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# Preparation of ferromagnetic carbon electrode from charcoal blocks

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A ferromagnetic carbon electrode, if it really exists, will have an interesting role in the electrochemistry because it attracts the paramagnetic species such as free radicals or ion radicals and still it may keep the stabilities that carbon has. Since ferromagnetic carbon has been prepared in a powdery form, to extend that technique for the preparation of a solid block of ferromagnetic carbon, have been expected in the present work. A wood charcoal piece was selected as the skelton of the ferromagnetic electrode. An aromatic hydrocarbon was adsorbed by the charcoal piece. Hydrogen reduction and vacuum heating was applied to this charcoal piece. Removing hydrogen atoms from both charcoal and the hydrocarbon were carried out in a $CCl_4$ atmosphere at 550°C. The results have shown that mechanically strong ferromagnetic carbon electrode can be obtained by the method described in this report. © *2001 Kluwer Academic Publishers*

## 1. Introduction

In electrochemistry, many solute ions in a solution are placed in an electric field to make them receive some driving forces toward one of the electrodes where redox reactions may take place [1]. Some of the species which can be in the electrolytic system may have magnetic field response when they have magnetic dipole in them. Such species like free radicals and radical ions are the examples. The presence of a ferromagnetic electrode will give a new kinetic behavior to these species. As a ferromagnetic electrode, ferromagnetic metals such as cobalt or nickel may work. But they are not stable in solution.

By these considerations it will be understood that the ferromagnetic carbon electrode will be useful as a chemically stable electrode.

A probable method for the preparation of a ferromagnetic carbon electrode is to bind ferromagnetic carbon powders or flakes which have become possible to be prepared by the works of the present author [2–4]. Here the problem is how to find a proper glue to combine carbon powders or flakes into a solid block. The binder must be chemically stable and electrically conductive. To find such a glue is not easy. In the present work, therefore, a trial is made to convert a charcoal block into a ferromagnetic carbon electrode.

## 2. Experimental

### 2.1. Preparation of ferromagnetic charcoal

Since the purpose of the present work is to get a ferromagnetic carbon block having practicable dimensions, the starting material is a charcoal piece having sides of several mm length. Some of the past works of the present author have indicated that the presence of ferromagnetic ions induces ferromagnetic carbon when organic substances are dehydrogenated by heat treatments [5]. For this reason, charcoal pieces were impregnated with cobalt ion. Charcoal used is the one commercially available, which has been obtained by baking oak. An aqueous solution of cobalt acetate was used. Amount of cobalt was 5.0% of the weight of charcoal. ESR sample $S_1$ was taken at this stage. After adsorption of cobalt ions, the charcoal piece was reduced by hydrogen at 350°C for one hour. ESR sample $S_2$ was taken at this stage. Ferromagnetization was made by heating this reduced Co/charcoal specimen at 720°C for 120 minutes. ESR sample $S_3$ was taken at this stage [5, 6].

### 2.2. Removal of cobalt from magnetized carbon specimens

In order to measure the magnetic properties of carbon specimens obtained apart from that of cobalt added, the cobalt removal from the carbon specimens was carried out as follows. Dilute hydrochloric acid, 1 : 2 (conc. HCl/water), was used to dissolve cobalt from the charcoal to which cobalt was adsorbed. A 50 mg sample of charcoal specimen was cut out from the entire charcoal piece, and was enclosed in a glass ampoule together with 10 ml of diluted HCl. The ampoule used had 25 ml of volume with a capillary end at the top. Thus it can be heated to 90°C for 48 hours without losing any of the acid. Then the acid was separated from the charcoal specimen. The latter was repeatedly washed by distilled water and was then dried. After doing so, the cobalt concentration in the specimen was measured by X-ray fluorescense analyser. In all the cases, almost no cobalt was detected in the carbon specimen after this washing procedure.

