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The Preparation and General Properties of Ion-exchange Carbon Fiber

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Cation-exchange carbon fibers were prepared from pitch-based carbon fiber by oxidizing treatment with a mixture of $K_2Cr_2O_7$, HNO_3, and water. Their most characteristic properties were a large electric conductivity, a large thermal stability, and their shape. Their exchanging properties varied with the composition of the mixture and the treating conditions. The following composition and the conditions were adopted as standard.

Composition of the mixture: $K_2Cr_2O_7$, 10 g; HNO_3, 20 m*l*; H_2O, 80 m*l*
Condition of the treatment: temperature, 104°C; period, 2.5 hr
Amount of carbon fiber: carbon fiber prepared at 1000°C 1 g

The cation-exchange capacity obtained by the standard procedure was 2.0 ± 0.1 mequiv/g. Carbon fiber prepared at 1000°C was a better material than that prepared at 2000°C. Even after the exchangers were heated at 220°C in air, no change was observed in the capacity measured at room temperature. The electric resistivity increased from 7×10^{-3} ohm-cm to 8×10^{-2} ohm-cm with an increase in the capacity, and no difference was obserbed between exchangers of the acidic form and the sodium form. The tensile strength of the filament(1.9 mequiv/g in the capacity) was 6.7×10^6 g/cm^2, and the breaking load of the spinning yarn of 1300 den. (2.0 mequiv./g) was 3.0 kg.

A number of investigations have been carried out on the preparation of high-modulus or high-strength carbon fibers and their applications. On the other hand, it seems that little attention has been paid to improving the application of low-modulus carbon fibers. However, we thought that the application of the low-modulus carbon fibers should also be developed as fully as possible. The present paper will, then, deal with ion-exchange carbon fibers prepared from low-modulus carbon fibers.

As compared with other ion-exchangers, the ion-exchange carbon fibers are characterized by their electric conductivity, their thermal stability, and their flexibility. Ion-exchange carbon fibers were prepared by oxidation. For the purpose of the surface treatment of high-modulus carbon fibers, the oxidation of carbon fibers has been attempted by various manners.[1] However, the ion-exchange capacity of the resulting carbon fibers is only less than 0.02 milliequivalents per gram. Therefore, the previous manners are not very good for preparing ion-exchangers.

On the other hand, some attempts have been reported to prepare the ion-exchangers by sulfonation from such carbonaceous materials as coal or char.[2][3] Sulfonation is effective for carbonaceous materials which contain same hydrogen atoms, but it does not give satisfactory results for carbon fibers practically composed only of carbon atoms.

After several preliminary examinations, it has been found that oxidizing treatment with a mixture of $K_2Cr_2O_7$, HNO_3 and water is a promising method for the preparation of ion-exchange carbon fiber without any intensive deterioration of its mechanical properties.

Experimental and Results

Preparation. The present ion-exchangers were prepared by the procedure shown in Fig. 1. This procedure is characterized by the use of a mixture of nitric acid, potassium dichromate, and water, and

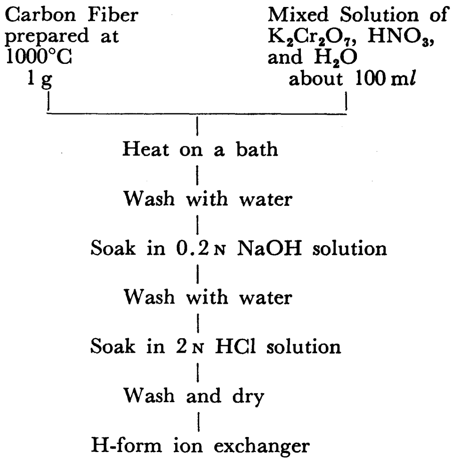

Fig. 1. Procedure of preparation.

