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Determination of Faradaic Current through a Bipolar Electrode in Acidic Bichromate

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Abstract

In order to elucidate the factors determining the proportion of the Faradaic current to the applied one, the Faradaic current through a bipolar electrode was measured under various conditions in acidic bichromate solutions.

A modified electrode was adopted for measurement of the Faradaic current in a compactly packed cell. The bipolar electrodes consisted of graphite disks with many drilled holes. The by-pass resistance, the electric resistance of the electrolyte filling the holes, widely varied with functions of the diameter and the number of the holes and the thickness of the electrodes. The interelectrode gaps were also varied.

The proportion of the Faradaic current to the applied one was substantially determined by the by-pass resistance independent of the diameter and the number of holes, and the thickness of the electrode. As continuous electrolysis was carried out in the acidic bichromate solutions, the proportion of the Faradaic current remarkably decreased in low concentrations of Cr(VI) and this was responsible for the decrease in the gross current efficiency in the bipolar electrode cell.

1. Introduction

In recent years a number of bipolar electrode cells have been developed for organic syntheses[1~5] and electrochemical treatments of waste water.[6,7] The bipolar electrodes are operable without lead wires in a bipolar manner when they are arranged between end electrodes. These characteristics make it possible to vary the shapes of the electrodes and the cell structures in such a way that the electrode system may have a significantly large electrode area per unti cell volume and/or enhancement of mass transfer: packed bipolar cell,[1,3,6,7] fluidized bed cells,[4] a thin film bipolar cell,[2] a bipolar trickle tower cell,[5] a rotating bipolar electrode stack cell,[8] etc.

The applied current to a bipolar electrode system is carried by the Faradaic current through the bipolar electrode and the by-pass current through the electrolyte. One of the most important problems in designing a bipolar electrode cell is to raise the proportion of the Faradaic current to a large extent as possible. Several investigators[3,9,10] have devoted their efforts to estimate the proportion of the Faradaic current and the energy consumption

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of the bipolar electrode systems by utilizing network models. However, there have been only a few studies on the function of bipolar electrodes and the network model itself has not been confirmed experimentally as yet.

In the present work, the controlling factors of the Faradaic current and its proportion to the applied current were invenstigated in acidic bichromate solutions using the bipolar disk electrodes with many drilled holes in relation to the Faradaic current and the electric resistance of the by-pass part. The Cr(VI) concentration, the proportion of the Faradaic current and various kinds of current efficiency were also measured as a function of the electrolytic time.

2. Experimental

2. 1 Electrolytic cell

The electrolytic cell is schematically described in Fig.1. The pyrex glass cell of an inner diameter of 26 mm was composed of three parts, namely, an electrolytic part, an electrolyte inlet, and an electrolyte outlet, which were connected with each part by acrylic flanges and silicon rubber packing. Five disk electrodes were stacked and end electrodes were arranged at the top and the bottom of the stack in the electrolytic part. A split electrode, the details of which will be described later, substituted for the center electrode when the Faradaic current through the bipolar electrode was measured. Interelectrode gaps (l_g) of 1 or 5 mm were supported by spacers of teflon rings. Applying electrolytic current to the end electrodes, cathodic and anodic reactions took place at the upper and

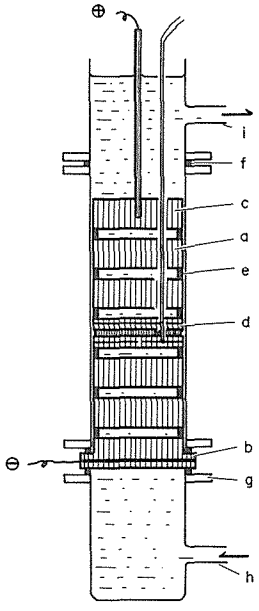

Fig. 1 Schematic diagram of the test cell. a-bipolar electrode, b-end cathode, c-end anode, d-split electrode, e-teflon spacer, f-silicon packing, g-acrylic flange, h-electrolyte inlet, i-electrolyte outlet.

lower surfaces of the stacked electrodes, respectively, that is, each stacked electrode operated in a bipolar manner.

