Experimental Investigation of the Components of Network Model at Bipolar Disk Electrode with Many Holes

Takeshi SASAKI* and Tatsuo ISHIKAWA*

The applicability of the network model to describing a bipolar electrode system has been investigated by the use of the disk electrodes with many holes as the by-pass parts in acidic bichromate solutions. A method of determining the Faradaic current through bipolar electrodes as packed compactly in the cell is also described. The by-pass resistance as determined by measuring the unit cell voltage at one bipolar electrode, the Faradaic current, and the by-pass current increased with the applied current. The increase is probably due to the reduction in the electrolyte region for the by-pass resistance, since the current flow lines may steeply be distorted in the vicinity of the electrode holes in the three-dimensional field composed of the electrode-electrolyte system. It is concluded that the network model of the bipolar electrode system must be modified as expressing the by-pass part by a variable resistance.

1 Introduction

The applied current to a bipolar electrode system is separated into the Faradaic current through the bipolar electrode and the by-pass current through the electrolyte; the first important problem on designing a bipolar electrode cell is to raise the proportion of the Faradaic current as large as possible. The proportion is determined by the relation between the characteristics of the Faradaic process at the electrode and the resistance of the by-pass current in the electrolyte, but the prediction of it is usually impossible from the electromagnetic theory, because of its complexity in three-dimensional field.

The proportion of the Faradaic current and the energy consumption of bipolar electrode systems have been estimated with network models¹⁻³⁾. In those models, the resistance of the Faradaic current which is referred to as a Faradaic resistance is expressed by a constant or a variable resistance and the resistance of the by-pass part which is referred to as a by-pass resistance, by a constant resistance; the former is determined by the characteristics of the Faradaic process and the latter, by the shape of the by-pass part and the specific resistance

of the electrolyte.

The ununiformity of current distribution at the electrode surface, however, may arise in the actual bipolar electrode system, since the reaction surface spreads in the direction of the current flow with the increase in the applied current. Even if the reaction surface little expands, the steep distortion of the current flow lines may occur in the vicinity of the by-pass part in the electrolyte, especially in a strong electric field. This leads to the fact that the proportion of the reaction current in the actual system may deviate from the current distribution expected from the network models. The deviation from the models may be pronounced at the bipolar electrode with many small holes, since the electrode areas in the neighborhood of the holes play a relatively important role in the electrode behavior.

In the present work, the by-pass resistance was experimentally determined at the bipolar disk electrodes with many drilled holes and it was compared with the by-pass resistance of the network model to elucidate the applicability of the model to describing the bipolar electrode system with many holes.

2 Experimental

2.1 Test cell, electrode, and electrolyte

The electrolytic cell and the measuring systems are schematically shown in Fig. 1. The

* Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University (Kitaku, Sapporo 060)
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Fig. 1 Schematic diagram of the test cell and measuring system

a-bipolar electrode, b-end cathode, c-end anode, d-split electrode, e-teflon spacer, f-silicon packing, g-acrylic fringe, h-Luggin capillary, i-SCE, j-electrolyte inlet, k-electrolyte outlet

cell was made of pyrex glass tubes of the inner diameter of 26 mm. It was composed of three parts, namely, a electrolytic part, a electrolyte inlet, and a electrolyte outlet, which were connected with each others by acrylic fringes and packing of silicon rubber. Five disk electrodes were stacked and two end electrodes were arranged at the top and the bottom of the stack in the electrolytic part. A split electrode described later was, if necessary, substituted for the center electrode for determining the Faradaic current through the bipolar electrodes. Interelectrode gaps (l_g) were maintained 1 or 5 mm by spacers of teflon rings. Applying electrolytic current to the end electrodes, cathodic reactions took place at the upper surfaces of the electrodes and anodic ones took place at the lower surfaces, that is, those electrodes operated in a bipolar manner.

The disk electrode were made of graphite rods (G-150, Tokai Electrode Co., Ltd.) Many holes were made through the electrode disks for the path of electrolytes and evolved gases. The diameter of holes (ϕ) was 1 mm and the number of them (n) was varied from 27 to 85. The electrode thickness (d) were 10 or 20 mm. The electrical resistance of the electrolyte filling the holes, which corresponds to the by-pass resistance of the network model in this work,

could be arbitrarily changed by varying n and d . The end electrodes had the same number of the holes as the bipolar electrodes under investigation.

