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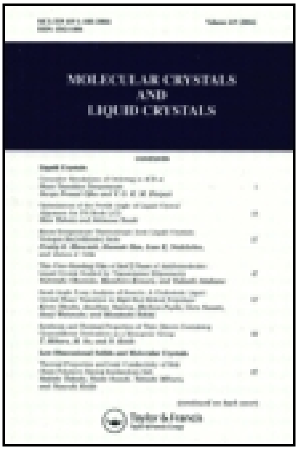

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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^{129}I Mössbauer Effect of Iodine Absorbed in Activated Carbon Fibers

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Version of record first published: 24 Sep 2006

To cite this article: Yoshiyuki Shibayama, Hirohiko Sato, Toshiaki Enoki, Makoto Seto, Yasuhiro Kobayashi, Yutaka Maeda & Morinobu Endo (2000): ^{129}I Mössbauer Effect of Iodine Absorbed in Activated Carbon Fibers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 301-306

To link to this article: http://dx.doi.org/10.1080/10587250008025483

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 301-306
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Printed in Malaysia

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Activated carbon fibers (ACFs) composed of a nano-graphite disordered network have huge specific surface areas ranging 1000–3000m^{2}g^{-1}. The electronic states of iodine adsorbed in ACFs were investigated by ^{129}I Mössbauer spectroscopy with a focus on charge transfer from nano-graphite to iodine. The observed spectra consisting of five different quadrupole octets demonstrate the coexistence of I_3^- ion and I_2 molecule in micropores. This fact implies that I_3^- ions are produced as a result of charge transfer from nano-graphite to iodine. The estimated charge transfer rate on the basis of the ratio of generated I_3^- is in good agreement with the previous results obtained by magnetic susceptibility.

Keywords: activated carbon fibers; nano-graphite; charge transfer; iodine-129 Mössbauer spectroscopy; iodine doping; micropore

INTRODUCTION

Activated carbon fibers (ACFs), which have huge specific surface areas (SSAs) ranging 1000–3000m^{2}g^{-1}, are microporous carbon consisting of a three dimensional disordered network of nano-graphites with an average in-plane size of L_a ~ 30Å [1]. In contrast with fullerenes and carbon nanotubes having closed π-conjugated systems, the nano-graphite is an open-edged π-electron system, which is currently focused in relation to the presence of novel edge inherited electronic structures [2-4]. In addition to this, micropores in ACFs, which are formed as nano-sized rooms surrounded by nano-graphites, are expected to accommodate various guest species with the aid of interaction with nano-graphites having the novel mesoscopic electronic states. Therefore, it is interesting to investigate the structures and the electronic properties of intercalated nano-graphite systems with the expectation of novel features that have never appeared in ordinary graphite intercalation

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compounds (GICs) or fullerene analogues. From this viewpoint, iodine is useful guest species that can work as a test probe to extract even a subtle difference in the electronic structures of host carbon systems. Actually, our previous work for iodine guests in ACFs has indicated that charge transfer takes place from nano-graphites to iodine [5] nevertheless bulk graphite gives no GICs with iodine [6], while polycyclic aromatic hydrocarbons such as perylene or carbon nanotubes give charge transfer complexes with iodine [7,8]. As nano-graphite is situated between polycyclic aromatic hydrocarbons and bulk graphite, charge transfer that is absent in bulk graphite shows one of novel features of nano-graphite. In the present work, ^{129}I Mössbauer spectroscopy for ^{129}I doped ACFs is investigated in order to clarify the electronic state of iodine atoms adsorbed in the ACFs and the charge transfer between iodine and nano-graphite.