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TABLE I The values of Ir (50 mT) for different measuring stages

| Hydrocarbon | $V_1$ | $V_2$ | $V_3$ | $V(CCl_4)$ | $V_4$ | $V_5$ | Type |
|---|---|---|---|---|---|---|---|
| 1,10-Phenanthroline | 2.04[a] | 1.44 | 0.844 | 0.107 | 0.0216 | 0.108 | A |
| Phenoxazine | 1.39 | 0.974 | 0.908 | 0.0785 | 0.0333 | 0.0549 | A |
| Phenazine | 0.874 | 0.328 | 1.88 | 0.0208 | 0.0578 | 0.0532 | B |
| Indigo | 0.674 | 1.10 | 1.32 | 0.00786 | 0.0264 | 0.507 | B |
| Phenothiazine | 0.632 | 1.46 | 0.854 | 0.0771 | 0.0500 | 0.0717 | C |
| Flavone | 0.618 | 1.29 | 1.99 | 0.022 | 0.0175 | 0.0391 | B |

[a] Values in emu/g unit. The matrix value before hydrocarbon impregnation is 0.688 emu/g. Some of the $V_1$ values are close to this value.

### 2.3. Impregnation of an aromatic hydrocarbon and heating in $CCl_4$ vapor or in a vacuum

A ferromagnetic carbon atom may be generated from the carbon atoms of charcoal itself. However, the C—C configurations in an aromatic hydrocarbon may be more convenient to form a ferromagnetic carbon atom network. By this reason, aromatic hydrocarbons, 1, 10-phenanthroline and 5 other aromatic compounds, as shown in Table I, were used. Impregnation was made by two methods, as shown in Fig. 1. "Impregnation-A" was a simple dipping of charcoal block in an alcoholic solution of phenanthroline (or other hydrocarbon) in order to coat only the surface of the charcoal block with phenanthroline. "Impregnation-B" was made in a vessel under a reduced pressure in order to let phenanthroline (or other hydrocarbon) penetrate into the inner tissue of charcoal. Impregnation-A was followed by a treatment with $CCl_4$ vapor at 650°C for 60 minutes. Impregnation-B was followed by a vacuum treatment at 650°C. This then was heated at 650°C for 60 minutes in vacuum again, in order to ascertain if this vacuum heating procedure is enough or not. Three ESR samples, $S_1$, $S_2$, and $S_3$, and 6 magnetization samples, $V_1$, $V_2$, $V_3$, $V_4$, $V_5$, and $V(CCl_4)$ were prepared. (Refer Fig. 1)

### 2.4. Measurement of ESR and magnetic susceptibility

ESR measurements were made with ME3X type spectrometer of Japan Electron Optics Co. using 100 kHz magnetic field modulation frequency. Magnetization measurements were made with VSM magnetometer of Tamagawa Corporation.

## 3. Results

### 3.1. ESR spectra of charcoal/cobalt composite system and those of the charcoal from which cobalt has been removed

It will be assumed that a mixture of cobalt/charcoal system will exhibit an ESR spectrum consisting of an overlapping of two ESR spectra namely that of cobalt and that of charcoal. This anticipation will be correct so far as there are no interactions between these two magnetic components. Fig. 2 seems to indicate that there actually is a mutual interaction between them.

The spectrum $S_1$ indicates the ESR spectrum of the charcoal which adsorbed cobalt acetate before hydrogen reduction. The central strong signal is due to charcoal ($g = 2.008$) and a broad spectrum appearing on both sides is due to cobalt ion adsorbed on charcoal surface. The spectrum $S_2$ indicates the ESR spectrum of the same specimen as $S_1$ after reduction in hydrogen,