King *et al.* developed a split electrode and determined the Faradaic current through the bipolar electrode by measuring it directly with an ammeter on organic syntheses⁴⁾. The measurements could be carried out, since the space between electrodes and the walls of the cell was relatively large and the electrodes were exposed to the gas phase in the cell. It was impossible, however, in the compactly packed cell as in the present work to measure the Faradaic current with such as their split electrode.

Fig. 2 Modified split electrode
a-graphite disk, b-acrylic insulator,
c-short-circuit wire, d-lead wire

The split electrode was modified to determine the Faradaic current in the compactly packed cell as shown in Fig. 2. A graphite disk was sliced perpendicularly to its axis and an insulating layer of acrylic resin was placed between the two halves, which were connected electrically with a short circuit wire. The fine wires covered with insulating tubes were soldered with the both ends of the short-circuit wire. The side of the electrode was coated with silicon resin to avoid the attack by electrolytes upon these wires. The Faradaic current could be determined by measuring the ohmic potential drop at the short-circuit wire with the fine lead wires. The electric resistance of the short-circuit wire was about 5 m Ω , which was precisely determined by electrical measurements. The value was negligibly small compared with the reaction resistance described later; the short-circuit wire did not hinder at all the passage of the Faradaic current through the split electrode.

Cr (VI) can be reduced to Cr (III) in bipolar

electrode systems composed of graphite electrodes in acidic bichromate solutions, since the electrochemical reduction of Cr (VI) to Cr (III) takes place irreversibly on graphite electrodes as on platinum electrodes⁵⁾ and the reverse reaction does not practically take place at the anodic surface of the bipolar electrode.

The test electrolytes were 0.01~0.1 M $K_2Cr_2O_7$ in 0.05~0.5 M H_2SO_4 which were prepared by dissolving guarantee grade reagent (Wako Junyaku Co., Ltd.) in distilled water. The solutions were maintained at 30°C and circulated by a pump at 400 ml·min⁻¹ during experiments.

2.2 Measurement

The applied current (J_t) and cell voltage (V_{cell}) were measured in the usual way. The Faradaic current (J_r) was determined by the use of the split electrode. The unit cell voltage of a bipolar electrode (ΔE_{bi}) was determined by measuring the potential differences between the two Luggin capillary probes set at the close vicinity of both surfaces of the bipolar electrode as shown in Fig. 1.

The network model for a bipolar electrode system is represented as a parallel circuit composed of a Faradaic resistance (R_r) and a by-pass resistance (R_{s1}), and a sandwich electrolyte resistance (R_{s2}) in series, as proposed by King and Wright⁹⁾. The Faradaic resistance expressing a decomposition voltage and a reaction resistance are represented by a variable resistance at the model, because of the non-linearity of the current-voltage characteristics of the Faradaic process. The by-pass resistance, however, is considered as a constant resistance determined by the specific resistance of the electrolyte and the shape of the by-pass part of the electrolyte.

In order to examine the applicability of the network model to the actual reaction systems, we consider an actual by-pass resistance (R'_{s1}) as a measurable resistance and compare it with R_{s1} . The actual by-pass resistance is defined as follows.

$$R'_{s1} = \frac{\Delta E_{bi}}{J_s} = \frac{\Delta E_{bi}}{J_t - J_r} \quad (1)$$

R'_{s1} is determined by the distribution of the current flow lines in three-dimensional field and there is no region of electrolyte assigned *a*

priori to R'_{s1} , since the flow lines are steeply bent to the electrode surface near the holes on the actual electrolysis and the distortion may be enhanced with applied current, that is, with the increase in the strength of electric field. R_{s1} , however, means the resistance of the electrolyte filling the holes of the electrodes under consideration; it is strictly determined by the cross section, the length, and the number of the holes, and the specific resistance of the electrolyte.

3 Results and Discussion

3.1 Polarization curves

Polarization curves were observed at both end electrodes. They are shown by closed circles in Fig. 3, where the potential is referred to SCE. Main cathodic reactions were the reduction of Cr (VI) to Cr (III) and the oxygen reduction, and anodic one, oxygen evolution. The cathodic potential decreased markedly in the range lower than 0.6 V, which was due to the additional overvoltage from Cr (VI) diffusion.