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by the use of carbon fibers prepared at 1000°C from pitch material. The cation-exchange capacity of the resulting exchangers was affected by several conditions, for example, the composition of the mixed solution, the oxidizing temperature, and the period. In this work, most of the cation-exchange capacities have been measured with sodium ions. Therefore, the cation-exchange capacity will be represented by the exchange capacity with sodium ions. Unless otherwise stated, the measurement of the capacity was carried out as follows: about 1 g of the exchangers, weighed exactly, was allowed to stand in a 0.2 N NaOH solution for 24 hours, and then the decrease in alkali was determined by titration with hydrochloric acid. Figure 2 shows the relationship between the composition of the mixed solution and the exchange capacity of the fibers finally obtained. The numbers in Fig. 2 represent the capacity. In this experiment, the weight of the original carbon fibers used was about 1 g, the oxidizing temperature was 104°C, and the oxidizing period was 2.5 hr. By the use of mixtures having compositions lower than the line denoted by 3.0, capacities larger than 3.0 mequiv/g were obtained. However, those fibers were remarkably weak in tensile strength, and some soluble matters were formes in an alkaline solution. Therefore, the composition and the conditions shown in Table 1 were adopted as standard. This standard procedure gave the exchange capacity of 2.0±0.1 mequiv/g.

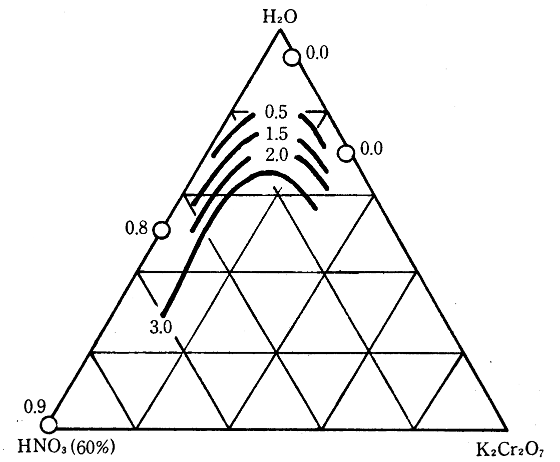


Fig. 2. Relationship between the composition of the mixed solution and the exchange capacity of the resulting fibers.

TABLE 1. STANDARD COMPOSITION AND CONDITIONS

Composition of the treating mixture	HNO_3	20 m*l*
	$K_2Cr_2O_7$	10 g
	H_2O	80 m*l*
Oxidizing conditions		
temperature	104°C	
period	2.5 hr	
Amount of carbon fiber		
Carbon fiber prepared at 1000°C		1 g

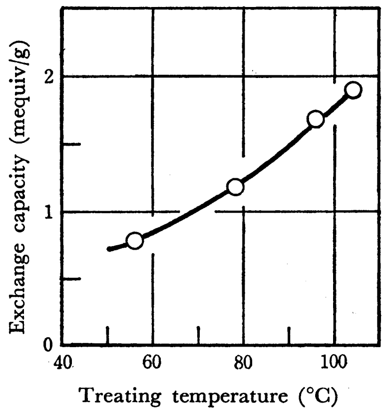


Fig. 3. Effect of the treating temperature. (Other treating conditions and composition of the mixture were the same as those of the standard procedure shown in Table 1.)

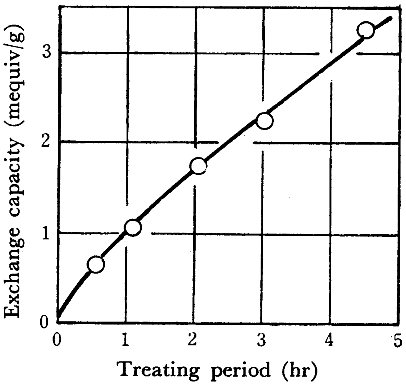


Fig. 4. Effect of the treating period. (Other treating conditions and composition of the mixture were the same as those of the standard procedure shown in Table 1.

Figures 3 and 4 show the effects of the oxidizing temperature and the oxidizing period respectively. These results indicate that it was possible to control the capacity of the fibrous exchangers by selecting well the composition of the mixed solution, the oxidizing temperature, and the oxidizing period.

Chemical Composition and Structure. The chemical composition and infrared spectrum of a typical ion-exchanger having a capacity of 2.0 mequiv/g are shown in Table 2 and Fig. 5 respectively.