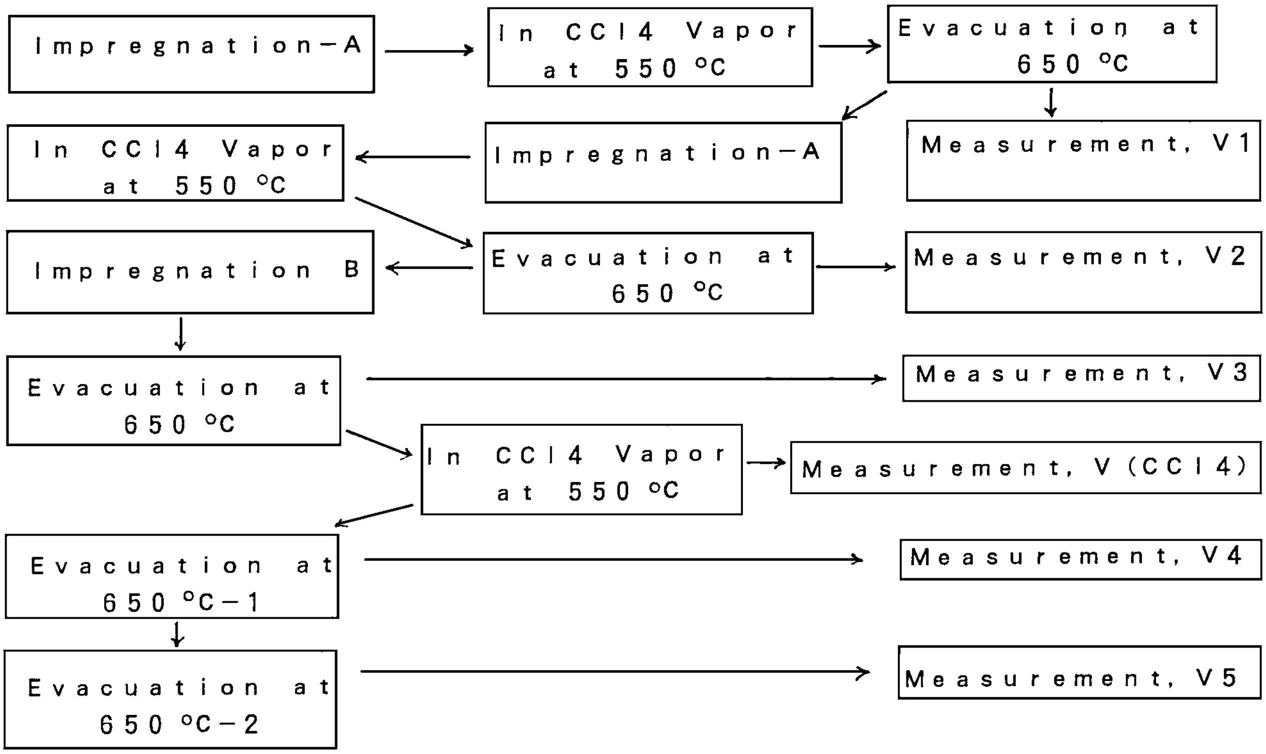


*Figure 1* The heating methods of hydrocarbons which appear in Table I. About Impregnation-A and Impregnation-B, see text. Measurements were made at 6 different phases of the processing and are named as $V_1$, $V_2$, $V_3$, V(CCl or $CCl_4$), $V_4$, and $V_5$.

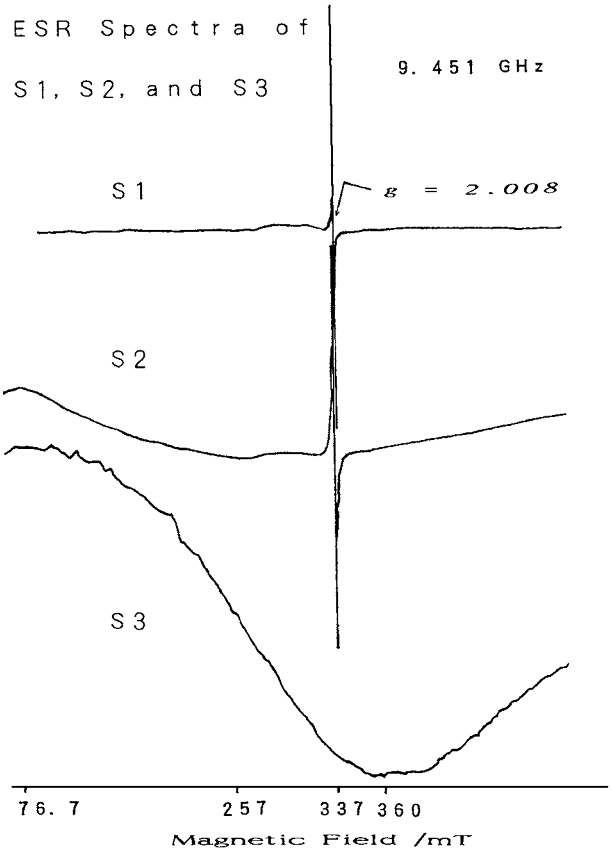


*Figure 2* The ESR spectra of charcoal/cobalt samples and magnetized charcoal ($S_3$). After cobalt impregnation ($S_1$), hydrogen reduction at 350°C ($S_2$), and after evacuation at 720°C ($S_3$). $S_3$ did not change by cobalt removal.