2. 2 Electrode

The disk shaped electrodes were made of graphite rods (G-150, Tokai Carbon Co., Ltd.). Many holes were drilled through the disks for transfers of electrolytes and evolved gases. The hole diameters(ϕ) varied in the range from 0.8 to 3 mm and the number of them(n), from 3 to 85. The electrode thicknesses(d) were within 6 and 20 mm. Varying ϕ, n, and d, we could widely change the electrical resistance of the electrolyte inside the holes, which we refer to as a by-pass resistance. The end electrodes had the same diameter and the same number of the holes as those of the bipolar electrode in each run.

King *et al.* developed a split electrode to determine the Faradaic current through the bipolar electrode on the organic synthsis.[2] They measured directly the Faradaic current with an ammeter, since the space between the electrodes and the walls of the cell was relatively large and the electrodes were exposed to the gas phase in the cell. It was found that the type of split electrode developed by King *et al.* was unadequate for the measurement of Faradaic current in the compactly packed cell adopted in the present investigation. Therefore, the split electrode was modified as shown in Fig.2. A graphite disk was sliced

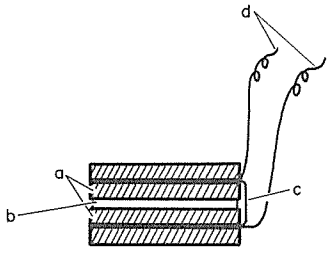

Fig. 2 Modified split electrode. a-graphite disk, b-acrylic insulator, c-short-circuit wire, d-lead wire covered with insulating tube.

perpendicularly to its axis and an acrylic resin insulator was placed between the two halves, which were connected electrically with a short-circuit wire. The fine wires covered with insulating tubes were fixed to both ends of the short-circuit wire. The wires and side faces of the electrode were coated with silicon resin. The Faradaic current was calculated from ohmic potential drop across the short-circuit wire by using the wire electric resistance of about 5 mΩ, which value was precisely determined. It seemed from the negligible wire resistance in comparison with the reaction that the short-circuit wire absolutely did not hinder the Faradaic current transfer through the split electrode.

2. 3 Experimental apparatus and measurements

The flow circuit and the measurement systems are schematically given in Fig.3. The test electrolytes containing 0.001～0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4 were prepared by dissolving test grade reagents (Wako Junyaku Co., Ltd.) in distilled water. The electrolyte

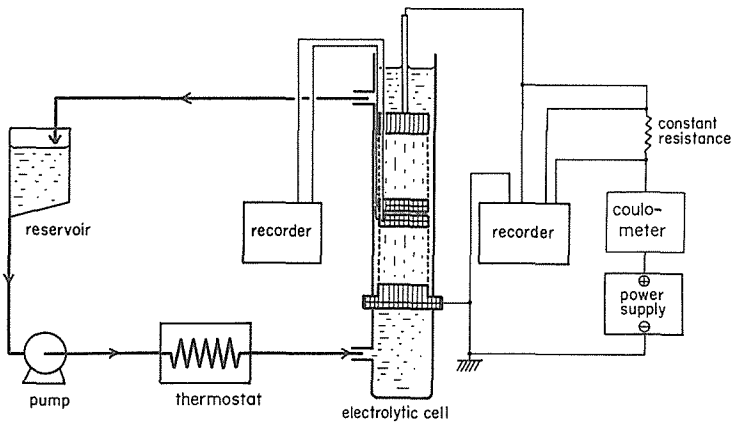

Fig. 3 Schematic diagram of flow circuit and measurement systems.

controlled at a constant temperature of 30°C was circulated by a pump at a flow rate of 400ml · min.$^{-1}$. The concentration of Cr(VI) with time was determined by colorimetric method with diphenylcarbazide. Cell voltage, applied current(J_t), and Faradaic current(J_r) were also recorded during the continuous electrolysis.

3. Results and Discussion

3. 1 Current distribution through bipolar electrode

Polarization curves were measured on both end electrodes by using the potential difference between the end electrodes and Luggin capillary probes set close to the electrode surfaces. They are presented by closed circles in Fig.4, where the potential is referred to S. C. E. Open circles in this figure indicate the J_r *vs.* E relations obtained for the split electrode, where E shows the potential difference between the split electrode and Luggin capillary probes set in the vicinity of the upper and the lower surfaces of the split electrode. They coincide with the polarization curves at the end electrodes. These results mean that the relationships between the Faradaic current and the electrode potential are the same both at the bipolar electrode and at the end electrodes. The potential difference between the upper and the lower surfaces of a bipolar electrode, ΔE_{bi}, was also determined with Luggin capillary probes. The relations between ΔE_{bi} and J_r obtained for different values of p are shown in Fig.5, where p is defined as the percentage of the cross sectional area occupied by holes to that of the bipolar electrode, and similar realtions for different values of d are presented in Fig.6. These figures show that the ΔE_{bi} *vs.* J_r curves are similar to each other independent of both values of p and d. Taking the results in Fig.4 into account, it can be seen that the J_r *vs.* E relations are the same for various bipolar electrodes. These results indicate that the Faradaic current was successfully determined with the split

