

Effect of electrochemically oxidized carbon colloid on lead acid batteries

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Abstract

An aqueous solution of carbon colloid was prepared by electrochemical oxidation of a graphite anode. It was found that the addition of this colloid into the electrolyte of lead acid batteries enhanced the charge–discharge capacity and extended life. The mechanism for this could be as follows: As a result of electrochemical oxidation the surface of the carbon particles is subjected to a chemical modification, and is endowed with hydrophilic groups such as carboxyl. This was confirmed with ESCA spectroscopy. When the carbon colloid is added to an electrolyte in a lead acid battery, the cathode (PbO₂) is electrochemically doped with the carbon particles. This is supported by the results of voltammetric and optical absorption spectroscopic studies. Since PbO₂ is a semiconductor and is used in a granular form, some of the particles probably do not have good electrical connection, and are not fully utilized. It is expected that doped carbon particles could provide electrical connection to non-utilized PbO₂ particles, which enhances the charge–discharge capacity and extends the life of lead acid batteries. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxidized carbon colloid; Lead acid batteries; Charge–discharge capacity

1. Introduction

In many cases, active materials for batteries are semi-conductors and are used in a granular form. Therefore, the net conduction is lower. It could happen that some grains do not have sufficient connection to the electrodes. Carbon powders are used sometimes in order to get good electrical contact between grains, for example, in the case of manganese dioxide dry cells. Much work has been reported concerning an improvement of electrical contact for active materials. For example, polymerization of polypyrrole in carbon-dispersed aqueous solution [1] and polymerization of polypyrrole on porous sheets of graphite fibers [2] where polypyrrole systems are used as cathodes of polymer batteries. An interesting example other than carbon is the formation of silver particles as a result of discharge ($2\text{Li} + \text{AgWO}_4 \rightarrow \text{LiOW}_4 + \text{Ag}$), which favors the charge process [3].

In spite of the fact that carbon is a useful material to improve the ability of batteries, only two examples [4,5] are known concerning the application of carbon to lead acid batteries except for the protection or reinforcement of

electrodes. In these cases, graphite or H₂SO₄-intercalated graphite was mixed with PbO₂ and pressed into Pb grids. Details have not been reported yet. It seems that some adhesive force between carbon and PbO₂ is necessary.

It is well-known that a carbon anode can be oxidized if a suitable potential is applied and that colloidal carbon is produced as a result of oxidation. This may be generally disadvantageous. Probably no one has made use of the carbon colloid thus formed because the efficiency to produce carbon electrochemically is not good. However, it was found by chance that the addition of the carbon colloid thus produced into the electrolyte of lead acid batteries, which were deeply discharged and unable to recharge, revived those batteries. It was also found that the carbon colloid increased the charge–discharge amount of new lead acid batteries. The purpose of the present work is to report the effect of the carbon colloid on lead acid batteries and to discuss the mechanism of the improvement. First, the result of cyclic charge–discharge testing is reported using two batteries where the one was treated with the carbon colloid and the other not. Secondly, analyses of the carbon colloid are reported. These include particle size distribution before and after electrochemical oxidation, dispersibility of the carbon colloid and surface analysis of the carbon by ESCA. Finally, the effects of

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carbon on lead acid batteries are discussed in the light of the analysis of voltammetry and optical absorption spectroscopy.

2. Experimental

Artificial graphite (TYK GL-500) was mixed with binder (pitch), pressed to a form of electrode and then heated up to 2800°C to form electrodes of the size $50 \times 50 \times 1.5$ mm.

Electrochemical oxidation of carbon was made with a carbon anode and a Pt cathode in de-ionized water and 7 V (DC) was applied between those electrodes. The current was low at first then gradually increased. At 10 h after the start the current was 200 mA and it increased to 1 A after 48 h. At this stage, the power was shut off. The content of the carbon in the colloidal solution thus formed was 0.2–0.3 wt.%. The pH value was about 2.6 implying the existence of –COOH groups. The solution showed good dispersibility.

