Behavior of a Model Bipolar Cell
with Cylindrical Electrodes

by

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Abstract

A type of bipolar cell, which consisted of graphite rods as bipolar elec-
trodes, was constructed as a model of the packed bipolar cell. Behavior of this
cell was investigated in the electro-deposition of copper from dilute solutions of
copper (II) sulfate. The effective cathode area on each electrode was dependent
on the applied voltage. The maximum energy efficiency was attained at a
certain voltage. These results are discussed on the basis of the concept of
threshold voltage and linear potential gradient in solution.

Introduction

The bipolar packed-bed cell, or briefly, the packed bipolar cell, is a type of
electrolytic cell which consists of a bed of conducting particles placed between
the main electrodes.[1] When the packing particles are electrically separated from
each other, and a sufficiently high voltage is applied between the main elec-
trodes, each particle can become a bipolar electrode. An anodic reaction occurs
at one end and a cathodic reaction at the other end. One way of achieving such
conditions is to use an appropriate mixture of conducting and non-conducting
particles.[1] Another way is to use particles having a high contact resistance, such
as carbon particles.[2] Since the effective reaction area is extended three-dimen-
sionally throughout the space between the main electrodes, this type of cell is
suitable for the electrolysis of dilute solutions of low electric conductivity.

The packed bipolar cell has been tested in the electrolytic treatment of waste
waters.[2-4] Large-scale operations have been tried in the treatment of industrial
waste water[5] and municipal sewage.[6] Also, the production of some organic

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chemicals such as propylene oxide and styrene oxide has been attempted.[1,7] Fleischmann et al.[1] have analyzed the performance of the packed bipolar cell using a simplified model. Goodridge et al.[7] have applied the model to their work. Since the packed bipolar cell is a complicated system, it may be helpful to use a model cell to learn the cell characteristics. From this point of view, we have constructed a model cell which consists of graphite rods as bipolar electrodes. Then, we investigated its behavior in the electro-deposition of copper from dilute solutions of copper (II) sulfate. An analysis of the cell performance is attempted using a simplified model.

Experimental

The model cell was made of poly (methyl methacrylate) plates and graphite rods. The inside dimensions of the cell were 85 mm in length, 20 mm in width, and 100 mm in depth (effective length of the graphite rods). As shown in Fig. 1, five
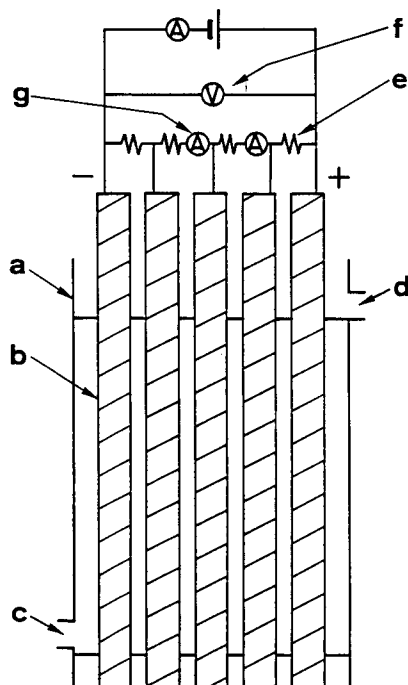

Fig. 1 Diagram of the bipolar graphite rod cell.
   a: poly (methyl methacrylate) case, b: Graphite rod,
   c: Solution inlet, d: Solution outlet,
   e: Inserted resistor, f: Voltmeter, g: Ammeter.

graphite rods of 10 mm in diameter were positioned vertically in a line with gaps of 5 mm from the adjacent rods and from the side walls, and 7.5 mm from the end walls. Resistors, which represented electronic contact between packing particles, were inserted. A dilute solution of copper (II) sulfate was continuously fed at the flow rate of 17 cm³ / min from the bottom of one end of the cell, and withdrawn from the top of the other end. A constant DC voltage was applied between the end rods, and the total current passing through the cell was recorded. Currents passing through the inserted resistors were also measured. The effective cathode area on each bipolar electrode was measured by observing the surface of the graphite rod through a microscope which was movable on a measuring device. The amount of deposited copper was determined by dissolving the copper with nitric acid and analyzing the copper (II) ion content in the resulting solution colorimetrically using sodium diethyldithiocarbamate as a chelating agent.[8] All experiments were conducted at room temperature. Concentrations are expressed in the units of $M = mol \cdot dm^{-3}$ throughout this paper.