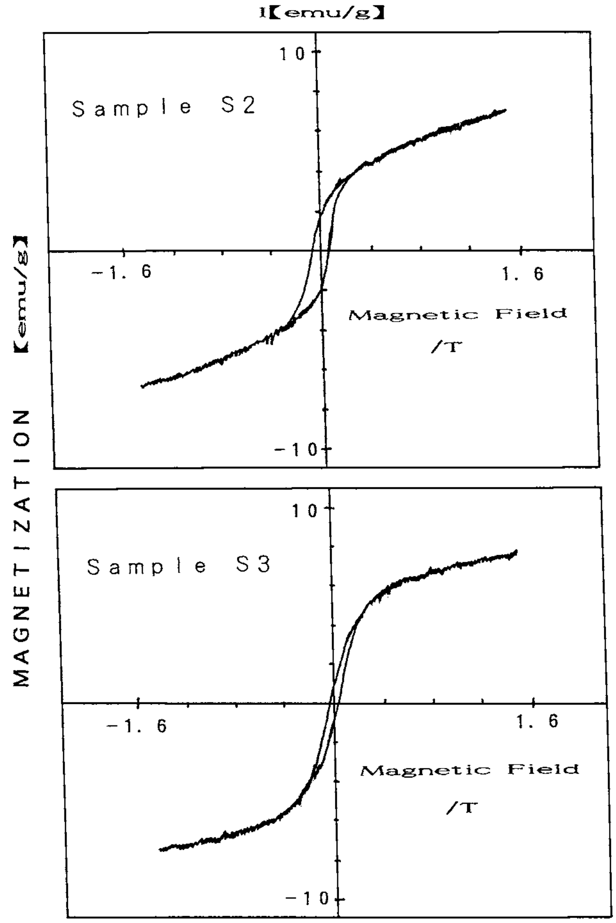


*Figure 3* The magnetization curves of charcoal/cobalt samples and magnetized charcoal ($S_3$ phase after cobalt removal). About $S_2$ and $S_3$, see text and the caption for Fig. 2. Vertical axis indicates the magnetization value, *I* in emu/g. Horizontal axis indicates magnetic field strength in T.

1 atm., at 350°C for 60 minutes. By doing so, cobalt had been reduced to metallic state and therefore the cobalt ESR had changed to a broader one. The central component had changed little. However, when the same specimen was heated at 720°C for 120 minutes in a vacuum, an ESR spectrum as shown by $S_3$ was observed. In this spectrum $g = 2.008$ absorption had completely disappeared and also a more intense signal had appeared. In $S_1$, $S_2$, and $S_3$ the signal amplification factors were the same, though in $S_3$ some weak signals observed in 76.7–500 mT region make the spectrum to look like the one taken at a higher noise level or with a higher amplification factor. Corresponding magnetization curves are as shown in Fig. 3. The specimen which gave $S_1$ ESR spectrum gave only paramagnetic magnetization curve, which is not shown in Fig. 3. The specimen which gave $S_2$ ESR spectrum gave the top magnetization curve in Fig. 3. This curve seems to consist of a paramagnetic carbon magnetization and a cobalt ferromagnetic magnetization. However, the bottom magnetization curve in Fig. 3 indicates that the ferromagnetism had changed in this specimen. The magnetization at 1.5 T increased from 7.098 to 7.529, and the coercive force decreased from 61.0 mT to 36.6 mT. This fact indicates that the major ferromagnetic component has changed from reduced cobalt to ferromagnetic carbon. The $S = 1/2$ state of the unpaired electrons has disappeared.

Effect of cobalt removal: In addition to the ESR spectrum $S_3$ in Fig. 2 and VSM data in Fig. 3 (the bottom curve), those measurements were made using the samples after cobalt-removal by diluted HCl solution. The charcoal sample $S_3$ used for Both Figs 2 and 3 was heated with diluted HCl in a capillary at 90°C for 48 hours and was then washed and dried. The results thus obtained were almost the same as those of Fig. 2 $S_3$ and Fig. 3 bottom figure. This indicates that the contribution of cobalt ions or cobalt metal to the ESR and VSM data of $S_3$ is very small.

