out. In the presence of manganese dioxide, however, the film could no more be repaired at 300 μA, but was broken down by passing the current as can be seen from Fig. 3, B and C. Therefore the presence of manganese dioxide would be the direct cause for the breaks. When the film breaks, the electronic current becomes predominant in place of ionic one, hence we considered that the rate of supply of oxygen ion into the film from manganese dioxide would be slower than that from aqueous electrolytes and would induce the electronic pass. It was also found from Fig. 7, F that once the film with manganese dioxide was broken by passing the current, it couldn’t be repaired after manganese dioxide was dissolved out.

4 Conclusions

The results are summarized as follows.
1) The tantalum anodic oxide film is deteriorated by the heating during pyrolysis of manganese nitrate on the film.
2) The weak spots generated by that heating can be repaired by the subsequent current flow.
3) The film is not deteriorated by the factors except heating in the pyrolysis.
4) The presence of manganese dioxide on the film is the direct cause of the electrical break down.

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References:

Technical Paper

Determination for Stage Transformations of Graphite Bisulfate Lamellar Compound

Rokuro Fujii

The transformation of stages of graphite bisulfate lamellar compound was studied quantitatively by cyclic voltammetry measurements. The steps of anodic oxidation which appeared on the cyclic voltammograms obtained for the pyrolytic graphite in 18 M sulfuric acid electrolyte at 25°C were resolved to five parts by mean of "Curve Resolver".

From the amount of electric quantity for each of separated curve, the relation between the various stages and its amount just after each oxidation steps were defined.

1 Introduction

The decomposition process of the graphite bisulfate lamellar compound has been studied with the X-ray diffraction by several investigators. Rüdorff2) and Riley3) suggested that the formation of the third stage from the second stage must involve the complete expulsion of certain bisulfate layers and their subsequent re-entry of other layers into the lattice, and they called it “peculiar step-wise”.

On the other hand, Inagaki4) concluded from the X-ray studies that on the decomposition process of lamellar compound, the transition of structure from the first stage to the second and third stages is established. In a previous investigation5), it was reported that the first stage of the bisulfate lamellar compound was transformed from the second and third stages. The observation was made by the X-ray diffraction measurements, which were performed simultaneously with the anodic oxidation of graphite electrode by the galvanostatic conditions. However, all of these reports have treated the processes of the transformation only qualitatively.

In this work, a trial was made to elucidate quantitatively the transformation of stages for each step of oxidation, by the graphical analysis of the i–E curves, which obtained by the cyclic voltammetry measurements.

2 Experiments

A graphite sample was prepared by recrystallization
of pyrolytic graphite at about 3,000°C, which was described in another paper. The chipped flake of the graphite (1.5mg weights), wrapped with a platinum net (100 mesh, $0.3 \times 0.5$cm) with a spot-welded platinum lead, was employed as the sample electrode. Platinum plate ($0.5 \times 0.5$cm) was used as the counter electrode. Electrode potentials were referred to the mercury/mercurous-sulfate electrode in the same electrolyte as used here. A potentiostatic isoscales-triangular wave was applied between the sample electrode and the reference electrode. The cathodic and anodic current-potential data were recorded on an X-Y recorder. For X-ray diffractometry, the sample electrode was taken up in situ on the way of anodic sweep from the electrolyte, and wrapped with a thin film (about 0.02 mm thickness) of polyethylene, due to the protection of water absorption in air.

3 Results and Discussion

A typical cyclic voltamgram obtained for the sample electrode dipped in 18 $M$ sulfuric acid electrolyte at 25°C is shown in Fig. 1. The oxidation current was higher for $i-E$ curve for the second sweep than for the initial one, and it approached the steady state after several repetition of cycles. The total electric quantity, $\int i \, dt$, corresponding to the area under the anodic oxidation curve was $9 \times 10^{-2}$ $\text{AH/g}$. This value is in good agreement with the theoretical one required to oxidize the graphite into the first stage which is the final product of the lamellar compound. Therefore, it is supposed that this anodic oxidation current is due to the formation of lamellar compounds. While, the cathodic reduction current, which occurs by the sweep toward negative potential, is due to the decomposition of them. The characteristic oxidation curve showed clearly five peaks corresponding to each step of stage transformation between about +0.3 volts and +1.3 volts as seen in the figure. The potential difference of two adjacent peaks is small from the peak I to the peak IV. On the contrary, there exists a large difference between the potential of the peak IV and of the peak V, and the peak V presents independently of others. This large potential difference may be related to the abrupt rise of about 0.2 volts on the potential-time curve obtained with the galvanostatic

![Fig. 1](image1.png)

Fig. 1 Current-potential curve in 18 $M$ sulfuric acid at a sweep rate of 10 mV/sec

![Fig. 2](image2.png)

Fig. 2 The diffraction pattern for the (001) line of lamellar compound formed during the oxidation step IV

![Fig. 3](image3.png)

Fig. 3 The diffraction pattern for the (001) line of lamellar compound formed during the oxidation step V
measurements, which have been explained as to correspond to the transformation from the higher stage to the first stage. In order to confirm this assignment, the X-ray diffraction measurements were made on the sample electrode in situ on the way of anodic sweep. The results indicated that the peak IV is related to the oxidation current which formed the second and third stage compounds from the higher stage and that the peak V is related to the oxidation which formed the compound of the first stage from the second and third stages, as shown in Fig. 2 and in Fig. 3.