A cyclic charge–discharge test was done as follows: Two lead acid batteries (Nihon Denchi GS6N4-2A, three cells in series, the capacity of 4 A h at 10-h discharge) were employed. One was used without adding the carbon colloid and for the other 6 wt.% colloidal solution was added to the electrolyte (dilute sulfuric acid). The carbon content was 0.018 wt.% in this case. These batteries were discharged through 2-W resistors until the voltages dropped down to 4.8 V. The charge process for the batteries was done by a constant current method where the charge current was controlled to 2 A. The charge process was terminated when the voltage reached 8.7 V. However, for the battery without the carbon colloid the voltage failed to reach 8.7 V because of a deterioration at cycle number 131. Therefore, an alternative method was taken in this case, where the amount of supplied charge was adjusted to correspond to the charge used in earlier cycles. This was found from another series of charge–discharge cyclic tests with the same type of battery. It was found that the amount of charge supplied by charging up to 8.7 V corresponded to that supplied from the charge process where the battery was charged up to 7.8 V and then continued the charge process further for 15 min. This process was taken for the battery without carbon colloid at charge cycles greater than 131. At each charge cycle when the charge process was terminated, the batteries were held during 2 min and then subjected to the discharge process. Control of charge–discharge cycle and the measurements of charge–discharge current and voltage were performed with a computer system.

ESCA was performed in UBE Scientific Laboratory with Electronics (Model-5600 ci). Calibration was done with graphite standard samples, which were prepared by cleaving the standard material immediately before the measurement.

Voltammetry was carried out with a functional generator (Hokuto Denko HB-104) and a potentiostat (Hokuto Denko HA-301) and signals were recorded on an X–Y recorder (Watanabe WX 4401). Au wire and Pt foil were used as reference and collecting electrode, respectively. For test electrodes, Pb and PbO₂ were employed. In both cases Pb wire were used covered with a heat shrink tube, except for one end in the solution, in order to decrease their surface area. In the case of PbO₂ the electrode was electrochemically oxidized in dilute sulfuric acid. The sweep rate of the voltammetry was 10 mV/s.

Optical absorption spectroscopy was performed for dilute carbon colloid (carbon content: 0.00455 wt.%). This concentration was chosen so that the optical density at an absorption maximum was less than 2.5. The solution (200 ml) was taken in a voltammetry cell with the three electrodes and 2.5 ml of the solution was taken out each time for the optical measurement at the beginning and at the end of the voltammetric cycle specified. After the optical measurement the solution was returned to the voltammetric cell. The optical absorption spectrum was taken with a spectrophotometer (Simazu UV-1600PC).

3. Results

3.1. Electrochemically oxidized colloidal carbon

The raw carbon material for the electrode did not disperse in water. Only an extremely small part did disperse in a very short period. The dispersibility of carbon increased as a result of electrochemical oxidation. It was found that about 80% of the carbon still remained in the solution after 10 days, as is described later. No dispersive agents were used in the solution. The particle size of the raw carbon material was about 1 μm, whereas carbon particles in the carbon colloid passed through a membrane filter with a pore radius of 0.3 μm. The distribution of particle sizes was measured for the raw carbon material and the oxidized carbon. Fig. 1 shows the distribution of particle size of the raw material carbon. In this case, a dispersive reagent was used for the measurement. The distribution of the smallest particles observed is about 33 wt.% (≤ 0.2 μm) and distribution of bigger sizes are also seen. Fig. 2 shows the particle size distribution of the carbon colloid. In this case, the colloidal solution which was produced by 24-h electrolysis (carbon content: 0.2 wt.%) was used for the measurement. It is seen in Fig. 2 that the content of the smallest size was clearly increased and those of bigger sizes were decreased correspondingly. However, much bigger sizes appear at the same time. This may be due to cleavage of the carbon electrode. This implies that electrochemical oxidation of carbon anode should not be done for too long a time.

The dispersibility of the carbon increased as a result of electrochemical oxidation. This is shown in Fig. 3 for the