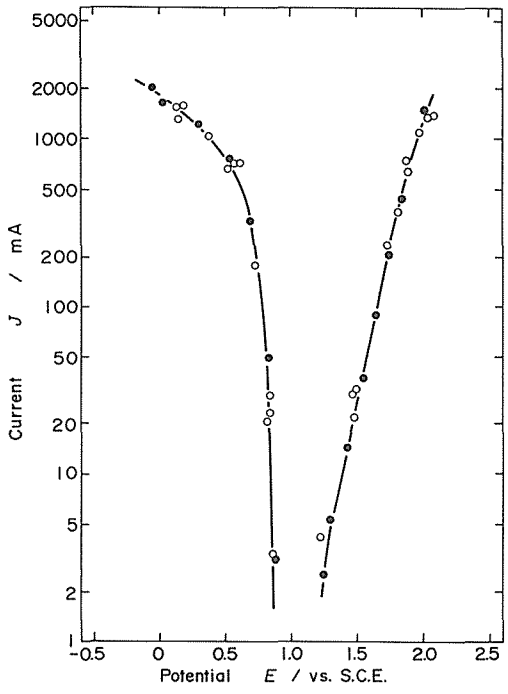

Fig. 4 Comparison between polarization curves (●) at end electrodes and Faradaic current vs. potential curves (○) at bipolar electrode of $p=12.6\,\%$ in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.

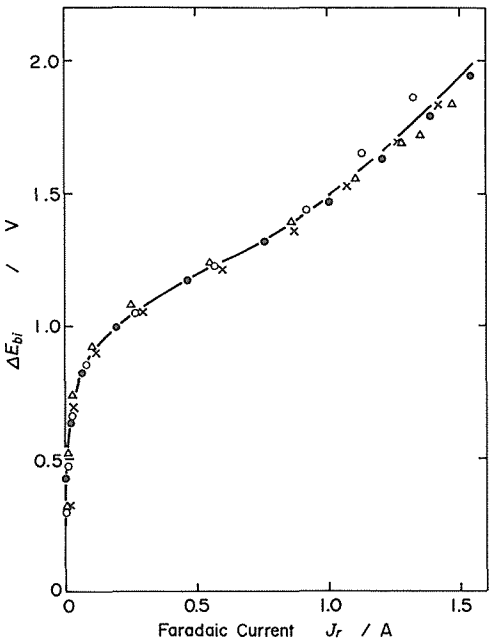

Fig. 5 Relation between ΔE_{bi} and J_r at bipolar electrodes of $\phi=1$ mm and $d=1$ mm in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.
$P(\%)$: ×-2.0, ○-4.0, ●-8.2, △-12.6.

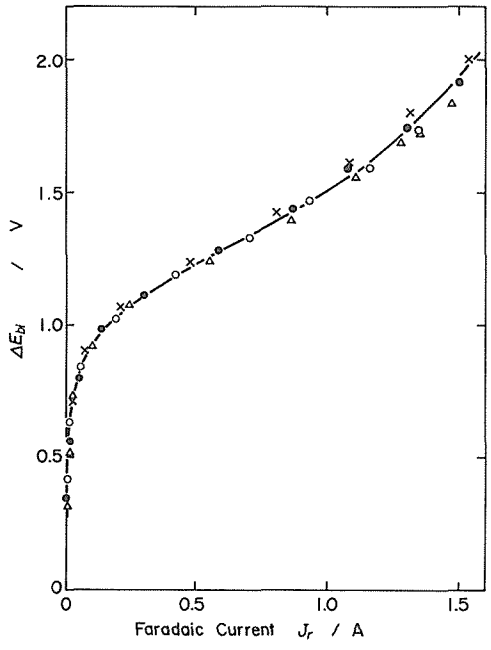

Fig. 6 Relation between ΔE_{bi} and J_r at bipolar electrodes of $p=12.6\,\%$, $\phi=1$ mm, and $n=85$ in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.
d(mm): ○-6, △-10, ×-15, ●-20.

electrode described above.

