Wettability and Surface Treatment of Carbon Powder[*]

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In investigating the relation between wettability and surface treatment of carbon powder for fuel cell, air cell, etc., the following results were obtained:

(1)　The surface area of carbon powder increased by steam treatment, but the contact angle to water decreased somewhat.

(2)　The contact angles to water of surface treated carbon powder were in the $90° - 94°$ range. The surface area, however, decreased considerably except under fluorine gas treatment.

(3)　It was found that in treatment with a H_2O_2 solution in 1 %, the contact angle of paraffin coated carbon decreased from $91°$ to $50°$ after 30 minutes. On the other hand, the contact angles of polyethylene, polystyrene and fluorine gas treated samples remained constant for 4-6 hours.

(4)　The waterproofing effect as a porous carbon electrode was discussed from changes in the electrode potential of air cell with time. The electrodes treated by polyethylene and fluorine gas gave good results. Particularly the electrode treated by fluorine gas showed great promise, despite some problems in respect to mechanical strength.

1　Introduction

As the air active mass in fuel cell or air cell is supplied through porous carbon electrode, three phase zone which takes place an electrochemical reaction must be formed on the electrode. The ability of the three phase zone are affected by the wettability of electrode material to electrolyte. From this standpoint, the porous carbon electrode is coated with paraffin, polyethylene, polystyrene, etc. The relationships between wettability and surface treatment of electrode have been investigated in recent years.[1][2] The wettability of carbon powder coated with some reagents was studied. The relation between wettability in carbon powder coated with those treatments and time change in potential as an air-electrode was also discussed from the formation of hydrogen peroxide on this electrode surface.

2　Experimental

2·1　Preparation of test powder

Sample of carbon powder was prepared by grinding the porous carbon electrode[3]

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for hydrogen-oxygen fuel cell or air cell. The mixture of charcoal, sawdust, and graphite with a ratio of 4 : 1 : 2 was molded by the binder which was the mixture of pitch and coaltar with a ratio of 1 : 3. The contents of the binder in the raw materials were fixed to 50%. The molded carbon electrode under about $100kg/cm^2$ was baked in an electric furnace at 900°C for 1 hour. In order to activate the baked carbon electrode by the water gas reaction, steam treatment was carried out. The preliminary baked carbon electrode together with charcoal powder in the furnace was heated up to 850°C and treated at same temperature for 1 hour by the steam from a quartz pipe by dropping water. Finally, the carbon electrode was ground to 50-100 meshes range.

2·2　Surface treatment of test powder

Paraffin treatment : After being immersed in trichloroethylene solution of 1% paraffin for 10 minutes under reduced pressure, the carbon powder was dried to evaporate the solvent.

Polyethylene treatment : After the samples were immersed in trichloroethylene solution of 1% polyethylene at near boiling point for 10 minutes, they were dried in an air bath at 120°C.

Polystyrene treatment : This treatment was carried out in benzene solution containing 1% polystyrene for 10 minutes under reduced pressure. The samples obtained were dried to evaporate the solvent.