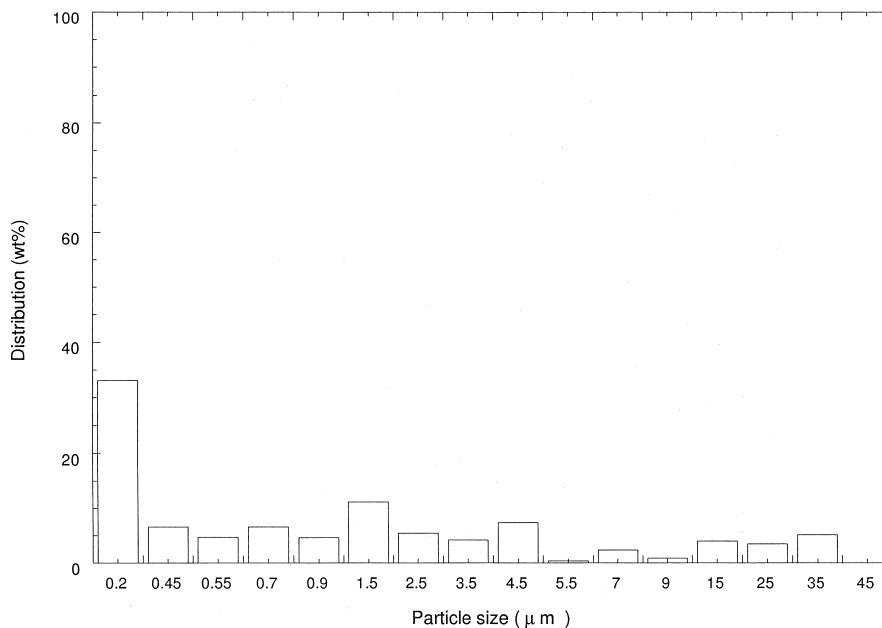


Fig. 1. Distribution of particle size of the raw carbon material for the electrode.

carbon colloid which was made by electrochemical oxidation for 48 h (carbon content: 0.029 wt.%). No dispersive reagent was included in the solution represented in Fig. 3. The time for the electrochemical oxidation for the carbon colloid in Fig. 3 was two times longer than that for the distribution test in Fig. 2. Therefore, the first drop in Fig. 3 could be due to bigger size as a result of cleavage at the electrode. Nevertheless, about 80 wt.% carbon was dispersed after 10 days. As is seen in Fig. 3, the sedimentation velocity is higher for the first period but lower in the

last period reflecting the particle size. Therefore, the amount of sedimentation after 10 days could be small.

3.2. Cyclic charge–discharge test

As is described already, the process of charge for the battery without the carbon colloid was changed after charge cycle 131. Although the difference of the charge estimated by the alternative method after cycle 131 could be less than 5%, the comparison of the charge amount of these

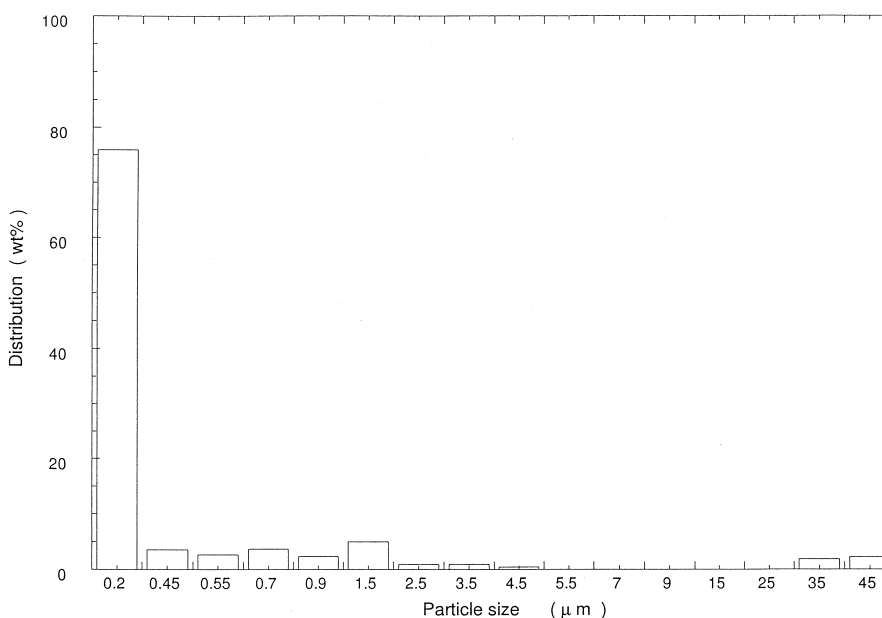


Fig. 2. Distribution of particle size of the carbon colloid obtained by electrochemical oxidation.

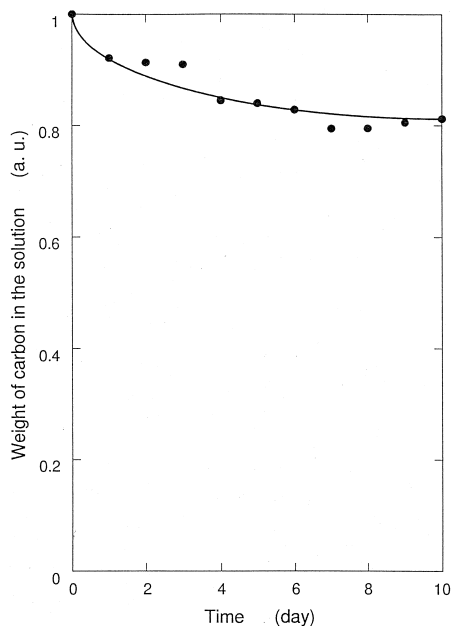


Fig. 3. Dispersibility of the carbon colloid.