Results and Discussion

Effective cathode area on the bipolar electrode. The surface of the three central rods was visually observed during the electrolysis of a copper (II) sulfate solution of $5.0 \times 10^{-3} M$. When the applied voltage was sufficiently high, the metallic copper was deposited on one side of each rod, and gas evolved on the other side. This observation suggests that the three central rods became bipolar electrodes on which the reactions of Eq. 1 and Eq. 2 took place.

$$Cu^{2+} + 2\,e^- \longrightarrow Cu \qquad\qquad (1)$$

$$H_2O \longrightarrow \frac{1}{2} O_2 + 2\,H^+ + 2\,e^- \qquad\qquad (2)$$

Figure 2 schematically shows the anodic (left) and cathodic (right) areas on each bipolar electrode. After some amount of copper was deposited on the electrodes, the effective cathode area was determined by observing the rod surface through a microscope. As shown in Fig. 3, the effective cathode area increased with an increasing voltage, approaching half the total surface of the rod (15.7 cm²).

The effective electrode area was also measured at a constant voltage when the inserted resistance was varied. As shown in Fig. 4, the effective cathode area was almost independent of the inserted resistance. Inserted resistance,
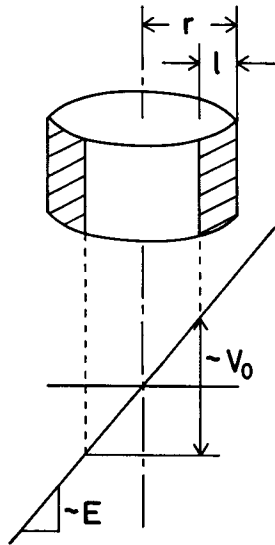
Fig. 2 Schematic representation of a
bipolar electrode.
V_0: Threshold voltage,
E : Potential gradient in
electrolyte,
r : Radius of graphite rod,
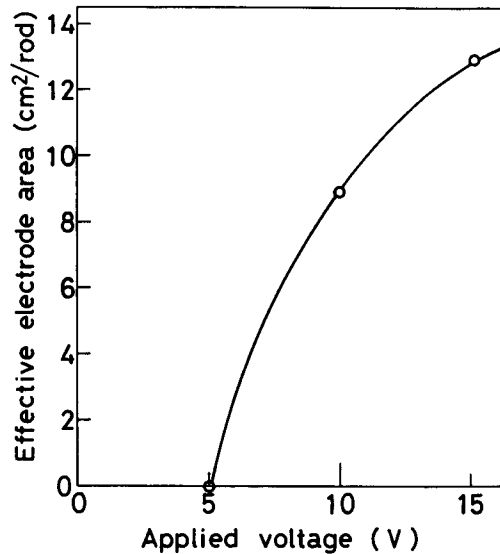l : Length corresponding to the
effective electrode area.

Fig. 3 Effective electrode area as a
function of applied voltage.
$CuSO_4$ concentration : 5.0 ×
10^{-3} M,
R_c: 1000 Ω.

which represents the electronic contact between the particles in a packed bipolar
cell, can be regarded as a partial short–circuit which does not affect the effective
electrode area.

If it is assumed that a linear potential gradient exists in the electrolyte, and
that the electrode reactions take place above a threshold voltage, as was consid-
ered by Fleischmann et al.,[1] the length "l" corresponding to the effective elec-
trode area (see Fig. 2) should be expressed by Eq. 3,