In order to elucidate the controlling factors of the Faradaic current, its proportion to the applied current was investigated at various electrodes. The percentages of J_r to J_t, $\eta_{el}=(J_r/J_t)\times 100$, are presented in Fig.7, where d is a constant of 10 mm. It is seen from

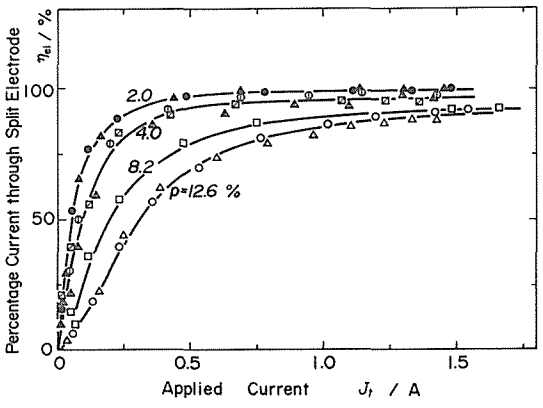

Fig. 7 Relation between η_{el} and J_t at various bipolar electrodes of $d=$ 10 mm, in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.
Electrode: ▲-$p=2.0$ %, $\phi=0.8$ mm, $n=21$,
●-$p=2.0$ %, $\phi=1.0$ mm, $n=13$,
①-$p=4.0$ %, $\phi=1.0$ mm, $n=27$,
⚠-$p=4.0$ %, $\phi=1.5$ mm, $n=12$,
⊠-$p=4.0$ %, $\phi=3.0$ mm, $n=3$,
□-$p=8.2$ %, $\phi=1.0$ mm, $n=55$,
○-$p=12.6$ %, $\phi=1.0$ mm, $n=85$,
△-$p=12.6$ %, $\phi=2.0$ mm, $n=21$.

the η_{el} *vs.* J_t curves that η_{el} increases with J_t and decreases with p independent of ϕ and n. η_{el} obtained for the electrodes with various thicknesses are shown in Fig.8, where p is a constant of 12.6 %. This figure indicates that η_{el} increases with d. The comparison of the η_{el} *vs.* J_t curves at two electrodes is shown in Fig.9, where the values of p and d of one electrode are twice as large as those of the other; these two electrodes possess the same by-pass resistance of 6.55Ω.

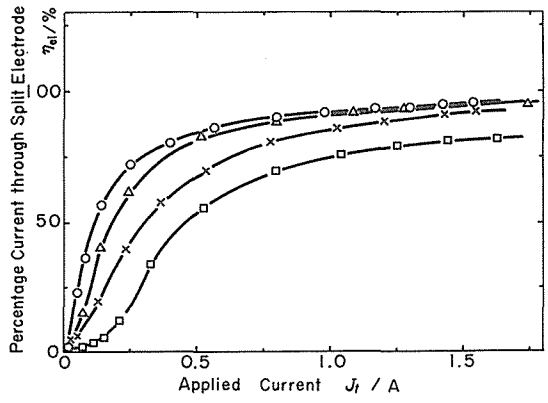

Fig. 8 Relation between η_{el} and J_t at bipolar electrodes of $p=12.6$ %, $\phi=1$ mm, and $n=85$ in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.
Electrode thickness (mm): □-6, ×-10, △-15, ○-20.

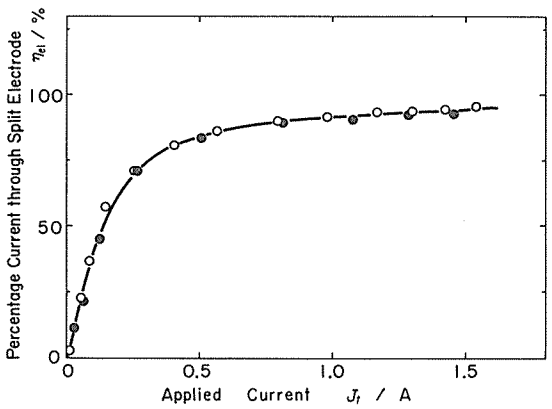

Fig. 9 Relation between η_{el} and J_t in 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4.
Electrode: ○-p=6.3 %, d=10 mm, ●-p=12.6%, d=20 mm.