### 3.2. Magnetization curves of charcoal treated with 1,10-phenanthroline

It has been demonstrated that charcoal carbon, if treated under the influence of cobalt at higher temperatures, becomes ferreomagnetic [5, 6]. This newly acquired ferromagnetism is not lost when the charcoal block was washed with diluted HCl solution. Then it will be hoped that if a new carbon rich layer is added on the top of the charcoal surface and this new carbon rich layer is treated by a process using $CCl_4$ vapor at 550°C, this newly added carbon layer will also become ferromagnetic. As the charcoal blocks, those charcoal pieces impregnated with cobalt acetate were used after following processing. They were first reduced with $H_2$ at 350°C, vacuum treated at 720°C, and then washed with diluted HCl solution at 90°C for 48 hours. 1,10-phenanthroline and 5 other hydrocarbons were impregnated into the

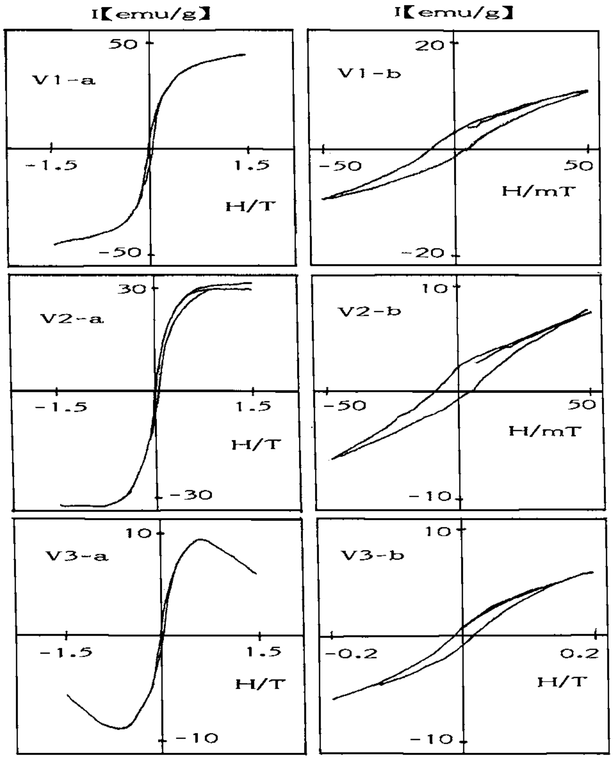


*Figure 4* The magnetization curves of 1,10-phenanthroline/charcoal sample. The coordination axes are identical to those in Fig. 3. The figure covers from $V_1$ to $V_3$ stages. "a" is for ±1.5 T region. "b" is for ±50 mT or ±200 mT region.

charcoal blocks thus prepared and then they were heat treated in $CCl_4$ and in a vacuum. After doing several combinations of these processings as shown in Fig. 1, VSM measurements $V_1$, $V_2$, $V_3$, CCl, $V_4$ and $V_5$ were made. The results are shown in Figs 4 and 5 and in Table I.

$V_1$; The hydrocarbon was impregnated into the charcoal by impregnation-A method, which means the HC (abbraviation for hydrocarbon) was adsorbed only by the external surfaces. Then it was treated in $CCl_4$ atmosphere to remove hydrogen atoms from the HC. Then it was heated in a vacuum at 650°C to remove chlorine atoms which may have combined with the carbon skelton. Then $V_1$ measurement was made.

$V_2$; By doing the same procedure as that for $V_1$ twice, this $V_2$ measurement was made.

$V_3$; After $V_2$ measurements, a different impregnation method, B, by which the inner surfaces of the charcoal block were also coated with HC, was used. Then heating in a vacuum only was made in order to see the reaction of the HC with ferromagnetized carbon.

The results obtained by $V_3$ measurement indicated that carbon atoms were still ferromagnetic in this specimen. This may indicate either newly added HC did not react with the ferromagnetic carbon already existed or newly added HC had changed to form a new ferromagnetic carbon layer. If the former possibility is true, it implies that newly added HC molecules do not reach ferromagnetic carbon site to react with it. Then, if $CCl_4$ vapor contacts with this HC//ferromagnetic carbon mixture, the distance between HC and the ferromagnetic carbon is to be shortened, because hydrogen atoms are removed, and the ferromagnetic carbon should be transformed to a paramagnetic species. For this reason, another measurement was made after $CCl_4$ treatment at 500°C. The result observed is titled as "CCl" in Fig. 5. This figure indicates that the ferromagnetic carbon has been destroyed by the combined action of newly added HC and $CCl_4$ vapor.