Fluorine gas treatment : The carbon powder treated by fluorine gas was coated with a fluorocarbon compound on the surface. This compound is of strong water repellency and stable in acids and bases[4]. Fluorine gas was supplied from the fluorine cell. The operation is following : The carbon powder was put in a nickel boat (40m m×40mm×5mm) which was kept in a closed nickel reaction vessel, and was heated by electric furnace. Then, the fluorination was carried out at 280°C for 30 or 60 minutes under the condition of fluorine gas pressure of 1/3 or 1/2 atm, respectively. The fluorinated carbon was determined from changes of weight of the sample. As a result of this the former increased in weight up to 7% and the latter up to 20%.
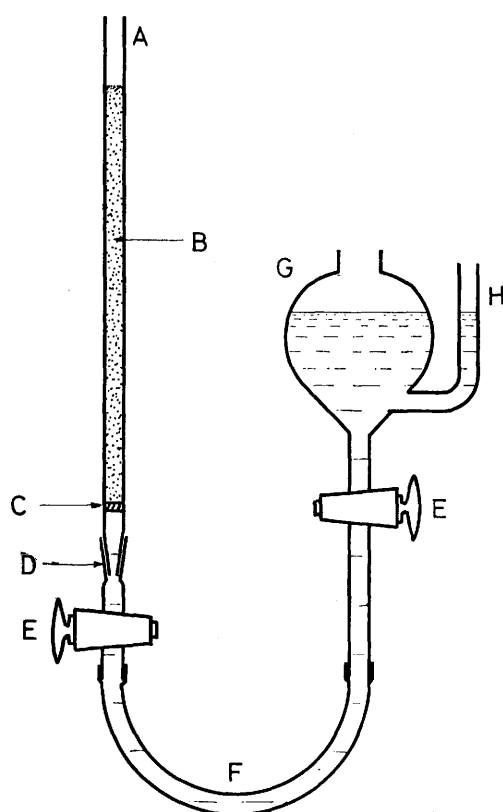
2·3　Measurement

(1)　Wettability : There are a few reports[5][6] related to wettability of powder. However, those are not always to have been established. In this experiment, then, the wettability of carbon powder was measured by the designed apparatus based upon permeation rate method[7] or a pressure-decline liquid permeability method.[8]

Fig. 1 gives the designed apparatus for the wettability measurement of carbon powder. A is a glass pipe with a scale. The sample, 1 g, was packed in to this pipe by a vibrator to become constant volume. Next, the sample was brought into contact with water by opening cock E. In this case, since the contact angle of the surface of treated sample with water was larger than 90° and the permeation of water has not been observed, the following operation was carried out. Reservior G was elevated slowly and when the permeation of water just began, the height of meniscus was measured

by a cathetometer. In a case of the untreated carbon powder, the permeation of water took place soon. Consequently, it was found that the contact angle of this sample was less than 90°. Then, the wettability of this sample was evaluated from the measurement of permeation rate of water under condition of keeping A in horizontal. The wettability measurement was carried out at 20°C.

(2) Surface area: Surface area of carbon powder was determined by an apparatus based upon the B. E. T. theory. Nitrogen molecule was selected as the adsorbing molecule.

(3) Specific gravity : Exactly 1 g of the sample was put into a picnometer with the dispersion medium of n-butyl alcohol. After air was removed, the specific gravity was determined at 25°C[9].

A : Glass pipe
B : Sample
C : Sintered glass disk
D : Ground glass joint
E : Cock
F : Silicon ruber tube
G : Reservoir
H : Branch

Fig. 1　Apparatus for the measurement of wettability

3　Experimental Results and Discussion

3・1　Wettability of carbon powder

Wettability of untreated carbon was evaluated from equation (1)induced as follows: Assuming that the vacant space of each carbon particle is to be a small pipe, the surface tension of solvent, γ, acts around across section of this pipe. The force of the surface tension is $2\pi\bar{r}\gamma$. Where $\bar{r}$ is average radius of the all pipes.

This force has the action which pushes the solvent, and is expressed to $-2\pi\bar{r}\gamma\cos\theta$. Where θ is a contact angle. Also, the force due to the pressure of the solvent is expressed to $\pi\bar{r}^2 dgh$. Where d, g, and h are density of solvent, acceleration of gravity, and height of solvent, respectively. When each force is balance, equation (1) is given. The value of $-\cos\theta/\bar{r}$ was calculated from this equation.