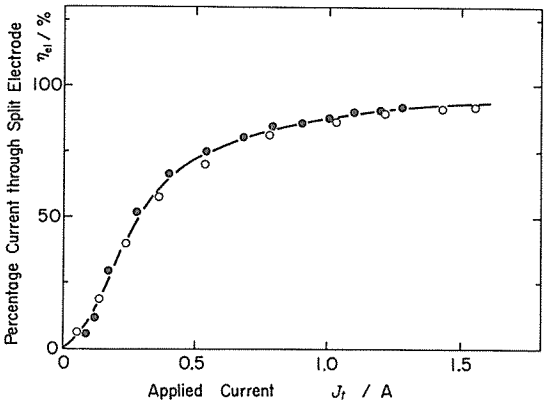

Fig.10 Relation between η_{el} and J_t at bipolar electrodes of p=12.6 %, ϕ=1 mm, n=85, and d=10 mm.
Interelectrode gap (mm): ○—1, ●-5.

In the figure, those curves nearly agree with each other. It is seen from Fig.10 that η_{el} is almost independent of l_g. From the results mentioned above, the bipolar electrode system seems to be explained in terms of a by-pass resistance. However, an approximate value of η_{el} should be calculated using the network model,[3,9,10] which includes a parallel circuit composed of a Faradaic resistance part and a by-pass resistance, and an electrolyte sandwich resistance in series, because the experimentally determined η_{el} becomes larger than that calculated by the network, in which model the increase in the by-pass resistance with the applied current was ignored. The details of the values of η_{el} will be discussed elsewhere[11].

3. 2 Continuous electrolysis of acidic bichromate solutions

3. 2. 1 Polarization curves

The current efficiency of the Cr(VI) reduction usually decreases with the decrease in Cr(VI) concentration when the continuous electrolysis is carried out in the acidic bichromate solution, because the reduction rate becomes gradually smaller in comparison with the side and reverse reaction rates. The applied current partly flows away bringing about no electrochemical reaction in the bipolar electrode cell. Therefore, in employing a bipolar electrode cell, the decrease in η_{el} might be responsible for the decrease in the current efficiency, since η_{el} also usually decreases with the decrease in Cr(VI) concentration owing to the increase in the Faradaic resistance.

The polarization curves in the solutions with various concentrations of potassium bichromate are demonstrated in Fig.11. The cathodic reactions were mainly the reduction of Cr(VI) to Cr(III) and the oxygen reduction. The potential decreased markedly in the range lower than 0.6 V, which was due to the additional overvoltage from Cr(VI) diffusion. Meanwhile, the current at the plateaus was not directly proportional to the Cr(VI) concentration, because the contribution of the oxygen reduction to the cathodic reactions became significant at low Cr(VI) concentration.

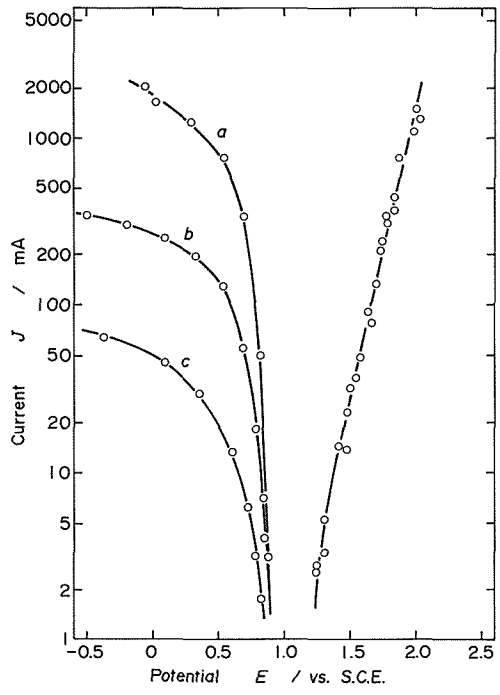

Fig.11 Polarization curves in various concentrations of $K_2Cr_2O_7$ in 0.5 M H_2SO_4. Concentration (M): a-0.1, b-0.01, c-0.001.

An anodic reaction is the oxygen evolution and the corresponding polarization curves are almost coincident with each other in all the solutions used. The oxidation reaction of Cr(III) to Cr(VI) readily takes place at the lead dioxide electrode due to its catalytic action, whereas this reaction is retarded on a platinum electrode[12]. As shown later, the oxidation rate of Cr(III) is also negligible on graphite electrodes, unless the concentration of Cr(VI) is extremely low in comparison with that of Cr(III). This fact makes the bipolar electrode of graphite for the reduction of Cr(VI) to Cr(III).