EXPERIMENTAL

Pitch-based ACFs having SSAs of 1500m^{2}g^{-1} (Osaka Gas Co., type A15) were used as samples after heat treatment at 1300°C for 15min in argon atmosphere. The reaction of ^{129}I$_2$ with the ACFs was carried out with the two zone vapor method of ACFs sample and ^{129}I$_2$, where ^{129}I$_2$ were obtained by pyrolysis of Pd^{129}I$_2$ over 350°C. Pd^{129}I$_2$ was synthesized by mixing aqueous solutions of commercial Na^{129}I (5.8×10^{-3} mol l^{-1}, 8ml) and PdCl$_2$ (1.2×10^{-3}mol l^{-1}, 20ml) [9]. An ACFs sample and Pd^{129}I$_2$ were placed in a Pyrex tube partitioned by a breakable seal. Here, three batches having different iodine concentration were prepared; the weight ratios $w_{\mathrm{ACFs}} : w_{\mathrm{Iodine}}$ = 1:0.11, 1:0.18 and 1:2.6, named as #1, #2 and #3, respectively. The ACFs sample was vacuum-sealed after vacuum heat-treatment at 200°C for 1 hour in order to remove adsorbing gases. Pd^{129}I$_2$ was vacuum-sealed as well, then it was pyrolyzed by heating with a torch. After the pyrolysis, the breakable seal was broken and iodine-doping started with the two zone vapor method, where the ACFs side and the iodine side were maintained at 105°C and 60°C, respectively, for 12 hours. After the iodine-doping, the sample sealed in the Pyrex tube was inserted into a polyethylene bucket and set in a cryostat for Mössbauer measurements. ^{129}I Mössbauer spectroscopy measurements were performed at 12K using a radiation source of ^{66}Zn^{129}Te ($t_{1/2}$=70min) prepared by irradiation of ^{66}Zn^{128}Te target (for #1 and #3) and Mg$_3$^{129m}TeO$_6$ ($t_{1/2}$=33.6d) prepared by irradiation of Mg$_3$^{128}TeO$_6$ target (for #2) in Kyoto University Reactor (KUR). The source produced sufficient 27.7keV γ-radiation for Mössbauer effect data collection, where the velocity calibration was accomplished with an ^{57}Fe foil.

EXPERIMENTAL RESULTS and DISCUSSION

FIGURE 1 shows the ^{129}I Mössbauer spectra at 12K for all the samples. All the spectra have considerably complicated features as compared with the spectrum of

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isolated $^{129}I_2$ molecule whose spectrum consists of one octet [10], suggesting the coexistence of more than two kinds of iodine species having different electronic states. The possibility of isolated I^- ion is excluded because of the absence of a single peak at about –0.5mm s^{-1} [11]. In ordered to analyze the spectra, the least square fit was taken with 3 adjustable parameters; quadrupole coupling constant $e^2q^{129}Q$ (eq and ^{129}Q are principle component of electric field gradient and nuclear quadrupole moment of ^{129}I nuclear, respectively), isomer shift δ and full-width at half maximum Γ. Here, asymmetric parameter η is assumed to be 0 judging from the structural disorderedness of ACFs. The fitting results are shown in FIGURE 1 with the experimental data and the obtained three parameters are summarized in TABLE I. The fitting line with five different quadrupole octet series resulted in a good quantitative agreement with the experimental data, demonstrating the presence of five types of iodine sites with different electronic states.

In the first place, we discuss the assignment of each site of iodine atom in the micropores of ACFs. I_3^- ion is one of the candidates for the sites. For I_3^- ion, $e^2q^{129}Q$ and δ have been reported as follows [12]. In a symmetrical I_3^- ion, $e^2q^{129}Q$ is –1725MHz and δ is 1.48mm s^{-1} for the central iodine atom, and –808MHz and 0.25mm s^{-1} for terminal iodine atoms. In a disordered I_3^- ion, on the other hand, $e^2q^{129}Q$ and δ are reported at –1787MHz and 1.14mm s^{-1} for the central one, and –1036MHz and 0.11 mm s^{-1}, and –616MHz and –0.24mm s^{-1} for two terminal iodine atoms. Compared with the present results, the obtained parameters for site 1 are close to those of the central iodine atom of symmetrical and disordered I_3^- ions in all the samples. And the ones for sites 2 and 3 are close to those of the terminal iodine atoms of disordered I_3^- ion in addition to that the absorption area ratios of site 2 to site 3 are almost 1:1. Moreover, the obtained parameters of site 4 are close to those of the terminal iodine atoms of symmetrical I_3^- ion. Here, the absorption area ratio of central iodine atom (site 1) to terminal iodine atom (site 2, 3 and 4) ranges 1:1.3–1.6, which is close to the reported value in I_3^- ion [10]. The derivation of the absorption area ratio from the composition ratio of 1:2 in I_3^- ion has been explained in term of the recoilless fraction and the saturation effect [13]. Eventually, site 1–4 are assigned to symmetrical and disordered I_3^- ions. Site 5, on the other hand, gives $e^2q^{129}Q$ ~ –1550MHz and δ ~ 0.5mm s^{-1} for all the samples. The obtained parameters are close to those for isolated I_2 molecule in hexane, $e^2q^{129}Q$ = –1587MHz and δ = 0.98mm s^{-1} [12]; hence site 5 is assigned to I_2 molecule.