$$\frac{-\cos\theta}{\bar{r}} = \frac{dgh}{2\gamma} \qquad \cdots\cdots(1)$$

On the other hand, since the contact angle of the untreated carbon to water is less than 90°, the value of $\bar{r}\cos\theta$ can be calculated by using the following equation[7] :

$$\frac{dl}{dt} = \frac{\bar{r}\gamma\cos\theta}{4\eta l} \qquad \cdots\cdots(2)$$

or, integrating

$$l^2 = \frac{\bar{r}\gamma\cos\theta\cdot t}{2\eta} \qquad \cdots\cdots(2)'$$

where dl/dt is permeation rate and η is viscosity of solvent. In equation $(2)'$ the relation between l^2 and t is shown in Fig. 2. Since the slope in Fig. 2 gives the $\bar{r}r\cos\theta/2\eta$, the value of $\bar{r}\cos\theta$ can be calculated.

It was attempted to determine the average radius of the vacant space, $\bar{r}$, from data of surface area and apparent and true specific gravity. These related equations are given as follows : [10]

$$S = 2\pi\bar{r}L \qquad \cdots\cdots\cdots(3)$$
$$V = \pi\bar{r}^2L \qquad \cdots\cdots\cdots(4)$$

or, using (3) and (4)

$$\bar{r} = \frac{2V}{S} \qquad \cdots\cdots\cdots(5)$$

where L is the total length of the small pipe, S is the surface area, and V is the total volume of the vacant space. The value of V is calculated by using following equation:

$$V = \frac{1}{\rho'} - \frac{1}{\rho} \qquad \cdots\cdots\cdots(6)$$

where ρ' and ρ are the apparent and true specific gravity, respectively. The average radius, $\bar{r}_s$, calculated by using equation (5) is shown in Table 1 together with the other characteristics. However, it was impossible to determine the contact angle, θ, from $\bar{r}_s$ and $\bar{r}\cos\theta$ or $-\cos\theta/\bar{r}$, that is, the $\cos\theta$ was greater than 1 or nearly equal zero. The value of $\bar{r}_s$ calculated by using surface area and specific gravity is order of 100Å as shown in Table 1. This fact suggests that the $\bar{r}_s$ does not only depend on the vacant space, but also is contributed by micro-pore of carbon.
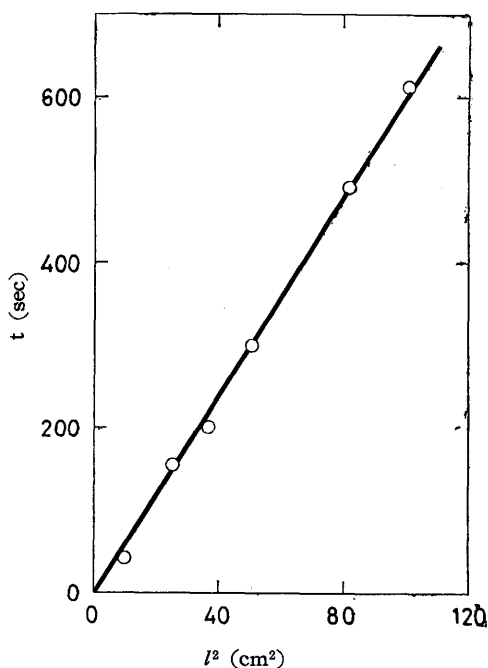
Then, the permeation rate of a few organic solvents for the test samples was measured by another method to determine the average radius of the vacant space, $\bar{r}$. The results obtained are given in Fig. 3. In this Fig., the slope of straight line is eqnal to $\bar{r}\cos\theta$ in equation $(2)'$. Where if the sample is perfectly wetted by the
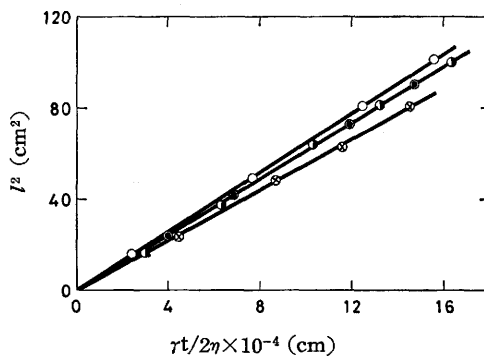