two batteries was made in a cycle range between 1 and 100 in order to avoid the uncertainty. In the case of the battery without the carbon colloid the charge supplied was consumed partly for the electrolysis of the electrolyte solution at charge cycles beyond 131. In spite of this it is obvious that the two batteries were fully charged at each charge cycle. Thus, comparison can be made for the discharge amount of these two batteries at all cycles studied, 1–192.

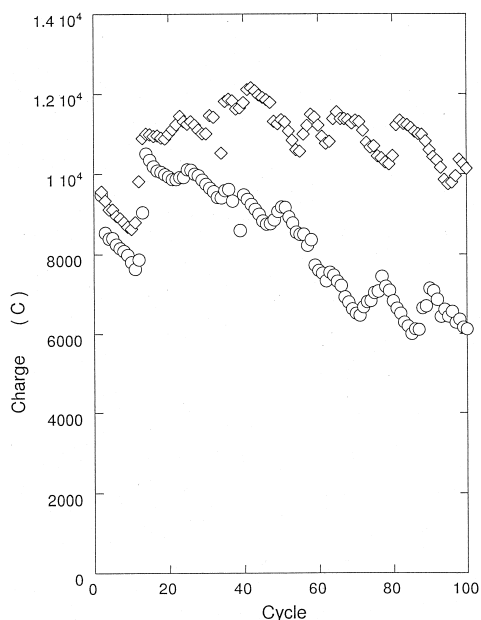


Fig. 4. Amount of charge vs. number of the charge cycle for the battery without the carbon colloid (O) and with the carbon colloid (◇).

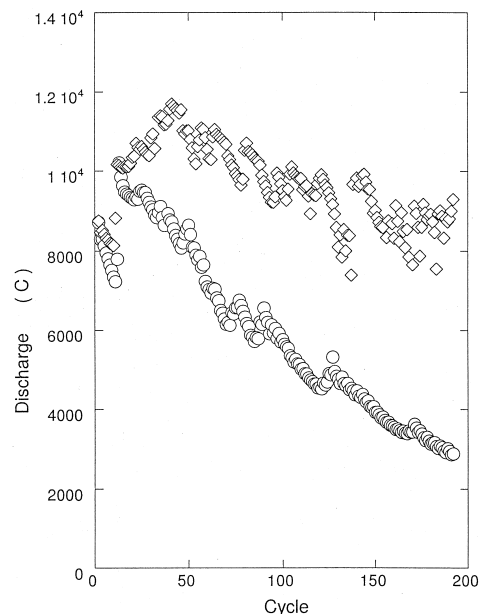


Fig. 5. Amount of discharge vs. number of the discharge cycle for the battery without the carbon colloid (O) and with the carbon colloid (◇).

Fig. 4 shows the amount of charge for the batteries with and without carbon colloid as a function of charge cycle. Fig. 4 shows that the amount of charge at the first cycle was nearly the same for two batteries, and the amount of charge for those two batteries decreases at first and the minimum appears at the ~10th cycle. For the battery without the carbon colloid the maximum appears at the 17th cycle and the amount of charge decreases with cycling. On the other hand, the amount of charge for the battery with the carbon colloid increases and the maximum appears at the 42nd cycle and then gradually decreases with cycling. However, even at the 100th cycle the amount of charge is still higher than that of the first. Thus, it should be noted that the carbon colloid increases the charge capacity of lead acid batteries.

Fig. 5 shows the amount of discharge as a function of cycle number for the batteries with and without the carbon colloid. As is the case of the charge test in Fig. 4, the amount of discharge at the first cycle was nearly the same for two batteries. For the battery without the carbon colloid

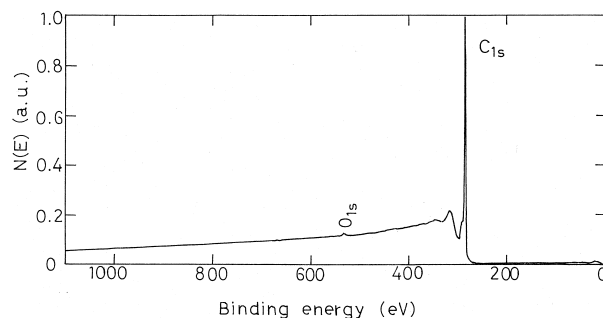


Fig. 6. ESCA spectrum of the raw material carbon.