$$l = r - V_0 / 2E \qquad\qquad (3)$$

where r is the radius of the graphite rods, V_0 the threshold voltage, and E the
potential gradient in the solution. Figure 5 shows the observed l–values
plotted against $1/E$. The straight line represents the expected relationship (Eq.
3), where V_0 is assumed to be equal to the thermodynamic decomposition
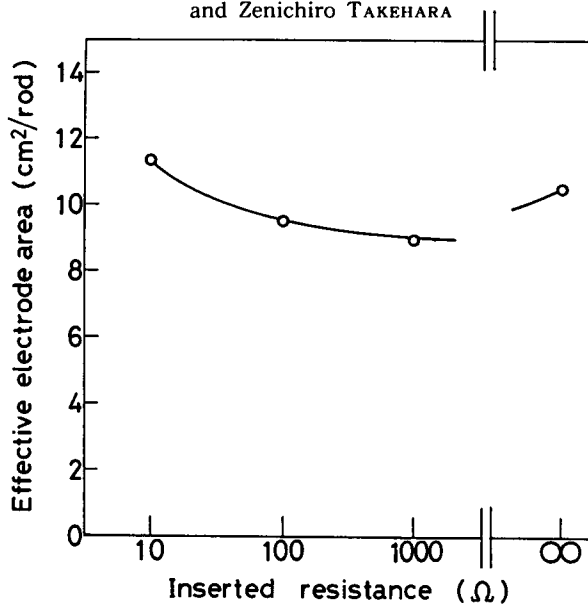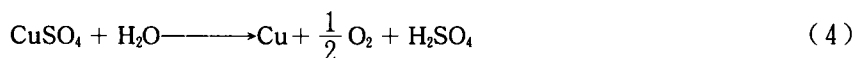voltage for the reaction of Eq. 4 (0.99 V).

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Fig. 4 Plot of the effective electrode area against inserted resistance.
        $CuSO_4$ concentration: $5.0 \times 10^{-3} M$,
        Applied voltage: 10 V.

$$CuSO_4 + H_2O \longrightarrow Cu + \frac{1}{2} O_2 + H_2SO_4 \qquad (4)$$

Although the observed data are somewhat scattered around the theoretical line, the above model seems approximately correct.

Figure 6 shows the amount of copper deposited in a certain duration of time plotted against the effective cathode area. The amount of copper increased with an increasing cathode area, but more rapidly at a larger cathode area. It seems that the process of electro–deposition of copper is not simply diffusion-controlled due to the migration of copper ion.

Current–voltage–resistance relationships and energy efficiency. Figure 7 shows the relationship between the total current and the applied voltage. It was seen that the current increased with an increasing voltage. The three central rods began to function as bipolar electrodes at about 5 V. The sum of the faradaic current (I_F) and the by–pass current through the solution (I_s) was obtained from the measurements of the total current (I_T) and the current through inserted resistors (I_c) according to $I_F + I_s = I_T - I_c$. Figure 8 shows the ratio ($I_F + I_s$) / I_T plotted against the applied voltage. The ratio depends mainly on the inserted
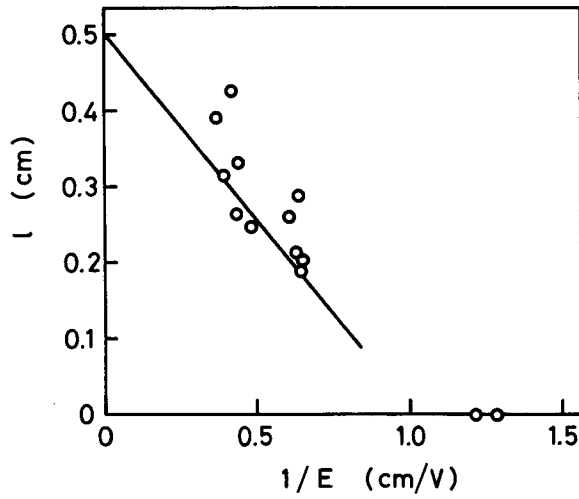
Fig. 5 Plot of the length 1 (defined in Fig. 2) against reciprocal of potential gradient.
CuSO$_4$ concentration: 5.0×10^{-4} M.
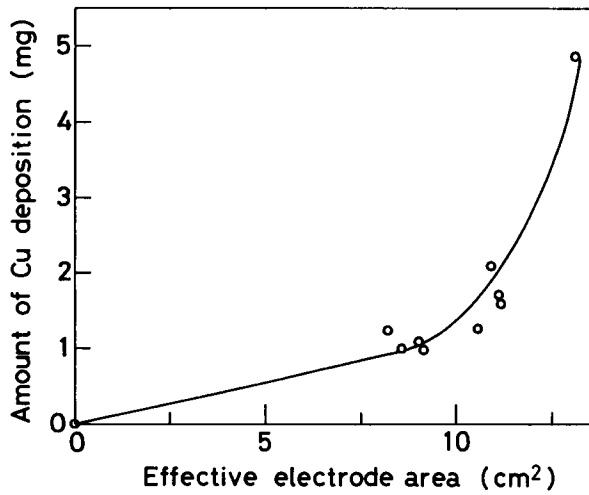