Fig. 2   Relationship between l^2 and t

⬤:C_6H_6,   ◯:CCl_4,   ◗:n-BuOH,   ⊗:$C_6H_5CH_3$

Fig. 3   Relationship between $rt/2\eta$ and l^2

organic solvents, that is, cos θ is equal to 1, the slope is equal to the average radius, $\bar{r}$. The assumption of cosθ =1 is valid from the following consideration. W. A. Zisman[11] has reported that in the experiments of wettability of polyethylene and polystyrene for several solvents, the relation between surface tension of each solvent and cos θ is linear in every case. The surface tension of intersection across the line of cosθ=1 is defined a critical surface tension. The critical surface tension of polyethylene is 31 dyne/cm and that of polystyrene is 33 dyne/cm. Since the surface tension of the organic solvents is less than these values, the carbon powder coated with polyethylene and polystyrene will be perfectly wetted. The critical surface tension of paraffin measured by using the various solvents which do not dissolve paraffin, is 15 dyne/cm[12]. There are still no data of polycarbon-monofluoride. However, the surface energy of sample powder gets larger in comparison with that of the flat surface and also the carbon surface might not be coated perfectly. It seems from this reason that the true critical surface tension may be little higher. Therefore, it seems that the assumption of cos $\theta = 1$ in this experiment is valid.

The average radius, $\bar{r}_p$, of the vacant space obtained from the slope in Fig. 3 is given in Table 1. These $\bar{r}_p$-values have a constant value in the order of 10^{-4}cm, being considerably greater than that of the above $\bar{r}_s$. The values of cos θ calculated substituting $\bar{r}_p$ for $\bar{r}$ cos θ or $-$cos $\theta/\bar{r}$ are shown in Table 1.

As compared with the contact angle in each sample, it was found that the value of the carbon treated by steam decreases from 85° to 74°. This fact suggests to form some hydrophilic surface compounds on its surface. The remarkable increase of surface area by this treatment is presumed to become even more hydrophilic for reason of the increase of the surface energy or others.

On the other hand, the contact angle of the sample coated with various waterproofing agents are 90°–94°. Though this is of favorable water repellency, the appreciable decrease of the surface area is observed in every treatment except fluorine gas treatment. This fact is considered that the pore of carbon is partially filled by those agents.
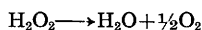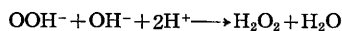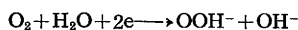
Table 1. Contact angles for the surface treated carbon powder

Desig-nation*	Surface area (m^2/g)	Specific gravity	$\bar{r}_s$ (cm)	$\bar{r}_p$ (cm)	$\bar{r}\cos\theta$ (cm)	$\cos/\theta\bar{r}$ (cm^{-1})	$\cos\theta$	θ (deg)
A	196	1.68	1.1×10^{-6}	5.4×10^{-4}	4.6×10^{-5}	—	0.085	85
B	520	2.03	0.63 ″	1.7 ″	4.8 ″	—	0.277	74
C	94	1.90	3.3 ″	2.0 ″	—	−54	−0.011	90½
D	54	1.81	5.8 ″	7.5 ″	—	−53	−0.040	92½
E	124	1.75	2.7 ″	5.8 ″	—	−71	−0.041	92½
F_1	257	2.07	1.2 ″	2.2 ″	—	−95	−0.021	91
F_2	187	1.95	1.3 ″	3.5 ″	—	−180	−0.063	93½