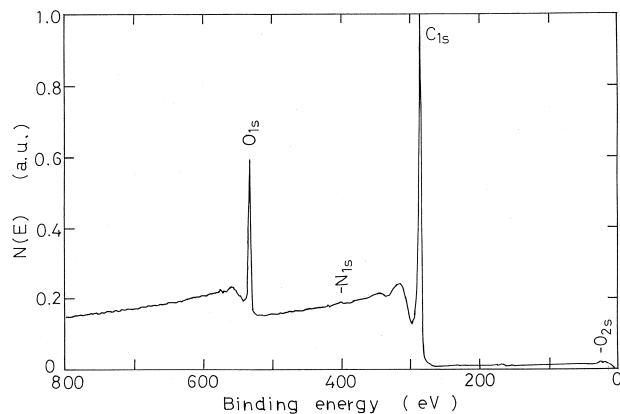


Fig. 7. ESCA spectrum of the oxidized carbon, obtained from the carbon colloid.

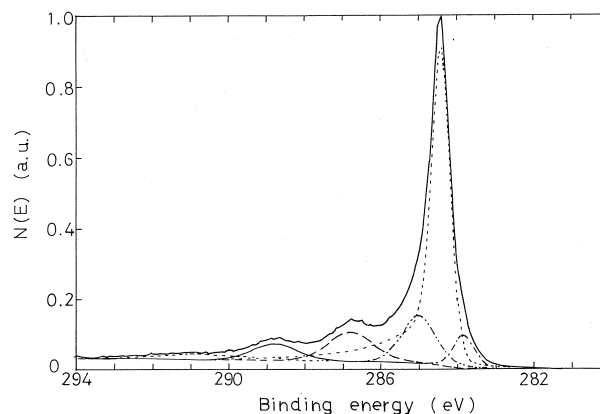


Fig. 9. C_{1s} band of the oxidized carbon in an expanded scale. Several sub-bands are given by computational work.

the maximum appears at the 13th cycle and then the amount of discharge decreases with cycles. On the other hand the maximum discharge amount was obtained at the 39th cycle in the case of the battery with the carbon colloid. It should be noted that the discharge amount at the 192nd cycle for the battery with the carbon colloid is still higher than that of the first cycle. The scattering of experimental points in Figs. 4 and 5 was reflected by the difference in the ambient temperature. As a conclusion, it can be said from Figs. 4 and 5 that the addition of the carbon colloid to the electrolyte of lead acid batteries results in an increase in the ability to charge and discharge.

4. Discussion

4.1. Chemical modification of carbon particles

It is well-known that carbon is intrinsically hydrophobic. The result in Fig. 3 indicates that carbon becomes dispersible as a result of electrochemical oxidation. The mechanism for this could be that hydrophilic groups such as $-\text{OH}$, $-\text{COOH}$ and/or $>\text{C}=\text{O}$ are formed by the electrochemical oxidation. In order to confirm this ESCA spectra were taken for the raw carbon material and the dried carbon obtained from the carbon colloid. Figs. 6 and

7 show ESCA spectra for the raw carbon material and for the dried carbon from the colloid, respectively. In Figs. 6 and 7, two peaks are observed at 284 and 533 eV. These are ascribed to C_{1s} and O_{1s}, respectively. For the raw material carbon in Fig. 6 only a trace of the O_{1s} peak is seen, whereas a high peak is observed for the dried carbon in Fig. 7 together with O_{2s} peak. It should be noted that ESCA spectroscopy gives us information concerning the surface of the material. From Fig. 7 the amount of oxygen on the surface was obtained to be 15.33 at.%. This implies that the surface of carbon particles was chemically modified by the electrochemical oxidation. The C_{1s} bands are shown in expanded scales in Figs. 8 and 9 for the raw material and the oxidized carbon, respectively. In the case of the oxidized carbon in Fig. 9 several sub-bands are seen in addition to the main band (284.43 eV). These sub-bands are separated computationally in Fig. 9. These sub-bands are hardly seen for the non-oxidized carbon. The sub-bands (chemical shift) are analyzed [6]. The existence of $-\text{COO}-$ and $\text{CO}-$ groups on the carbon particle surface seems to imply that $-\text{COOH}$ and $-\text{COH}$ groups are produced as a result of electrochemical oxidation. The reaction could be initiated by electrons from the cathode and these could