The original carbon fiber had, before treatment, a carbon content of 99.2 wt%, and it had no characteristic absorption band in its infrared spectrum. By

TABLE 2. CHEMICAL COMPOSITION OF ION EXCHANGE CARBON FIBER
(2.0 mequiv/g)

Element	Content	
	wt%	atom%
C	87.4	82.3
H	0.8	9.3
N	1.3	1.1
O(diff.)	10.5	7.3
Cr[a)]	trace	trace

a) by emission spectroscopoy

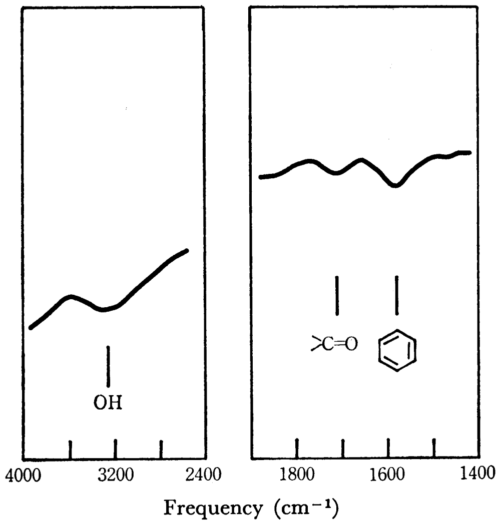


Fig. 5. Infrared spectrum of the ion exchange carbon fiber having 2 mequiv/g in the capacity.

Table 3. Changes of d_{002} and L_c by the oxidizing treatment

State	Original	Exchanger	
		H-form	Na-form
Inter-layer distance	3.7_7	3.6_7	3.6_3
Crystalline thickness	17	19	18

the oxidizing treatment, the weight of the fiber increased by about 10% in the case of preparing a fibrous exchanger with a capacity of 2.0 mequiv/g. The resulting ion-exchange carbon fiber was very hydroscopic and was found to take up water of about 10 wt% upon exposure to the atmosphere. Its infrared spectrum indicates that some carbonyl and hydroxyl groups were introduced by the treatment.

In order to get some information on the structural changes upon treatment, the powdered samples were used for X-ray diffraction analysis. X-ray diffraction profiles of the original and the treated carbon fibers were composed of (002) and (10) diffraction bands. The two bands were very broad in all cases. The structural parameters of the original one, calculated from the (002) diffraction band, were 3.7_7 Å in inter-layer distance, d_{002}, and 17 Å in the crystalline thickness, L_c. By the oxidizing treatment, the (10) band was weakened to some extent, and the inter-layer distance was decreased slightly, as is shown in Table 3. On the basis of these data, it seems that the structure was not affected very much by the oxidizing treatment.

Exchanging Properties. The first examination of the exchanging properties consisted of measuring the variation in the exchange capacity upon a repetition of the cycle of exchanging and regenerating. The H-form carbon fiber was allowed to stand in a 0.2 N NaOH solution for one day to measure the exchange capacity, and then the resulting carbon fiber-(Na-form fiber) was regenerated with the 0.2 N HCl solution over a one-day period. The exchange capacity of the regenerated H-form fiber was again measured by the above method, and then the cycles of the exchanging and regenerating were repeated. As is shown in Fig. 6, even after the cycles had been repeated 8 times, the exchange capacity remained at the same value as that of the original exchanger.

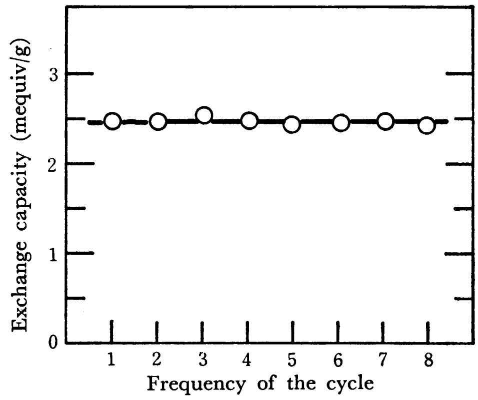


Fig. 6. Variation of the capacity by repeating the cycle of exchanging and regenerating.

In order to determine the exchanging rate, a 50-ml portion of the 0.2 N NaOH solution was placed in each of 7 flasks, and one gram of the H-form exchanger was taken into each alkaline solutions, then the decreases in alkali after 5, 10, 15, 20, 30, 40, and 50 min were determined by titration with the 0.2 N HCl solution. The results are shown in Fig. 7. Two curves, (1) and (2), were obtained for the present ion exchangers, while curve (3) was that of a weakly acidic exchange resin obtained commercially. The value of 100% exchange was considered to be reached at the end of 2 days.