* A : Untreated, B : Steam treated, C : Paraffin treated, D : Polyethylene treated, E : Polystyrene treated, F : Fluorine gas treated
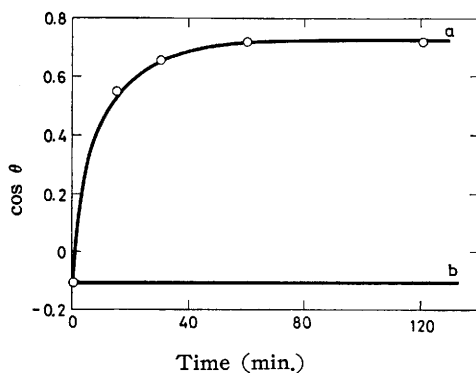
3・2 Hydrogen peroxide treatment of carbon powder

In general, the electrochemical reactions of oxygen electrode in an alkaline solution are expressed as follows :[13][14]

$$O_2 + H_2O + 2e \longrightarrow OOH^- + OH^-$$
$$OOH^- + OH^- + 2H^+ \longrightarrow H_2O_2 + H_2O$$
$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

Though the first step reaction takes place rapidly, the second or other is slow. The intermediate products such as hydrogen peroxide or its ion, etc. are accumlated on the electrode surface and these products will affect to the rate of electrochemical reactions. It is expected that the concentrated hydrogen peroxide accumulated on the carbon electrode decomposes the waterproofing agent or makes the carbon surface wettable. From this standpoint, the waterproofed carbon sample was treated by hydrogen peroxide solution and its hydrophobicity was discussed. The experimental procedure is as follows: The 1% hydrogen peroxide solution was prepared under the condition of pH=9.0. The pH-value was controlled by potassium hydroxide solution. The hydrogen peroxide solution containing the carbon sample in a 100ml beaker was slowly rotated by a stirrer. The relation between wettability and treating time was observed by using the apparatus shown in Fig. 1. The results obtained are given in Fig. 4. As shown in Fig. 4, the cos θ of the sample treated by paraffin increases remarkably after 15 minutes. After this, it increases gradually. Subsequently the change of the contact angle was not observed during the treatment for 1-2 hours, that is, it has a constant value, cos $\theta = 0.71$ (θ=45°). This value is smaller than that of sample A or B shown in Table 1. This fact suggests the formation of some surface active compounds on the carbon surface by the oxidizing force of hydrogen peroxide. Consequently, the surface energy of the carbon may be little higher.

The changes of the contact angle of the samples treated by polyethylene, polystyrene, and fluorine gas are not observed as shown by the b in Fig. 4. These samples are still stable in the treatment for 4-6 hours and their contact angles are greater than 90° in every case. However, the appreciable quantity of the carbon sample coated with polystyrene dispersed into the solution during the treatment for 2-4 hours, and the evolution of the oxygen, also, was observed.

Time (min.)

a : Paraffine treated carbon
b : Polyethylene, polystyrene, and fluorine gas treated carbons

Fig. 4 Relationship between H_2O_2 treating time and contact angle

3・3 Time Changes of electrode potential

The lowering of carbon electrode potential during continuous discharge has been considered owing to the wetting of the electrode. In order to test the hydrophobicity, the time change of air-electrode potertial

was measured during the continuous discharge. The carbon electrode used is the baked carbon plate (baking temperature, 900°C ; porosity, 45–50%) of Nippon Denchi Co. Ltd. This sample was baked at 800°C for 1 hour under the atomosphere of the nitrogen. The 5N–KOH solution was selected as electrolyte and the nickel was used as a counter electrode. The air-carbon electrode was compulsively polarized by external battery and ionization reaction of the oxygen was carried out at the current density of 20mA/cm². The air-electrode potential was measured by a potentiometer vs. HgO reference electrode. As shown in Fig. 5, the untreated carbon electrode is poor in waterproofing effect, namely, the remarkable lowering of potential is observed after about 8 days.