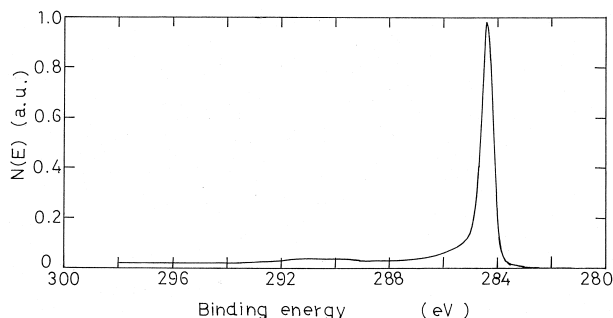


Fig. 8. C_{1s} band of the raw material carbon in an expanded scale.

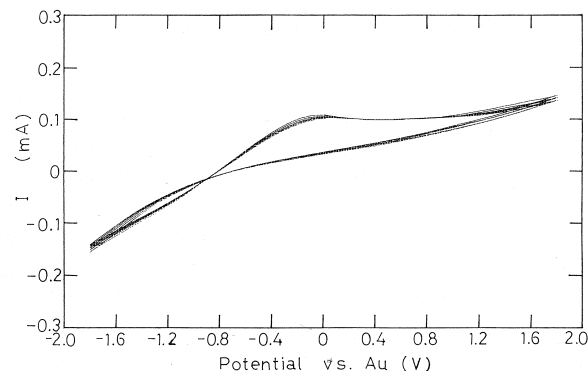


Fig. 10. Cyclic voltammogram of the PbO₂ electrode in the carbon colloid (carbon content : 0.018 wt.%). Five cycles are shown.

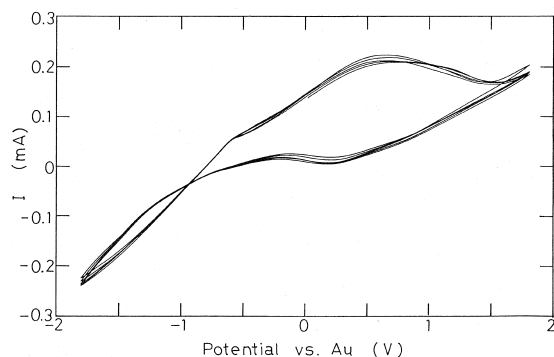


Fig. 11. Cyclic voltammogram of the Pb electrode in the carbon colloid (carbon content : 0.018 wt.%). Five cycles are shown.

then react with oxygen molecules to produce OH^- through multi-step reactions.



The OH^- ions could drift to the carbon anode to initiate the oxidation of carbon. No information is obtained concerning $-\text{H}$ from ESCA spectra. We have tried to observe on FTIR spectrum but it was unsuccessful because of the strong absorption of carbon. However, taking Eq. (1) into consideration, $-\text{COO}-$ and $-\text{CO}-$ groups observed in the ESCA spectrum could probably be due to $-\text{COOH}$ and $-\text{COH}$. The existence of $>\text{C}=\text{O}$ and $-\text{COH}$ is reported for oxidized graphite [7,8]. Carboxyl and hydroxyl groups could play an important role in the dispersion of carbon particles if the particle size is small enough. In conclusion of this section, it can be said that the surface of carbon particles was chemically modified as a result of electrochemical oxidation and particles become dispersible in water.

A calibration with standard graphite was taken immediately after cleaving. The sample for ESCA spectroscopy

consisted of aggregated particles. The particles were not separated. It is felt that the effect of particle size on the ESCA spectrum can be neglected in this case.

4.2. Electrochemical doping of PbO_2 cathode

After the cyclic charge–discharge test the battery with the carbon colloid was opened and examined. It was found that carbon particles were stuck around the PbO_2 cathode. This seemed to imply that the PbO_2 cathode was doped with carbon by an electrochemical process. In order to confirm whether electrochemical doping does occur or not cyclic voltammetry was carried out. Fig. 10 shows the cyclic voltammogram of the carbon colloid (carbon content: 0.018 wt.%) with a PbO_2 working electrode. The carbon content was adjusted to be the same as that for the cyclic charge–discharge test. As is seen in Fig. 10, current appears over a wide range of the potential against Au. This can be ascribed to a doping current. This was confirmed by the following procedure. As soon as the carbon colloid was put in to the cell equipped with the three electrodes, the potential of the PbO_2 electrodes was set to -1.2 V against Au and maintained for 20 min. No carbon was observed on these electrodes. In the next step, the potential of PbO_2 electrode was changed to $+0.2$ V against Au and maintained 5 min. Then carbon was observed on the surface of PbO_2 electrode. Therefore, the current observed in the potential region from -0.8 to $+1.2$ V could be ascribed to a doping current. As is described later, voltammetry was performed using the carbon colloid with a much lower carbon content than that in Fig. 10. The carbon content was monitored by photoabsorption spectroscopy every 10 or 20 cycles. It was observed that the intensity of the voltammogram decreased corresponding to the decreasing carbon content in the solution. This result indicates that