On the basis of these assignments, we discuss the ratio of I_3^- ion to I_2 molecule in ACFs and their iodine concentration dependence. As for site 5 assigned to I_2 molecule, the adsorption area ratios in #1 and #2 are small compared with the ratio in #3. This fact suggests that in the initial stage of iodine doping almost iodine changes to I_3^- ions, which are considered to be generated through charge transfer from nano-graphite to iodine. As increasing in the concentration of iodine doped in ACFs, the ratio of the iodine without charge transfer increases. According to oxygen adsorption isotherms for ACFs, the ACFs has two kinds of adsorption sites; that is,

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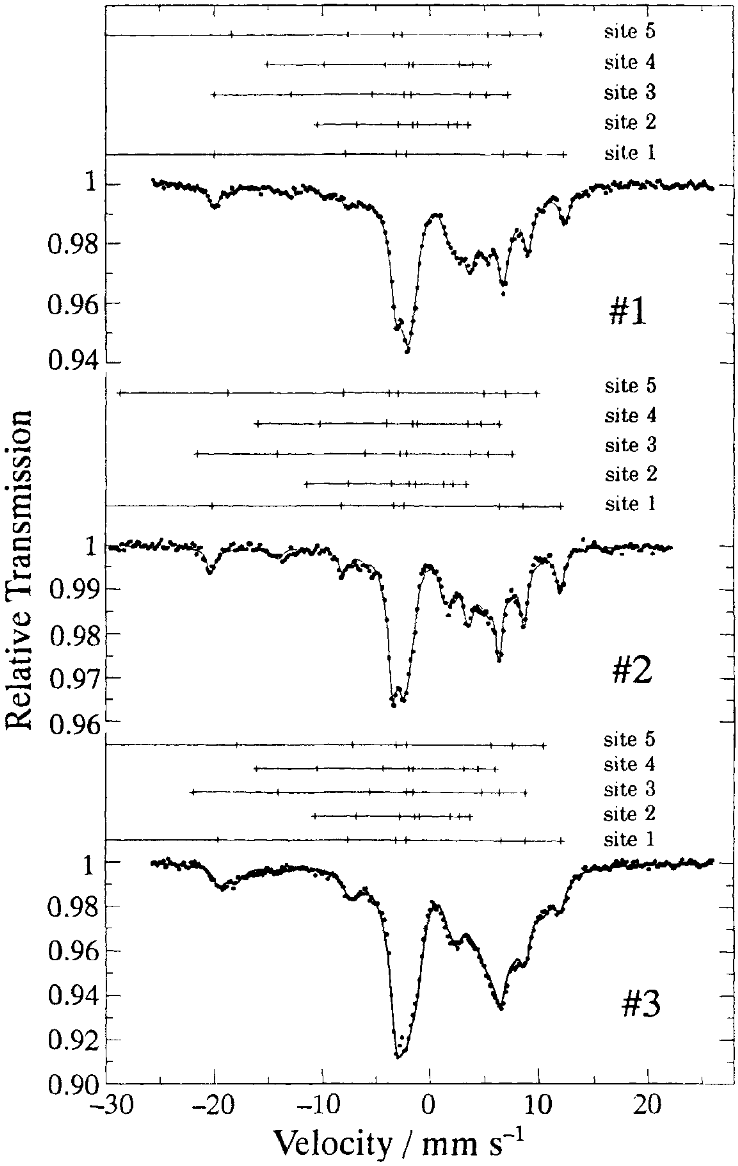

FIGURE 1 : ^{129}I Mössbauer spectra for samples #1, 2 and 3 (solid circle) and the least square fitting results (solid line) with five different quadrupole octets. The horizontal line with vertical bars indicates each octet. Here the velocity for #2 was converted the value relative to the ^{66}Zn^{129}Te source.