Both the samples treated by polyethylene and fluorine gas, however, are shown to be superior to the untreated sample. In comparison with both the samples treated by polyethylene and fluorine gas, the potential of the former lowers gradually with passing the discharge time. The potential of the latter has a constant value up to 15 days, after this time the potential lowers remarkably. In consideration of these results and those mentioned in section 3 • 2, it is reasoned that the water-proofing surface compounds on the carbon, especially polyethylene, are not only decomposed by oxydation of hydrogen peroxide formed on the carbon surface, but also the surface properties change gradually with the formation of surface active compound. On the other hand, since the carbon electrode treated by fluorine gas is weak in mechanical strength, the water-repellent surface compound is easily removed by physical impact. This may be an important factor of the lowering of the potential. It seems that the carbon electrode treated by fluorine gas is superior as the air-carbon electrode to the others.
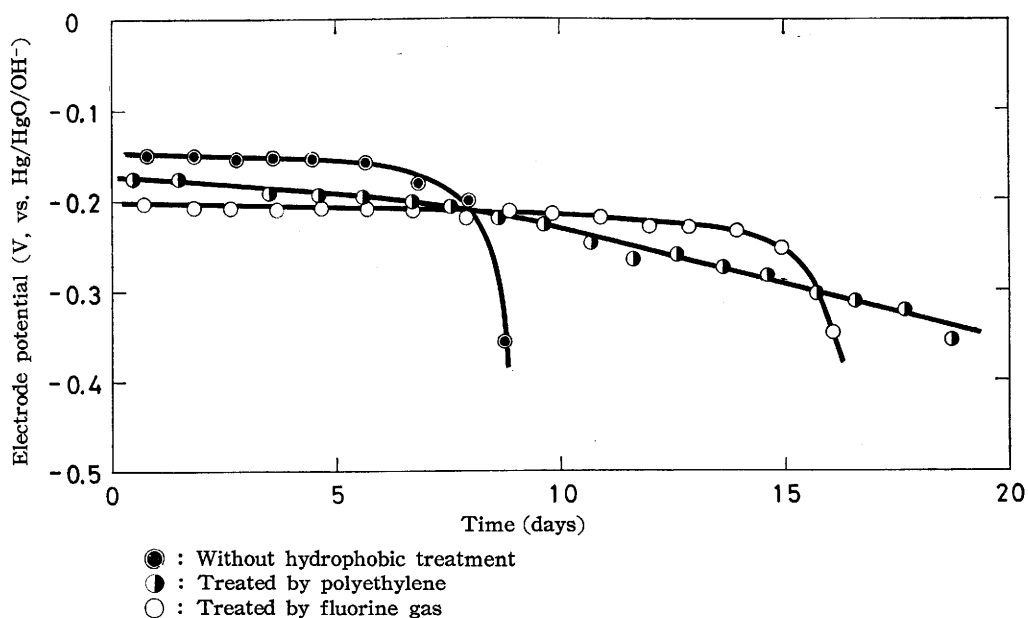

● : Without hydrophobic treatment
◑ : Treated by polyethylene
○ : Treated by fluorine gas

Fig. 5   Changes in the air-electrode potential with time

4 Conclusion

In investigating the relation between wettability and surface treatment of carbon powder for fuel cell, air cell, etc., the following results were obtained:

(1) The surface area of carbon powder increased by steam treatment, but the contact angle to water decreased somewhat.

(2) The contact angles to water of surface treated carbon powder were in the 90°–94° range. The surface area, however, decreased considerably except under fluorine gas treatment.

(3) It was found that in treatment with a 1% hydrogen peroxide solution, the contact angle of paraffin coated carbon decreased from 91° to 50° after 30 minutes. On the other hand, the contact angles of polyethylene, polystyrene, and fluorine gas treated samples remained constant for 4–6 hours.

(4) The waterproofing effect as a carbon electrode was discussed from changes in air-electrode potential with time. As a result, polyethylene and fluorine gas treatments were shown to be superior. Fluorine gas treatment in particular shows great promise, despite some problems in respect to mechanical strength.

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