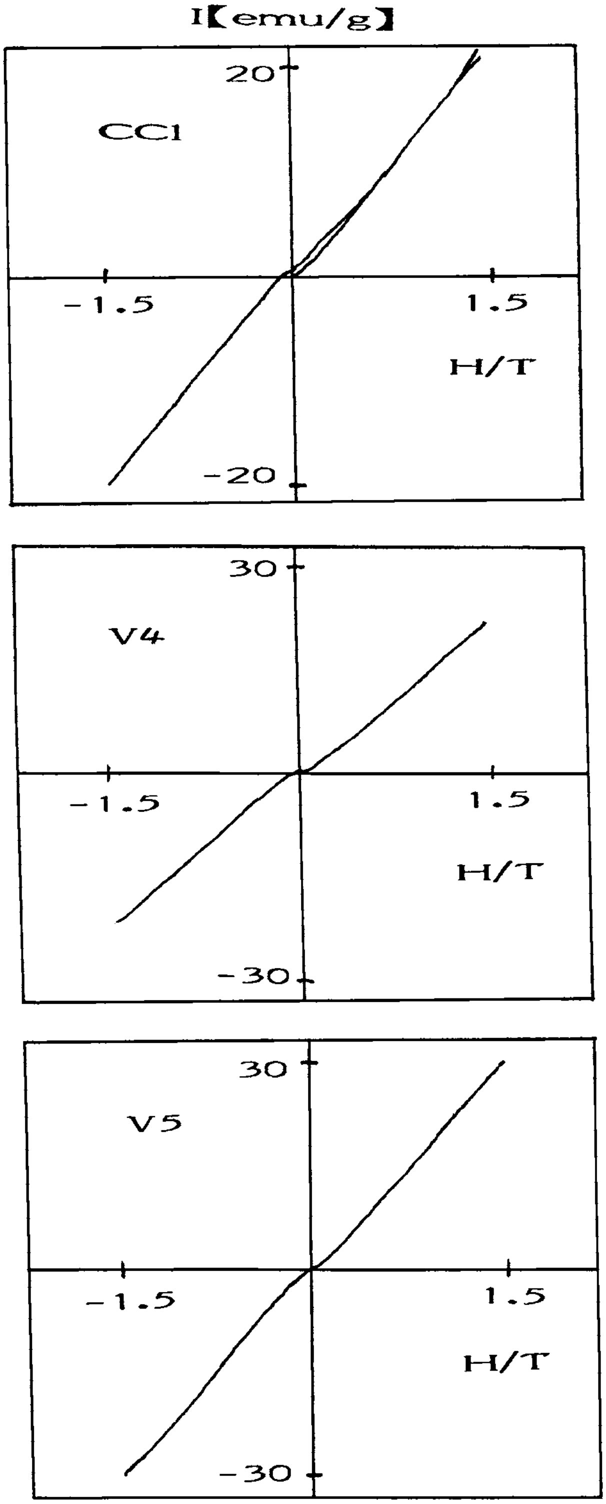


*Figure 5* The magnetization curves of 1,10-phenanthroline/charcoal sample obtained by CCl, $V_4$ and $V_5$ measurements.

$V_4$; The disappearance of ferromagnetism might be due to the halogen addition to the carbon atoms, so a vacuum-heating was made to remove the assumed

Cl atoms from the imagined C—Cl bonds which may have formed. The result, $V_4$ curve, indicates that this kind of reaction is not taking place or the hypothesis is untrue.

$V_5$; As shown in Table I, the differences between $V(CCl_4)$ values and $V_4$ values are not small. In order to see if this change occured has already been completed in $V_4$ or not, another vacuum heating at 650°C for 60 minutes was made. The result, $V_5$ curve had changed somohow from $V_4$, but has not reproduced the s-type shapes of $V_1$–$V_3$ curves.

## 4. Discussion

### 4.1. Preparation of a solid ferromagnetic carbon rod with practicable dimensions has been possible

As it has been mentioned in the introduction section, the preparation of a ferromagnetic carbon block having a practicable dimensions may be prepared from ferromagnetic carbon powder. The preparation of ferromagnetic carbon has been made from organic polymers, sugars, or aromatic hydrocarbons having condensed rings [2–5]. All of them give powders of ferromagnetic carbon. Therefore, it may be more convenient to prepare ferromagnetic carbon block having a practicable dimensions either by glue-cement method or by press-compression method. In the case of the glue-cement method, the binding substance must be both electrically conductive and chemically stable in an electrolyte solution. It is difficult to find this type of substance to bind ferromagnetic carbon powders.