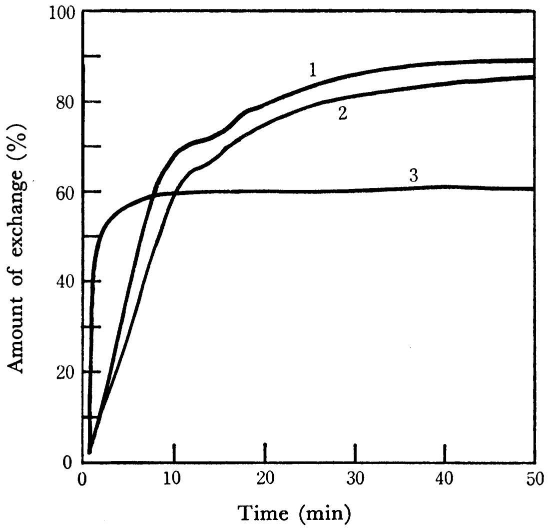
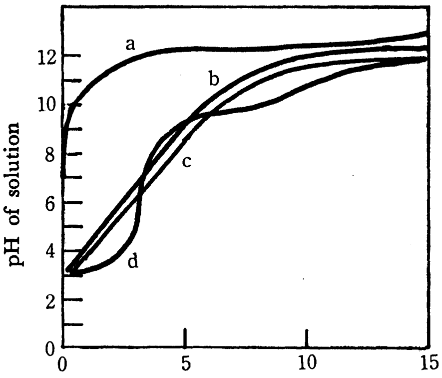


Fig. 7. Rate of ion exchange
1) exchange carbon fiber, 2.1 mequiv/g in the capacity
2) exchange carbon fiber, 1.9 mequiv/g in the capacity
3) weakly acidic exchange resin (as control)

When one gram of the exchange carbon fiber in 100 ml of distilled water was titrated with the 0.2 N NaOH solution, the pH of the solution varied as is shown in Fig. 8. The curve (a) is the result of a blank



0.2 N NaOH added (ml)

Fig. 8. Titration curves with NaOH solution.
a) pure water (blank test)
b) exchange carbon fiber, 2.1 mequiv/g in the capacity
c) exchange carbon fiber, 3.5 mequiv/g in the capacity
d) mixture of strongly acidic and weakly acidic exchange resins (as control)

test with distilled water alone, while curve (d) is that on a mixture of strongly acidic and weakly acidic exchangers obtained commercially. The titration curves of the present carbon fibers gradually rose from 3 to 12 in pH value.

Figure 9 shows the thermal stability of the present ion-exchange carbon fiber. After heating in air for one hour, the ion-exchange capacity was measured at room temperature. Until the heating temperature was over 220°C, no change was observed in the capacity, at 320°C, the capacity decreased by 20%.

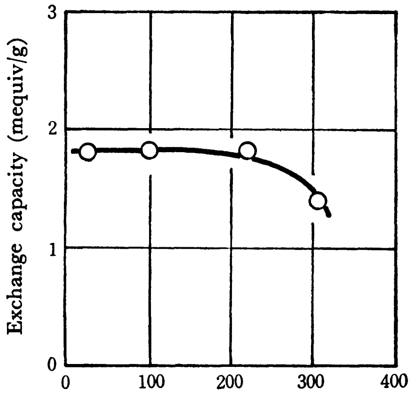


Fig. 9. Change of the exchange capacity after heating in air for one hour.

The effect of the exchanging temperature is shown in Fig. 10. Since the experimental error was about ±0.1 mequiv/g, it seems that an increase in the exchanging temperature up to 100°C caused scarcely no change in the capacity.

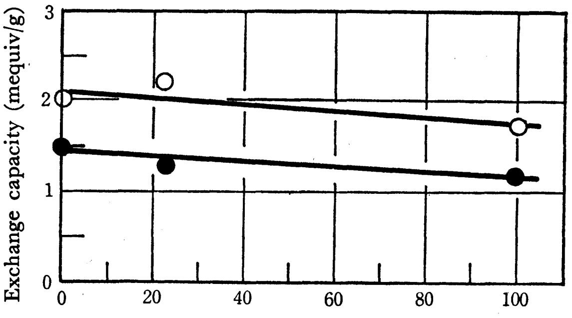


Fig. 10. Effect of the exchanging temperature.