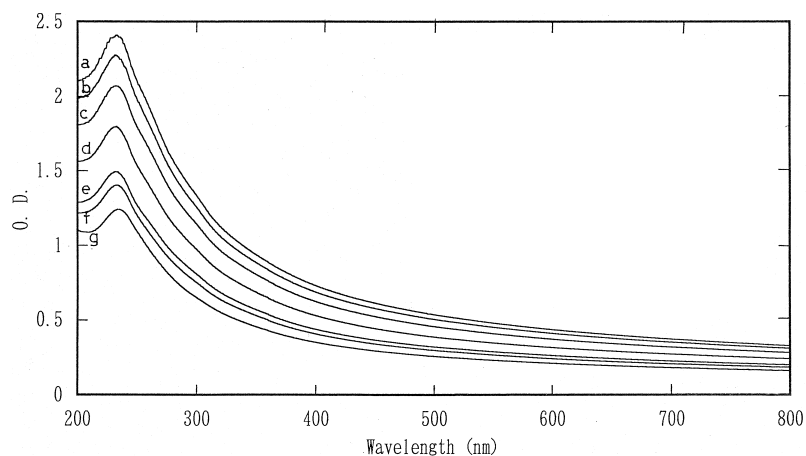


Fig. 12. Optical absorption spectrum of the carbon colloid (carbon content : 0.00455 wt.%), taken after the cyclic voltammetry. The condition of the voltammetry was the same as that in Fig. 11 except for the carbon content. The spectrum was taken before the start of voltammetry (a), after 10 (b), 30 (c), 50 (d), 70 (e), 90 (f) and 110 (g) cycles.

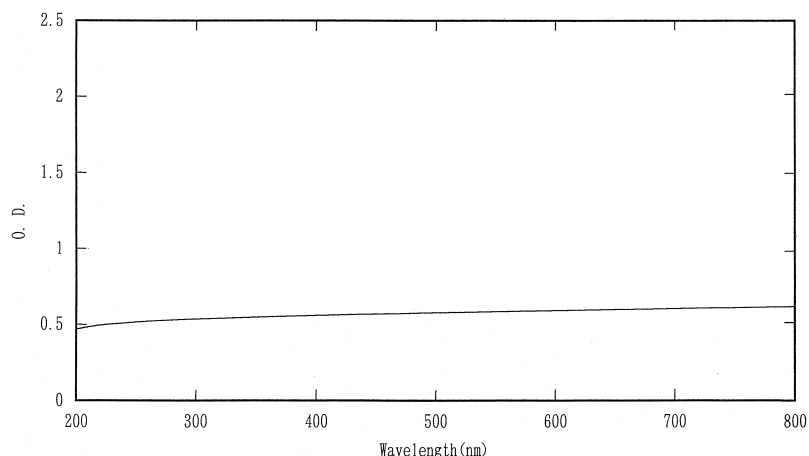


Fig. 13. Optical absorption spectrum of the raw material carbon.

features in the voltammogram reflect the doping current. From Fig. 10, the undoping current is hard to recognize. Therefore, it seems that undoping does not occur in this system. This seems to be supported by the fact that carbon accumulated on the PbO_2 surface did not appear to decrease when the potential was set to -1.2 V.

Fig. 11 shows a cyclic voltammogram of the carbon colloid (carbon content: 0.018 wt.%) with a Pb working electrode. No substantial differences were seen between the results of Figs. 10 and 11. This voltammetric works supports the theory that Pb and PbO_2 working electrodes are electrochemically doped with the oxidized carbon particles.