To compress ferromagnetic powder into a pellet is also difficult. Due to magnetic repulsion force, the pellet prepared always split into several pieces. For these reasons, to prepare a ferromagnetic carbon electrode from ferromagnetic carbon powder is very difficult. In the present work, however, a charcoal frame could be used as the core of the ferromagnetic carbon block which may be used as an electrode. One unexpected fact found is that the charcoal itself can become ferromagnetic by the action of ferromagnetic substance [6].

### 4.2. Further coating of the ferromagnetic charcoal block by ferromagnetic carbon of aromatic origin

The skelton of the ferromagnetic carbon body has been made by the heat treatment of charcoal/cobalt system. The cobalt impregnated could be extracted out by heating this charcoal in diluted HCl solution for 48 hours. This ferromagnetism created in carbon can be strengthened by a coating/decomposition process using an aromatic hydrocarbon. Table I indicates the change of the magnetization values at 50 mT external field strength. As the original charcoal skelton has 0.825 emu/g, the increment of ferromagnetism by the first stage ($V_1$) is 1.22 for 1,10-phenanthroline. At the second stage, ($V_2$), this value decreases to 0.62 emu/g for the same compound. At the third stage, ($V_3$), this value for the same compound decreases to 0.02. This type of change is named as group A in Table I. A different tendency is found for phenothiazine ($V_2$ gives the largest value). This type is named as group C in Table I. Another group is consisted of phenazine, indigo, and flavone ($V_3$ gives the largest values) and they are named as group B in Table I. One possible explanation for these different tendencies may be as follows.

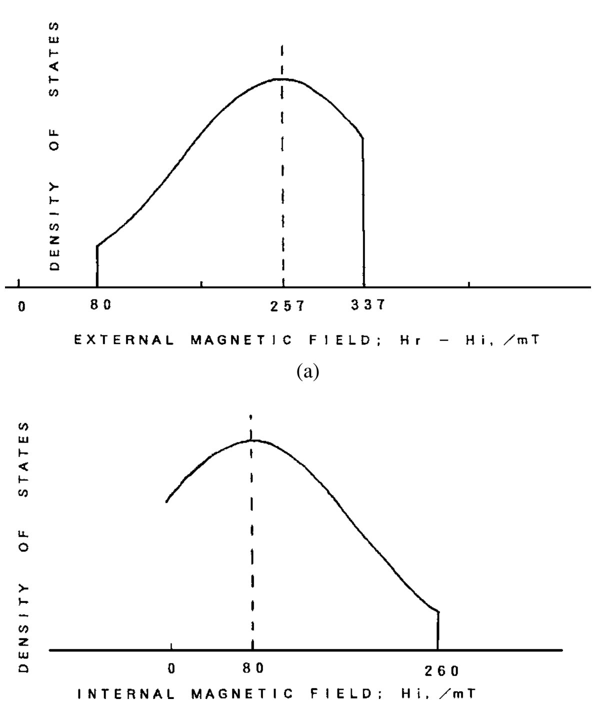
It may be possible to assume two different fates for the hydrocarbon added to the ferromagnetic carbon specimen. One fate is to become ferromagnetic carbon after proper heat treatment. Such possibility exists when the HC added is adsorbed at the not-ferromagnetic carbon site or at the paramagnetic site: $HC + C_n$ (pmg) $\rightarrow$ CC· (fmg) $+ C_{n-1}$ (pmg) $+$ mH. Another fate is to become paramagnetic carbon after heat treatment. Such possibility exists when the HC added is adsorbed at ferromagnetic carbon site. A HC and a ferromagnetic carbon when heat treated reacts; $HC + C\cdot$ (fmg) $\rightarrow$ CC· (pmg) $+$ mH.

### 4.3. Complex formation between aromatic compound and ferromagnetic carbon

In Table I, it will be found that $V(CCl_4)$ is considerably less than $V_3$ values. This indicates that impregnation B followed by $CCl_4$ processing at 550°C decreases carbon ferromagnetism greatly. There will be two possible theories to interpret these facts. One theory is that ferromagnetic carbon is destroyed by a quenching reaction with HC (hydrocarbon) or with the combination of $HC + CCl_4$. Another theory is that the ferromagnetic carbon makes a complex with the HC added and the product complex is not ferromagnetic. The former possibility is denied by the fact that in Table I, $V_5$ is larger than $V_4$ values except in the case of phenazine. In the case of phenazine $V_5$ is larger than $V(CCl_4)$. These values will indicate that ferromagnetic carbon can be partially restored by evacuation and that the disappearance phenomenon is not due to a complete quenching of the ferromagnetic species but due to a temporal trapping by HC.