As seen from Fig.11, the Faradaic resistance increases with the decrease in Cr(VI) concentration, since the resistance is calculated by $\Delta E_{bi}/J_r$ and ΔE_{bi} is given by the potential difference between cathodic curves and anodic one. On the other hand, the variation in the by-pass resistance is negligible owing to the existence of the excess H_2SO_4. It can therefore be predicted that η_{el} will decrease with the decrease in Cr(VI) concentration.

3. 2. 2 Current efficiency of the bipolar electrode cell

There are m places for each of the cathodic and anodic reactions in the bipolar electrode cell composed of $m-1$ bipolar electrodes. This bipolar electrode cell is referred to as a m compartment cell and corresponds to the cell which is composed of m monopolar electrodes in series. Therefore, the total applied current should be regarded as the product of m and J_t, although the total Faradaic current is given by $\{(m-1)\eta_{el}/100+1\}\times J_t$, The gross current efficiency, η_{gs}, of the bipolar electrode cell is given as follows,

$$\eta_{gs}=\frac{\mathrm{nF}\Delta CV}{mJ_t\Delta t\,\mathrm{M_{Cr}}}\times 100 \tag{1}$$

$\Delta C(\mathrm{g\cdot l^{-1}})$ is the variation in Cr(VI) concentration within small time intervals of Δt, V(l) is the volume of the electrolyte, $\mathrm{M_{cr}(g\cdot Mol^{-1})}$ is the atomic weight of Cr, F(Coulomb) is a Faradaic constant. The value of n in the eq. (1) is 3 in the reduction process of Cr(VI) to Cr(III).

The gross current efficiency is expressed by two elements, as follows,

$$\eta_{gs}=\eta_{cl}\times\eta_{nt} \tag{2}$$

where η_{cl}, cell efficiency[13], is the proportion of the total Faradaic current to mJ_t and η_{nt}, which we call net current efficiency, is the percentage of the Faradaic current used in the considered reaction similar to that of the monopolar electrode cell. They are given as follows,

$$\eta_{cl}=\frac{(m-1)\eta_{el}/100+1}{m} \tag{3}$$

$$\eta_{nt}=\frac{\mathrm{nF}\Delta CV}{\{(m-1)\eta_{el}/100+1\}J_t\Delta t\mathrm{M_{Cr}}}\times 100 \tag{4}$$

As seen from eq.(3), η_{cl} is determined by η_{el} which represents the proportion of the Faradaic current at a bipolar electrode, and η_{nt}, on the other hand, evaluates the considered reaction rate in comparison with side and reverse reaction rates. η_{el} and η_{nt} are basic information on η_{gs}.

3. 2. 3 Variation in concentration and current efficiency with time

The potentiostatic electrolysis is preferable when the concentration of the considered ions varies with time. In order to electrolyze a definite solution such as the waste water as fast as possible with low energy consumption, we must set up a working electrode at the potential range where the diffusion overvoltage of the considered ions does not appear or only slightly even if it does.

The conductivity of the electrolyte is kept nearly constant during the electrolysis in this work, because of the existence of the excess H_2SO_4. Therefore, the electrolysis under the constant cell voltage can be adopted instead of the potentiostatic electrolysis. It can be seen from Fig.11 that the application of the potential difference of about 1.5 V to every one bipolar electrode is needed for the desirable electrolysis. This condition was almost satisfied at the cell voltage of 9 V, and the electrolysis was carried out at that constant cell voltage. η_{el} was measured by the use of the split electrodes and the variation in Cr(VI) concentration was followed by analysis of the electrolyte sampled at every a definite amount of electricity. η_{gs} was calculated from eq.(1) using the relation between the concentration and the amount of electricity, and η_{nt} was also evaluated from eqs.(2) and (3) using η_{gs} and η_{el}.