Fig. 6 Relationship between the amount of deposited copper and the effective electrode area.
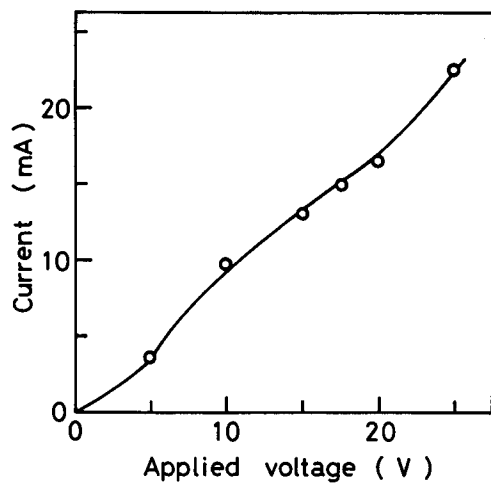CuSO$_4$ concentration: 5.0×10^{-3} M,
Duration of electrolysis: 20 min.

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Fig. 7 Total current passing through the cell as a function of applied voltage.
CuSO$_4$ concentration:
2.5×10^{-4} M,
R$_c$: 1000 Ω.

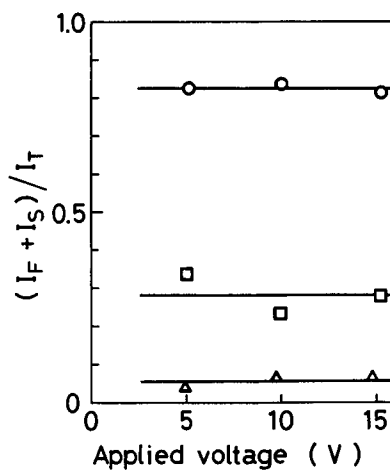Fig. 8 Plot of (I$_F$+I$_S$) /I$_T$ against applied voltage.
CuSO$_4$ concentration:
5.0×10^{-4} M,
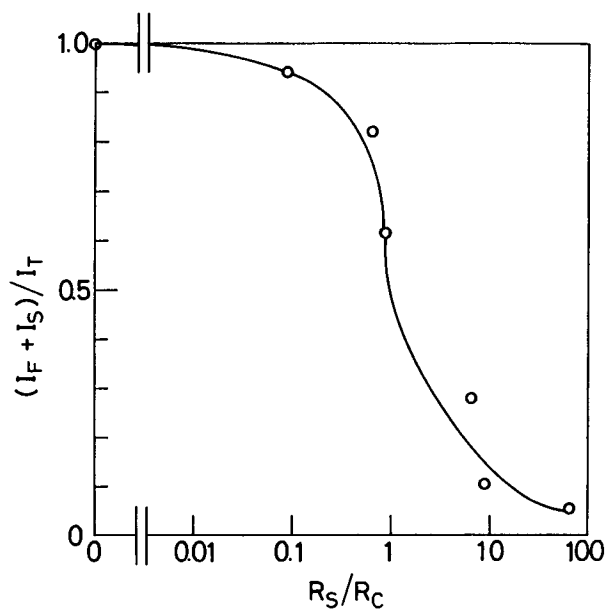R$_c$: 10 Ω (△), 100 Ω (□),
1000 Ω (○).

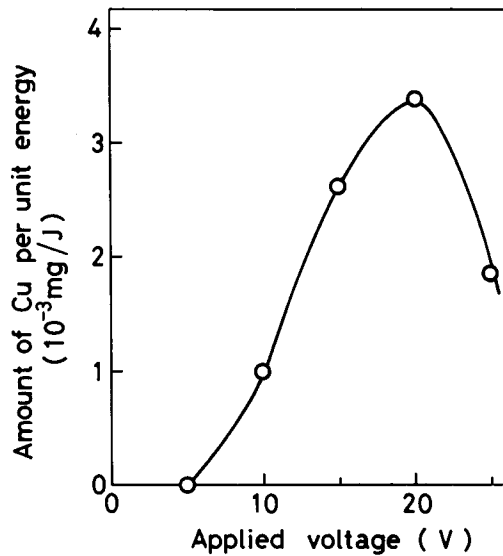Fig. 9 Relationship between (I$_F$+I$_S$) /I$_T$ and R$_S$/R$_c$.