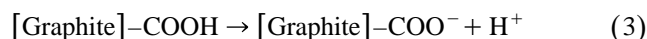
Electrochemical doping is qualitatively supported by the cyclic voltammetry. However, it is also necessary to show this quantitatively. In order to do this the carbon content in the solution was measured by an optical method. Fig. 12 shows the optical absorption spectrum of the carbon colloid (carbon content: 0.00455 wt.%) before and after cyclic voltammetry. It should be noted that a maximum appears in each spectrum at about 230 nm. The optical absorption spectrum of de-ionized water dispersed with the raw carbon material is shown as a reference in Fig. 13, where no absorption peak was observed. Thus the absorption peak in the ultra-violet region in Fig. 12 could be due to carboxyl groups. As is seen in Fig. 12, the absorption decreases with successive cycles of voltammetry. However, the shape of the optical spectrum in Fig. 12 does not change at all. This is confirmed in Fig. 14, where optical absorption densities at the peak (230 nm) and that at 500 nm are shown as a function of cycle number. The two straight lines in Fig. 14 are parallel with each other. It could be noted that the ordinate in Fig. 14 is given as a logarithm. Thus, the decay of the carbon content in the solution, shown in Fig. 14, is a first order reaction, namely the decay rate is given as,

$$-d[C]/dt = k \quad (2)$$

where $[C]$ is the carbon concentration, t is the time (or cycle number) and k is a constant. The constant k could

be a function of current density, viscosity and temperature. The fact that Eq. (2) holds could be further evidence for the electrochemical doping. Namely, the decay rate of carbon should not depend on its concentration under a certain electric field and the viscosity of the solution.

The mechanism of the electrochemical doping can be speculated as follows. Carboxyl groups on the surface of carbon particles dissociate to give anions.



These anions drift to the positive electrode and lose their charge. Then the positive electrode can be doped with carbon particles.

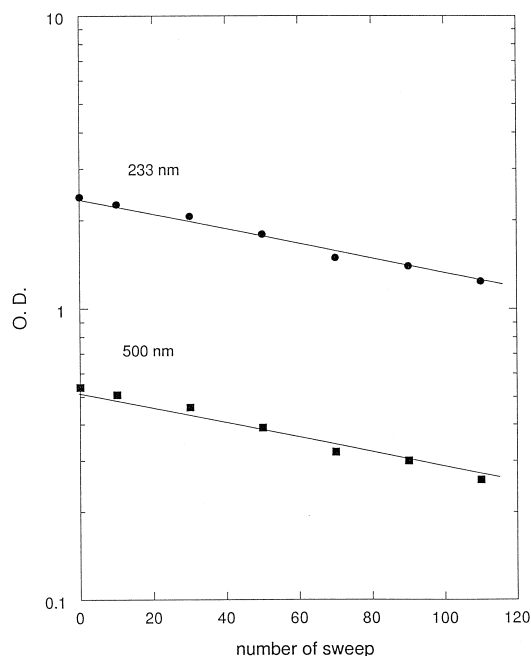


Fig. 14. Optical densities at 233 (●) and 500 nm (■) for the photoabsorption spectra of the oxidized carbon shown in Fig. 12.

4.3. The mechanism of the improvement of the charge–discharge ability of lead acid batteries

As is described above, positive electrodes can be doped with oxidized carbon. However, the problem is whether reaction (3) really occurs in the electrolyte of lead acid batteries. The electrolyte of lead acid batteries is a strong acid. In this case the existence of a high concentration of H^+ causes the reverse reaction. Therefore, the existence of the anion shown above cannot be expected. However, the concentration of H^+ could probably be low in a region very close to the positive electrode. In such a situation the existence of $-COO^-$ can be expected. As is described already the active material of the positive electrode, PbO_2 , is a granular semiconductor. Therefore, some PbO_2 grains have inadequate electrical connection. When PbO_2 electrodes are doped with carbon particles, these carbon particles can be expected to improve the electrical connection for the PbO_2 grains that are poorly connected.

4.4. Particle size of the oxidized carbon

The particle size of the oxidized carbon was extremely small. Measurements by SEM (scanning electron microscope) were unsuccessful. We have succeed in obtaining photographs with TEM (transmission electron microscope), where a dilute carbon colloid with a dispersive reagent was

developed on a thin Al foil (0.8 μm) and the thickness of the foil was decreased by a bombardment with Ar^+ ions from the back side. We could observe particles of 4–5 nm. Unfortunately, the quality of the photograph is not suitable for publication.

Raman spectroscopy was made which gave a result that the size of particles is 4.5 nm in average. We have also obtained a result by AFM (atomic force microscope) that the particle size is a few nanometer. We are preparing the publication of these results.

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