by-pass current density for different pellet sizes

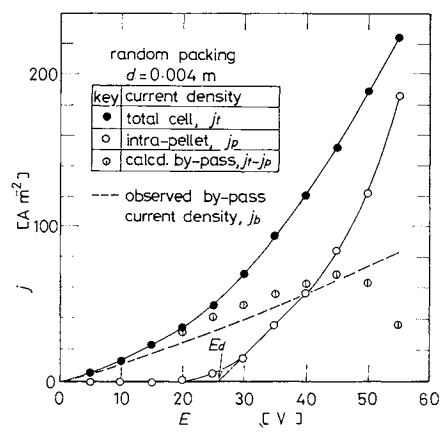


Fig. 10 Current densities via different paths in randomly packed bed

the plate electrode.

When the voltage between adjacent pellets reached the decomposition voltage, e_d, the Faradaic current began to flow, and the electrodeposition of copper was observed on the cathodic side of each pellet. This minimum bipolar cell voltage, E_d, is given by[3]

$$E_d=(1+n_r)e_d \tag{5}$$

where n_r is the number of pellets placed in parallel with the current between the plate electrodes. The calculated values of E_d for the HT type and SS type beds were 23.5 and 24 V, respectively, and were in agreement with the observed ones.

The broken line in Fig. 6 and 7 shows the observed by-pass current density flowing in the electrolyte phase of the inert bed. The difference between total cell current density and Faradaic current density, j_t-j_f, agrees with the observed by-pass current density. Therefore, the interaction between Faradaic and by-pass current is considered to be small for the regular packing modes, and the general model can be simplified to Case 3 in Fig. 4.

2) Randomly packed bed **Figure 8** shows the effect of electrolysis time on total cell current density j_t, and the short-circuiting current density, j_c, in the randomly packed bed of 0.004-m pellets. Total cell current density increased with time in the same manner as the short-circuiting current density. At higher cell voltages, copper deposited more rapidly between adjacent pellets and lowered the contact resistance.

Figure 9 shows the effect of cell voltage on total cell current density and by-pass current density for different pellet sizes. The by-pass current density was not affected by pellet size. The minimum bipolar cell voltage for a randomly packed bed is given by the following equation, based on the free volume of the pellet.

$$E_d=(1+L\varepsilon_s^{1/3}/d)e_d \tag{6}$$

where L is the distance between two plate electrodes and ε_s is the solid holdup. The term $L\varepsilon_s^{1/3}/d$ corresponds to n_r of the regularly packed bed. The calculated values of E_d from Eq. (6) were 25.6, 49.8, and 98.1 V for d=0.004, 0.002, and 0.001 m, respectively. These values agreed with the experimental ones.

Figure 10 shows current densities via different paths in the randomly packed bed of 0.004-m pellets. The intra-pellet current density, j_p, is a mean of the data

obtained with the composite pellets A and B. The value of j_p is the sum of j_f and j_c for the random packing mode. In the range of $E<50$ V, however, the short-circuiting current can be neglected, and j_p is nearly equal to j_f. As shown in Fig. 10, the value of j_t-j_p agrees with the by-pass current density observed in the inert bed. Thus, the current paths can be expressed by Case 3. In the range of $E>50$ V, the calculated by-pass current density decreased with increasing cell voltage, and the Faradaic resistances, R_{ra} and R_{rc}, became sufficiently small. Therefore, the interaction resistance, R_{f1}, was not negligibly small compared to R_{ra} and R_{rc}. The network model of Case 2 is more suitable in this region.

3. 3 Current efficiency and energy consumption

The overall current efficiency, C_e, and the energy consumption, E_c, are dependent on time because the short-circuiting current increases with time as shown in Fig. 8. The values of C_e and E_c averaged over the electrolysis period are given by the following equations.

$$C_e=100\Delta cnF/I_t t \tag{7}$$

$$E_c=I_t Et/\Delta c \tag{8}$$

where Δc is the amount of deposited copper, I_t is the total cell current, and t is the electrolysis period. The overall current efficiency exceeds 100% in the bipolar packed-bed electrodes as shown in **Fig. 11 (a)**. This means that the electrochemical reaction takes place on each pellet surface as well as the plate electrodes. Therefore, the bipolar packed-bed electrodes behave as if many plate electrodes were arranged in series. The optimum cell voltage appears for the following reasons.

1) Bipolarity of pellets is not sufficient at lower voltages.

2) Hydrogen evolution at higher voltages decreases the current efficiency of copper deposition. **Figure 11 (b)** shows the energy consumption per unit mole of deposited copper. In the randomly packed bed electrodes the minimum value of E_c increases with decreasing pellet size. The energy consumption is strongly related to the value of j_f/j_t, which decreases with increase in electrolysis time as shown in Fig. 8, and with decrease in pellet size as shown in Fig. 9.