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TABLE I : Quadrupole coupling constant $e^2q^{129}Q$ converted to ^{129}I nucleus, isomer shift δ relative to the ^{66}Zn^{129m}Te source, full-width at half maximum Γ and absorption area ratio normalized with respect to site 1 after the least square fits of ^{129}I Mössbauer spectra.

sample		$e^2q^{129}Q$ / MHz	δ / mm s^{-1}	Γ / mm s^{-1}	Area Ratio
#1	site 1	-1760	1.37	1.1	(1.00)
	site 2	-564	-0.01	1.3	0.55
	site 3	-1100	0.40	1.4	0.57
	site 4	-829	0.20	1.1	0.48
	site 5	-1550	0.57	1.9	0.38
#2	site 1	-1750	1.02	0.87	(1.00)
	site 2	-597	-0.44	1.1	0.55
	site 3	-1170	0.19	1.1	0.62
	site 4	-900	0.69	0.87	0.13
	site 5	-1570	0.17	1.9	0.33
#3	site 1	-1710	1.31	1.3	(1.00)
	site 2	-582	0.18	1.4	0.68
	site 3	-1240	0.95	1.7	0.62
	site 4	-890	0.32	1.3	0.00
	site 5	-1540	0.82	2.0	1.33

chemisorption and physisorption sites,[14] where physisorption sites start to work after chemisorption sites become full with adsorbates through chemical reaction. In the present cases, similar to oxygen adsorption, it is considered that the initial stage of iodine adsorption is dominated by the chemisorption-type process accompanying the charge transfer, resulting in the generation of I_3^- ion, although it is not clear how the actual reaction proceeds. With chemisorption sites occupied, the ratio of iodine without charge transfer increases. The generation of I_3^- results in the lowering of the Fermi level of the nano-graphites in ACFs because of the role of iodine as electron acceptor. Here, we can estimate the charge transfer rate in iodine-doped ACFs on the basis of the estimated ratio of I_3^- ion to I_2 molecule. For the estimation, we assume that the absorption area ratio of site 1 to site 5 gives the I_3^- / I_2 ratio, where site 1 corresponds to central iodine atom of I_3^- ion and site 5 to I_2 molecule. Under this assumption, the charge transfer rates per carbon atom f_C for #1, #2 and #3 are estimated at 0.0027, 0.0046 and 0.0043, respectively. In the previous investigation on magnetic susceptibility for iodine-doped ACFs, f_C was estimated at 0.0079 for the sample having similar iodine concentration to #3 [3], being in good agreement with present results. In (perylene)$_2$(I$_2$)$_3$, where perylene ($C_{20}H_{12}$) is one of polycyclic aromatic hydrocarbons, the charge transfer rate was estimated at 0.02 from ^{129}I Mössbauer spectroscopy [10]. The fact that iodine is not intercalated in bulk graphite composed of an infinite π-electron system, on the other hand, suggests the weakness in the interaction between iodine and bulk graphite. The finite charge transfer between the nano-graphite and iodine demonstrates that the less graphitized ACFs having small conjugated π-electron systems are considered to have similar electronic state to that of condensed polycyclic aromatic molecules.

In summary, ^{129}I Mössbauer spectroscopy for $^{129}I_2$ doped ACFs was investigated. The spectra indicate the coexistence of I_3^- ion and I_2 molecule, demonstrating charge transfer from nano-graphite to iodine. The presence of charge transfer reveals novel features in the electronic state of nano-graphite which gives considerably different intercalation activity from bulk graphite.

Acknowledgments
The authors express their gratitude to Dr. N. Shindo in Osaka Gas Co. for providing ACFs samples. The present work has been carried out in part under the Visiting Researcher's Program of the Research Reactor Institute, Kyoto University. Y. S. was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. The present work was supported partly by the Grant-in-Aid for Scientific Research No. 08404048, No. 10137214 and No. 10354011 from the Ministry of Education, Science and Culture, Japan.

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