Fig. 10 Amount of deposited copper per unit energy plotted against applied voltage.
CuSO$_4$ concentration: 2.5×10^{-4} M,
R$_c$: 1000 Ω.

resistance (R$_c$), but not on the applied voltage. Figure 9 shows a plot of (I$_F$ + I$_s$) /I$_T$ against R$_s$ / R$_c$ where R$_s$ is the resistance of the solution. The ratio (I$_F$ + I$_s$) / I$_T$ becomes very small when R$_s$ / R$_c$ becomes larger than one. This suggests that packing particles with high contact resistance are needed in packed bipolar cells when solutions with low ionic conductivity are to be electrolyzed.

Figure 10 shows the amount of copper deposited on each bipolar electrode per unit energy, which is a measure of the efficiency with respect to the energy utilization, as a function of the applied voltage. When the voltage was relatively low, the efficiency increased with an increasing voltage due to an increasing cathode area. It reached a maximum and then decreased, probably due to increasing currents in the solution (I$_s$) and in the inserted resistance (I$_c$), and also due to a side reaction, i. e., the hydrogen evolution reaction. It seems to be important to know how the maximum efficiency is related to the cell dimensions and operating conditions.

Calculation of the energy efficiency by a simplified model. Fleischmann et al.[1], and later, Goodridge et al.[7] have applied a simplified model to the analysis of the performance of packed bipolar cells. Their model is based on the following two

assumptions:

    (1) Potential gradient in solution is linear.

    (2) Electrochemical reactions are characterized by two parameters, i. e., the threshold voltage V_0 and the diffusion limiting current density i_d.

Although the conditions for a pure diffusion-controlled reaction are not satisfied in the present work, it seems worth trying to calculate the energy efficiency based on the above model, and then compare it with our experimental results. In the following treatment, further assumptions are made:

    (3) No side reactions occur on the electrodes, i. e., the faradaic current efficiencies for concerned reactions are 100%.

    (4) The by-pass current in solution is proportional to the potential gradient and to the apparent conductivity of the solution, which is calculated by Rayleigh's equation[9] $\kappa' = \kappa(1-f) / (1+f)$, where κ is the specific conductivity of the solution and f is the volume fraction of graphite rods in the cell.

Applying this model to the present graphite-rod cell, we calculate the energy efficiency in a unit cell which is located between two adjacent rods of the three central rods. From the assumptions (1) and (2), the effective electrode area is given by[7]

$$A = 2\,rh\,\cos^{-1}\,(V_0 / 2\,rE) \qquad\qquad (5)$$

where h is the length of the graphite rods. Since the faradic current is assumed to be controlled by a diffusion process, it is given by

$$\begin{aligned} I_F &= i_d A \\ &= 2\,rhi_d\,\cos^{-1}\,(V_0 / 2\,rE) \end{aligned} \qquad\qquad (6)$$

where i_d is the diffusion limiting current density. The by-pass current through the solution and the short-circuit current through the inserted resistor are

$$I_S = V_{cell} / R_S \qquad\qquad (7)$$
$$I_C = V_{cell} / R_C \qquad\qquad (8)$$

where V_{cell} is the voltage applied to the unit cell, R_S the apparent resistance of the solution, and R_C the resistance of the inserted resistor. R_S is calculated by
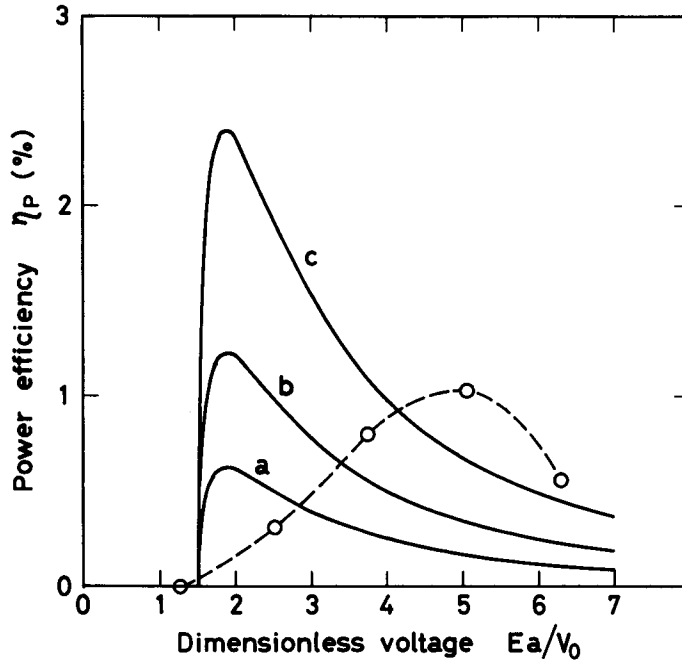
$$R_S = [\kappa(1-f) / (1+f)]^{-1} (a / bh) \qquad\qquad (9)$$