In order to determine the composition of these oxidation steps, the oxidation curve was resolved to five parts (each corresponds to peak I～V) by Du Pont Curve Resolver model 310 with the assumptions as follows: (a) The oxidation curve is composed from five curves. (b) The maximum position of each curve is the same as that of the each peak. (c) A molecular sulfuric acid and a bisulfate ion which have entered into the graphite lamellar remove the lamellar only through the decomposition reaction. (d) The shape of each curve is of the Gaussian type. Thus, the resolved curves and the synthesized curve by mean of the curve resolver are shown in Fig. 4. For these results, the percentage of electric quantity for each of separated curves were determined from the ratio of each area to the total area. The results are shown in Table 1.

If it is assumed that all of transformation to the first stage are transformed from the second stage, the electric quantity in the oxidation step of the curve V is estimated as 50 % of that required for the oxidation of graphite to the final lamellar compound. Also, electric quantity of 66.67 % is required for the anodic oxidation of the first stage transforms only from the third stage. The value of 58 % obtained here for the curve V suggests that the transformation to the first stage was occurred from the second and third stages, and this agrees with the results obtained on the X-ray studies in the previous investigation9. Therefore, it is possible to determine the composition of the second and third stages formed in the oxidation step of IV from this value of 58 %. In a similar way, the amount of each stage formed in each oxidation step can be calculated, if each compound is formed through the simple transformation process: for example, from the third stage to the first and second stages, as well as from the fourth stage to the second stage, and from the fifth stage to the second and third stages. The results of this calculation are shown in Table 2 as the relation between the various stages and its amount just after each oxidation step.

Table 2 Relation between the various stages and its amount just after each oxidation step

<table>
<thead>
<tr>
<th>Oxidation step</th>
<th>I (%)</th>
<th>II (%)</th>
<th>III (%)</th>
<th>IV (%)</th>
<th>V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n th stage</td>
<td>4</td>
<td>6</td>
<td>11</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>8 th stage</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 th stage</td>
<td></td>
<td>4</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 th stage</td>
<td></td>
<td></td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 th stage</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>3 rd stage</td>
<td></td>
<td></td>
<td></td>
<td>26</td>
<td>100</td>
</tr>
<tr>
<td>2 nd stage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 st stage</td>
<td></td>
<td></td>
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</tbody>
</table>

In this table, the quantity Q is the percentage of the electric quantity, corresponding to the formation of each stage, against the total quantity. Just after the oxidation step III, the third, fourth, and fifth stages co-exist with the Q value of 4, 11, and 12 %, respectively. In the step IV, the second and third stages co-exist with 16 and 26 %, respectively. As a result, it proves that the transformation processes of stages during the anodic oxidation of graphite can be discussed quantitatively without contradiction to the results of measurements by the X-ray diffraction. It was also indicated that the transformation processes among the higher stages, which could not be observed by the X-ray measurements, could be elucidated. However, the intrinsic mode of the transformation process

![Graphical analysis of i-E curve and the synthesized curve](image)

Fig. 4 Separated curves obtained by the graphical analysis of i-E curve and the synthesized curve
cannot be treated quantitatively with the data in Table 1 and 2, because they are dependent upon the properties of graphite and the experimental conditions such as the potential sweep rate. For instance, when a graphite sample is more isotropic and potential sweep rate is rapid, the positions of peaks in the oxidation curve are less clear, and therefore the analysis of this curve is difficult. Nevertheless, if a single crystal of graphite and a suitable sweep rate are used, the method used here may be valid for the quantitative investigation on the intrinsic mode of the transformation process.

Reference:
2) H. L. Riley, Fuel 24, 8 (1946).
4) R. Fujii, to be published in Denki-kagaku.

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**Technical Paper**

The Structures of One-electron Reduction Products of Quinolinium and Isoquinolinium Perchlorates, and their Re-oxidation Reactions*

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and Eiji IMOTO****

As one of an integrate study on the Reduction of azinium salts, some quinolinium and isoquinolinium perchlorates were electrolyzed at the potential corresponding to the first d.c. polarographic reduction waves.

Quinolinium salts that have substituent at 2-position form 4,4'-dimer, which have substituent at 4-position form 2,2'-dimer, and isoquinolinium salts form 1,1'-dimer by the reduction. A neutral radical produced by the one-electron reduction of these salts generally gives dimer through rapid association. However, existence of a substituent such as phenyl group at the active site gives an opportunity to detect a radical intermediate. Oxidation of a dimer with silver perchlorate, chloranil, et. al. gives corresponding azinium salt through an oxidative cleavage of a C-C bond of dimerizing position.

1 Introduction

Azines are transformed into the corresponding anion radicals by electrochemical or metallic reduction. On the other hand, it may be easily suggested that the neutral radicals are produced by one-electron reduction of azinium salts. As for pyridinium salts, dimers derived from the association of neutral radicals are obtained in some cases. In spite of many attempts to isolate one-electron reduction products of quinolinium salts, the structures as well as reactivities have not yet been clarified. In order to synthesize one-electron reduction product of quinolinium salt, choice of a reducing agent preferable to one-electron reduction and a system where one-electron reduction product will not disproportionate, will be at least necessary. From this point of view, reduction with chemical reagents such as sodium dithionite, sodium borohydride, lithium aluminium hydride, and sodium metal is undesirable. On the other hand, controlled potential electrolysis, the power of which can be regulated willingly, may be an extremely useful technique for the preparation. Thus, mainly by use of electrochemical methods, the present authors investigated the dimerized sites and reactivities with some oxidizing agents of one-electron reduction products of several quinolinium and isoquinolinium salts having inactive substituent in polarographic reduction, as one of the integrate study for the organic reduction-catalysis.