### 4.4. Interpretation of charcoal/cobalt ESR specta

As shown in Fig. 2, the ESR spectrum of this system changes drastically by heat treatment. This phenomenon may be interpreted by using Figs 6 and 7. Original charcoal has $S = 1/2$ unpaired electrons which are paramagnetic and have only paramagnetic interactions with surrounding $S = 1/2$ electrons. However, if several pairs of $S = 1/2$ electrons form a ferromagnetic state, it exerts local magnetic power on a $S = 1/2$ unpaired electron which exists at nearby site. Let's observe the ESR spectra of this $S = 1/2$ electron as a probe species, $e_p$. The internal magnetic field, $H_i$, which works on this probe electron, will be distributed like Fig. 6B. If there is an external field, $H_{ex}$, Fig. 7A, $H_i$ must be aligned to $H_{ex}$ direction to some extent as shown in Fig. 7B, and so the magnetic field component on $e_p$ must be positive (its $H_{ex}$ direction component is a plus value) and has a density of state distribution as shown in Fig. 6B. Since at those external magnetic

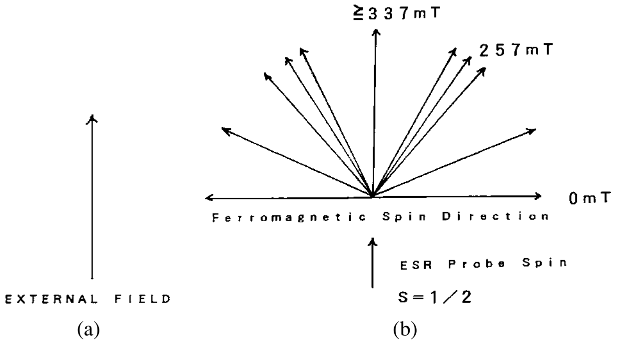


(a)

(b)

*Figure 6* ESR spectra calculated from internal magnetic field, $H_i$. 6B indicates the density of states distribution of $e_p$ (S = 1/2) electron receiving internal magnetic field. 6A indicates the density of states of $e_p$ which is in the resonant condition at the designated external magnetic field value, 80–337 mT.

field values; $H_{ex} = H_{resonance} - H_i$, the ESR absorptions occur, the shape of the ESR spectrum as a function of the external magnetic field values should look like Fig. 6A. Therefore, Fig. 6A must be the ESR spectrum of $e_p$ surrounded by ferromagnetic carbon spins. If a first derivative curve of Fig. 6A is calculated, it should resemble to the curve Fig. 2-$S_3$. Actually it is. Therefore, the change of $e_p$ ESR spectrum from $S_2$ to $S_3$ reflects the change of its environment, namely, from paramagnetic carbon atmosphere to ferromagnetic carbon atmosphere.



(a)

(b)

*Figure 7* The partial alignment of ferromagnetic carbon spins when an external magnetic field, 7A, exists. They are pointed to diversified directions as shown in 7B, but their $H_{ex}$ components are all positive. $(H_i, H_{ex}) > 0$.

### 4.5. Possible application of ferromagnetic electrode technique to another heterogeneous reactions in which electron spin plays a rôle

One possible application of this technique is to the ferromagnetic carbon catalyst. A solid catalyst particle should have active surfaces and some "free space around its particle" through which the reactant gases move with considerable space velocity. Therefore, ferromagnetic carbon powders are not convenient to use for solid catalyst. By the same reason described for ferromagnetic electrode, tabletting or pellet formation with ferromagnetic carbon powder is not easy. Then, a preparation method of ferromagnetic carbon catalyst from charcoal and an aromatic hydrocarbon will be useful for this purpose, too.

## 5. Summary

1. Charcoal/cobalt mixed system becomes ferromagnetic when heated in vacuum.

2. This ferromagnetism is not lost after removing cobalt by thermal extraction with diluted HCl. The ferromagnetism can be strengthened if an aromatic hydrocarbon is added to this charcoal system and then the hydrocarbon is dehydrogenated.

3. In the aromatic hydrocarbon/charcoal system, a paramagnetic complex may be formed, and therefore, the ferromagnetism may be weakened, under some condition, by the hydrocarbon added.

4. To prepare a ferromagnetic electrode with practicable dimensions has been possible. This technique can be applied for the preparation of pellets of ferromagnetic carbon catalyst.

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