Open circles indicate the relation between the Faradaic current through the split electrode and the potential of the bipolar electrode as mea-

Fig. 3 Comparison between polarization curves (●) at end electrodes and Faradaic current-potential curves (○) at bipolar electrode of $p=12.6\%$ in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4 .

sured by Luggin capillary probes set at close vicinity to the upper and the lower surfaces of the split electrode. They coincide with the polarization curves at the end electrodes in all range; the relation between the Faradaic current and the electrode potential is the same both at the bipolar electrode and the end electrodes. This fact indicates that J_r was exactly determined by the use of the modified split electrode.

3.2 Faradaic current through bipolar electrode

The Faradaic current (J_r) through the bipolar electrode was determined using the split electrodes at various applied current (J_t). The percentage of J_r to J_t , [$\eta_{el} = (J_r/J_t) \times 100$], are presented in Fig. 4, where p is defined as the percentage of the sum of cross section of the holes to that of the bipolar electrode. In this figure, p and d of one electrode are twice as large as those of the other; the two electrodes are equal in the by-pass resistance calculated as $R_{s1} = 6.55 \Omega$. The figure indicate that the curves nearly agree with each other. It seems from this fact that the bipolar electrode system is explained in terms of a by-pass resistance and can be represented by the network model. But it will be elucidated later that η_{el} values in the figure must necessarily be higher than that values as calculated by the use of the network model due to the increase in the actual by-pass resistance (R'_{s1}) with the applied current.

Fig. 4 Plot of the fraction of the cell current via the Faradaic process against applied current in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4
Electrodes: $\circ$ — $p=6.3\%$, $d=10$ mm, $\bullet$ — $p=12.6\%$, $d=20$ mm

3.3 Comparison between R_{s1} and R'_{s1}

J_r and J_s determined by the use of the split electrode are plotted against J_t in Fig. 5. ΔE_{bi} observed simultaneously are presented in Fig. 6. It is remarkable from Fig. 5 that each J_s reaches practically a constant value and each J_r increases straight with J_t except the very early stage of J_t . The reached values of J_s increase with p . Figure 6 shows that ΔE_{bi} steeply increase with J_t in the early stage where J_r is small and J_s takes the most part of J_t ; then ΔE_{bi} increase relatively slowly as J_r becomes significantly large. It also shows that ΔE_{bi} decrease with p , that is, with the decrease in R_{s1} . It is noticeable by comparing Fig. 6 with Fig. 5 that ΔE_{bi} continue to increase with J_t .

Fig. 5 Relations of J_r and J_s to J_t in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4
 p values: a-4.0%, b-8.2%, c-12.6%

Fig. 6 Relations between ΔE_{bi} and J_t in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4
 p values: a-4.0%, b-8.2%, c-12.6%

Fig. 7 Variations in resistance components with applied current at graphite electrode and dummy electrode of $p=12.6\%$ in $0.1\text{ M K}_2\text{Cr}_2\text{O}_7$ in $0.5\text{ M H}_2\text{SO}_4$

even after J_s reached the constant value, therefore it is easily seen that R'_{s1} estimated from equation (1) will increase with J_t .

The plot of R'_{s1} against J_t is shown with those of R_r and R_{s1} vs. J_t in Fig. 7, where R_r was calculated from $\Delta E_{bi}/J_r$ and R_{s1} was experimentally determined in the same manner as R'_{s1} using a dummy electrode instead of the split electrode. The dummy electrode was made of nonconducting resin of which shape and holes were identical with the test graphite electrode. In the figure, R_{s1} is constant in all range of the experimental current. R'_{s1} , however, increases with J_t and R_r shows an exponential decrease with J_t . The constant value of R_{s1} coincides with the resistance of the electrolyte filling in electrode holes which was calculated from the cross section, the length, and the number of the holes, and the specific resistance of the electrolyte. The specific resistance was measured with a Universal Bridge (type 4265 A, Yokogawa Hewlett-Packard, Co., Ltd.) at 1000 Hz. The above fact indicates that the experimental measurements of R_{s1} at the dummy electrode were correctly carried out; the ohmic potential drop which might be contained in ΔE_{bi} was negligibly small and R_{s1} was little affected by the gas which was evolved at the electrodes as arranged lower than the dummy electrode, and so on. Therefore it is reasonable to conclude that R'_{s1} also was not

influenced by the ohmic potential drop which might be contained in ΔE_{bi} and the evolved gas, since it was determined in the same manner as R_{s1} using the split electrode. It is impossible to elucidate to what extent the reaction surfaces expand, but in any event, the increase in R'_{s1} with J_t may be attributed to the reduction in the electrolyte region for R'_{s1} due to the steep distortion of the current flow lines in the vicinity of the electrode holes; the applied current is distributed to the bipolar electrode or the by-pass electrolyte according to the distribution of the flow lines in the three-dimensional field composed of the electrode-electrolyte sys-