Fig. 11 Calculated and observed energy efficiencies as a function of dimensionless
quantity Ea/V_0.
———: Calculated, i_d (A/cm^2) : (a) 5.0×10^{-6}, (b) 1.0×10^{-5}, (c) 2.0×10^{-5},
————: Observed (recalculated from Fig. 10).

where a is the length of the unit cell, and b the width of the cell. The energy
efficiency can be defined as the ratio of $V_0 I_F$ to $V_{cell} I_T$, where I_T is the total
current passing through the cell;[*]

$$I_T = I_F + I_S + I_C \tag{10}$$

Using Eqs. 6, 7, 8, and 10, and the equation $V_{cell} = Ea$, the energy efficiency is
given by:

$$\eta_p = V_0 I_F / V_{cell} I_T$$

$$= \frac{2 V_0 \, rhi_d \cos^{-1} (V_0 / 2 rE)}{Ea[2 \, rhi_d \cos^{-1} (V_0 / 2 rE) + Ea(1 / R_s + 1 / R_c)]} \tag{11}$$

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[*] According to this definition the energy efficiency is unity when
$I_s = I_c = 0$ and $V_{cell} = V_0$.

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In order to simulate the experimental results shown in Fig. 10, the following values are substituted: $r = 0.5$ cm, $a = 1.5$ cm, $b = 2.0$ cm, $h = 10.0$ cm, $v_0 = 1.00$ V, $r_c = 1.0 \times 10^3 \, \Omega$, $R_s = 2.1 \times 10^3 \, \Omega$*, and $f = 0.26$. Figure 11 shows the energy efficiency η_p in percent for three different values of i_d, as a function of the dimensionless quantity Ea / V_0. The broken line in the Figure shows the experimental result which is recalculated from Fig. 10.** Although the calculated curve exhibits the features of the experimental curve to some extent, the agreement is not very good. A possible reason for the poor agreement is that the assumption of a linear potential gradient and the concept of a threshold voltage may not be appropriate to the present case. In order to give a more reasonable explanation, we need to know a precise picture of the potential and current distributions in the cell. Such problems will be treated in succeeding papers.

List of symbols

A	Effective electrode area (cm^2)
a	Length of unit cell (cm)
b	Width of unit cell (cm)
E	Potential gradient in solution (V / cm)
f	Volume fraction of graphite rods (dimensionless)
h	Depth of cell (effective length of graphite rods) (cm)
I_F	Faradaic current (A)
I_s	By-pass current through solution (A)
I_c	Short-circuit current through inserted resistor (A)
I_T	Total current (A)
i_d	Diffusion limiting current density (A / cm^2)
l	Length defined in Fig. 2 (cm)
R_s	Apparent resistance of solution across unit cell (Ω)
R_c	Resistance of inserted resistors (Ω)
r	Radius of graphite rods (cm)
V_0	Threshold voltage (V)

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* R_s is calculated by Eq. 9 with $\kappa = 6.0 \times 10^{-5} \, \Omega^{-1} \, cm^{-1}$ which is obtained from Ref. 10.

** The obtained values of η_p are very small since no optimization has been made on the cell design.

V_{cell}	Voltage applied to unit cell (V)
η_p	Energy efficiency (dimensionless)
κ	Specific conductivity of solution $(\Omega^{-1}cm^{-1})$
κ'	Apparent conductivity of solution $(\Omega^{-1}cm^{-1})$

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