Electric and Mechanical properties. The electric resistivity of the present exchangers is shown in Fig. 11. The measurement was carried out at room temperature by the use of the Universal Bridge TF 1313A made by Marconi Instrument, Ltd. As is shown in Fig. 11, the electric resistivity increased with the increase in the capacity, and no difference was observed between the H-form and the Na-form.

The mechanical properties of a typical ion-exchanger

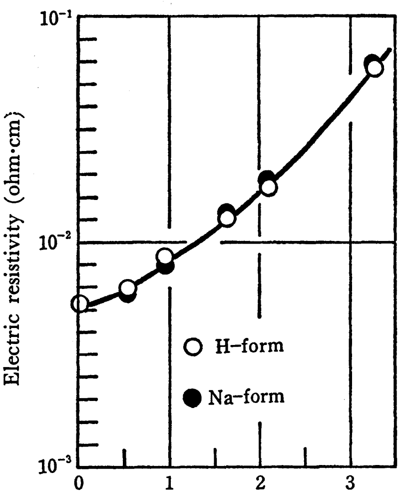


Fig. 11. Relationship between elecctric resistivity and the ion exchange capacity.

TABLE 4. MECHANICAL PROPERTIES OF THE ORIGINAL AND THE ION EXCHANGE CARBON FIBER

Sample	Tensile strength ($\times 10^6$ g/cm^2)	Breaking load (Kg)	Elongation (%)	Young's modulus ($\times 10^6$ g/cm^2)
Filament				
original	8.7	—	2.1	420
ion exchanger (1.9 mequiv/g)	6.7	—	2.5	260
Spinning yarn (1300 den.)				
original	—	4.0	—	—
ion exchanger (2.0 mequiv/g)	—	3.0	—	—

are shown in Table 4. The tensile strength decreased by 20% as compared with that of the original carbon fiber, and Young's modulus decreased by 33%. When the graphite fiber prepared at 2000°C was used as the original fiber in the standard procedure, the resulting fibrous exchanger had a tensile strength of only one half of these values and an exchange capacity of less than one third. Carbon fiber heated at 1000°C was a much better material for the exchanger than that prepared at 2000°C.

Discussion

From the results presented above, it has been found that the new ion-exchangers can easily be prepared from carbon fiber. The resulting fibrous exchangers have a satisfactory tensile strength for common use and several other characteristic properties. The most interesting properties other than their shape and mechanical properties are their large electric conductivity and their large thermal stability.

The exchanging properties shown in Fig. 8 resemble those of amorphous zirconium phosphate[4)] rather than a commercial strongly or weakly acidic resin exchanger which has a single functional group. From this result, it seems that the ion-exchange carbon fibers have many kinds of functional groups and/or exchanging mechanisms. It is a well known fact that graphite oxide is formed from graphite crystallites or graphitized carbon materials by oxidizing treatment with various agents, such as a mixed solution of phosphoric acid and sulfuric acid.[5,6)] Graphite oxide, however, is a very complicating material, and its chemical composition and structure are not known definitely. According to Hofmann *et al.*,[7,8)] the chemical composition can be represented by C_8O_2-$(OH)_2$ and oxygen atoms exist in both the *keto*-type and the *enol*-type. The inter-layer distance, d_{002}, of the graphite oxide was expanded to 7.96 Å even in a dry state. However, on the basis of the results obtained in the present work, it is doubtful that the previous considerations of the graphite oxide are applicable to the present investigation. In the present work, use was made of a new oxidizing agent and the carbon material not graphitized. Carbon fiber prepared at 1000°C had a larger exchange capacity than that produced from carbon fiber prepared at 2000°C. The inter-layer distance of the exchanger, in spite of the large amount of oxygen introduced, kept almost the same value as that of the original fiber. The exchangers have acidic functional groups, and their infrared spectra indicate the presence of carbonyl and hydroxyl groups. Moreover, it is also well known that mellitic acid is formed from carbon materials by oxidation with some oxidizing agents, such as nitric acid. From these results, it seems most reasonable to assume that the ion-exchange properties are due mainly to the carboxyl groups substituted at various positions of the carbon structure.

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