Fig. 8 Relations between R'_{s1}/R_{s1} and η_{el} in $0.1\text{ M K}_2\text{Cr}_2\text{O}_7$ in $0.5\text{ M H}_2\text{SO}_4$
 p values: $\times$ -4.0%, Δ -8.2%, $\circ$ -12.6%

Fig. 9 Relations between R'_{s1}/R_{s1} and η_{el} at electrode of $p=12.6\%$

Solutions: Δ -0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ in $0.05\text{ M H}_2\text{SO}_4$, $\times$ -0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ in $0.5\text{ M H}_2\text{SO}_4$, $\circ$ -0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ in $0.5\text{ M H}_2\text{SO}_4$

tem, though the distribution in the three-dimensional field is not considered on the network model.

The resistance ratios R'_{s1}/R_{s1} at three electrodes with different p are plotted against η_{el} in Fig. 8, where the electrodes have nearly equal R_r because of the same solution and R_{s1} varies from 6.55 to 20.6 Ω according to p . The same relations at a electrode in various solutions are presented in Fig. 9. In this case, R_{s1} varies from 6.55 to 53.6 Ω according to the specific resistance of electrolytes and R_r also indicates the different values in each solution. Three curves seem nearly coincident with each others in Fig. 8 and the ratios increase obviously in the region beyond 60% η_{el} . Those in Fig. 9 also show the similar behavior. In these figures, $R'_{s1}/R_{s1}-\eta_{el}$ plots indicate analogous behavior even under the different values of R_{s1} and R_r at various p and in various solutions. It seems from above results that the ratio of the Faradaic current to the by-pass current may be related with important factor to determine the distortion of the current flow lines near the holes. It is noticeable, in any case, that the deviation of R'_{s1} from R_{s1} becomes large at high η_{el} region where we consider the cell design in most cases.

3.4 Proportion of by-pass current to applied current

Fig. 10 Plot of the fraction of by-pass current against applied current in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4

○—direct measurement, ●—calculated from network model, p values : a—4.0%, b—8.2%, c—12.6%

The percentage of J_s to J_t was calculated from the network model by the use of J_t , ΔE_{bi} , and R_{s1} to elucidate the effect of the deviation of R_{s1} from R'_{s1} on the by-pass current. The values are shown with those from J_s as determined experimentally using the split electrode in Figs. 10, 11, and 12. It is seen from Fig. 10 that the calculated values become larger than the experimental ones at all electrodes in large J_t region, that is, in relatively high η_{el} region. The deviations reach about 2% at $p=4.0\%$

Fig. 11 Plot of the fraction of by-pass current against applied current at the electrode of $p=12.6\%$ in 0.01 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4

○—direct measurement, ●—calculated from network model

Fig. 12 Plot of the fraction of by-pass current against applied current at the electrode of $p=12.6\%$ in 0.01 M $K_2Cr_2O_7$ in 0.05 M H_2SO_4

○—direct measurement, ●—calculated from network model

Fig. 13 Modified network model

R_f -Faradaic resistance, R_{s1} -by-pass resistance, ΔR_{s1} -increment of by-pass resistance, R_{s2} -sandwich electrolyte resistance, J_t -applied current, J_f -Faradaic current, J_s -by-pass current

and 4%, at $p=8.2$ and 12.6%. Those in Figs. 11 and 12 also reach 4% at high J_t region, though the hydrogen evolution takes place at that region in addition to the reduction of Cr (VI).

Since it was proved that the actual by-pass resistance increased with the applied current, the network model for the bipolar electrode system should be modified as shown in Fig. 13, where R'_{s1} is expressed by the sum of R_{s1} and ΔR_{s1} . ΔR_{s1} , expressed as a variable resistance, is the increment of R_{s1} to become significantly large at high η_{el} region. If the by-pass current at the bipolar electrode with the small holes as in this work is calculated by the use of the simple network model where ΔR_{s1} component is not considered, it will be always

large estimated in high η_{el} region, though the size effect of the holes on ΔR_{s1} cannot be elucidated by the present work.

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.

The by-pass resistance determined by experiments increases with the applied current at the disk bipolar electrode with many small holes as the by-pass part. It has been shown that the simple network model of the bipolar electrode system must be modified as expressing the by-pass part by a variable resistance.

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