The results obtained for the electrolyte containing 0.1 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4 using the electrodes of $p=4.0$ %, $d=10$ mm are shown in Fig.12 and those for the electrolyte containing 0.01 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4 using the electrodes of $p=4.0$ %, $d=20$ mm are presented in Fig.13. It is shown in Fig.12 that the concentration of Cr(VI) decreases steeply

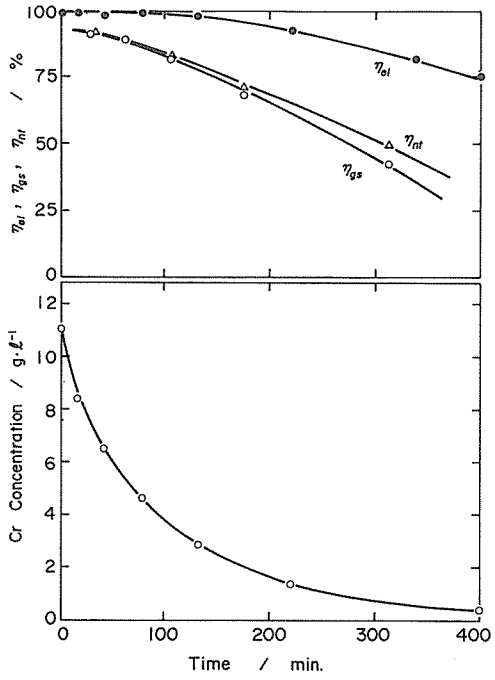

Fig.12 Variation in Cr(VI) concentration and various kinds of current efficiency with time at electrolysis (cell voltage is 9 V) of 500 ml bichromate in 0.5 M H_2SO_4. Bipolar electrode: p=4.0 %, d= 10 mm.

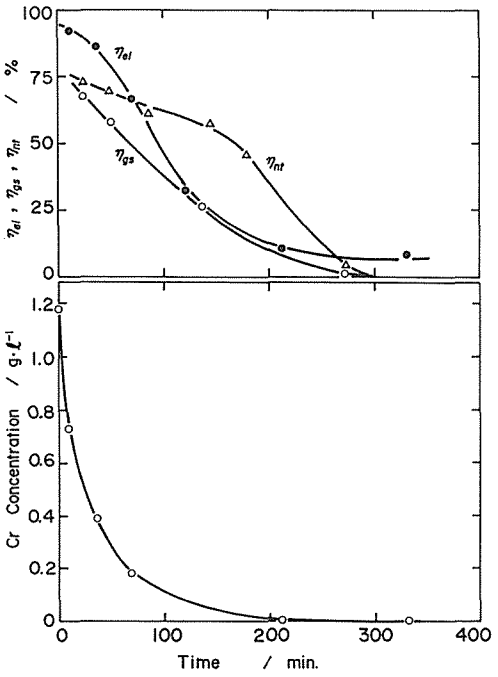

Fig.13 Variation in Cr(VI) concentration and various kinds of current efficiency with time at electrolysis (cell voltage is 9 V) of 500 ml bichromate in 0.5 M H_2SO_4.

at an early stage of the electrolysis and decreases slowly after that. η_{el} and η_{nt} also decrease with time and it leads to the decrease in η_{gs}. As seen from Fig.11, the decrease in η_{el} with time is attributable to the increase in the Faradaic resistance owing to the decrease in Cr(VI) concentration. The decrease in η_{nt}, on the other hand, is probably due to the decrease in the reduction of Cr(VI) relative to that of oxygen in a low concentration range. The decrease in η_{nt} is large compared with that in η_{el} and it becomes the main cause of the decrease in η_{gs}.

η_{el} remarkably decreases in low concentration as in Fig.13, although the by-pass resistance of the electrodes is higher than that of the electrodes employed and its decrease becomes the main cause of the decrease in η_{gs}, although η_{nt} also decreases. So long as the bipolar electrode cell is used, the decrease in η_{nt} is unavoidable to some extent, but the improvements in η_{el} will be possible by the use of the electrodes with high by-pass resistance and by the application to the solution of low H_2SO_4 concentration. Then a reduction in electrolysis time may be possible to a great extent, considering that the Cr(VI) concentration, even in Fig.13, becomes lower than 1×10^{-5} M $K_2Cr_2O_7$ after the electrolysis for 320 minutes.

4. Conclusions

A method of measuring the Faradaic current through the bipolar electrode packed compactly in a cell has been developed by modifying the split electrode.

The proportion of the Faradaic current to the applied current is substantially de-

termined by the by-pass resistance of the bipolar electrodes.

The proportion of the Faradaic current remarkably decreases in low concentration of Cr(VI) and it is responsible for the decrease in the gross current efficiency in the bipolar electrode cell.

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