Figure 12 shows the effect of packing modes on energy consumption. The regular SS-type bed is the most efficient under the present conditions.

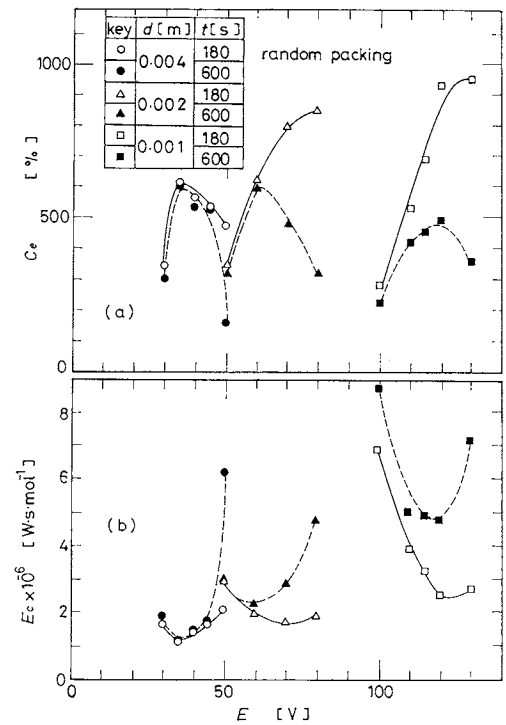


Fig. 11 Electrolysis efficiency for different pellet sizes (a) Overall current efficiency (b) Energy consumption

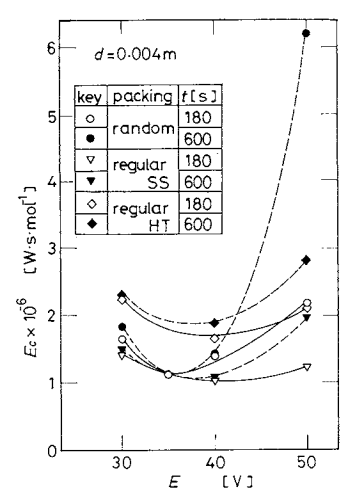


Fig. 12 Effect of packing modes on energy consumption

Conclusion

1) The minimum voltage of a bipolar cell is given by Eq. (5) and Eq. (6) for the regular packing modes and the random packing mode, respectively.

2) Current densities via different paths in bipolar packed-bed electrodes were evaluated separately. For the regularly packed beds, the interaction between Faradaic and by-pass current was small, and the electrodes are well described by the network model of Case 3 in Fig. 4. For the randomly packed bed of 0.004-m pellets, the electrodes are expressed approximately by the model of Case 3 in the range of $E<50$ V and by that of Case 2 in the range of $E>50$ V.

3) The minimum value of energy consumption was observed at a particular cell voltage which was a function of pellet size and packing mode. Energy consumption in the randomly packed bed increased with increase in electrolysis time. This is because the short-circuiting current increased due to copper de-

position. The regular SS-type packing mode was the most efficient for the bipolar electrode cell under the present experimental conditions.

Acknowledgment

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Nomenclature

A	=	area of plate electrode	[m^2]
C_e	=	overall current efficiency	[%]
Δc	=	amount of deposited copper	[mol]
d	=	pellet diameter	[m]
e_d	=	decomposition voltage	[V]
E	=	cell voltage	[V]
E_c	=	energy consumption	[$W \cdot s \cdot mol^{-1}$]
E_d	=	minimum bipolar cell voltage	[V]
E_0	=	cell voltage without ohmic potential drop	[V]
I_p	=	intra-pellet current	[A]
I_t	=	total cell current	[A]
j_c	=	short-circuiting current	[$A \cdot m^{-2}$]
j_f	=	Faradaic current density	[$A \cdot m^{-2}$]
j_p	=	intra-pellet current density	[$A \cdot m^{-2}$]
j_t	=	total cell current density	[$A \cdot m^{-2}$]
L	=	distance between two plate electrodes	[m]
n_c	=	number of pellets between two net separators	[—]
n_r	=	number of pellets placed in parallel with the current between two plate electrodes	[—]
R_b	=	resistance of by-pass current path	[Ω]
R_c	=	resistance of short-circuiting current path	[Ω]
R_{f1}, R_{f2}, R_{f3}	=	resistances of electrolyte between adjacent pellets	[Ω]
R_{ra}	=	resistance associated with anodic reaction at the double layer	[Ω]
R_{rc}	=	resistance associated with cathodic reaction at the double layer	[Ω]
t	=	time	[s]
ε_s	=	solid holdup	[—]

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