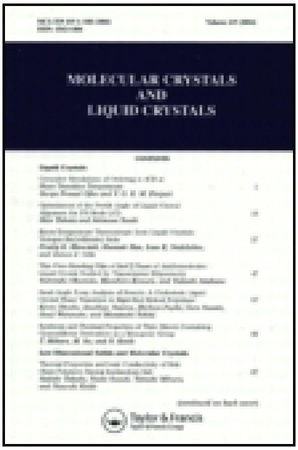

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Characterization of Unsaturated Organic Molecule—Alkali Metal—Ternary Graphite Intercalation Compounds

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Characterization of Unsaturated Organic Molecule – Alkali Metal – Ternary Graphite Intercalation Compounds

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Raman scattering and X-ray diffraction measurements were made to identify stage structure of $CsC_{24}(C_2H_4)_n$ and $CsC_{24}(C_2H_3CN)_n$, which were exposed to air for a long time. Their electric conductivities were also measured during the long exposure to air. Raman spectra suggest that the gradual degradation of their electric conductivities in air is caused by the slow decomposition of the ternary GIC's from the periphery region, although results of X-ray diffraction for all samples indicate the retention of the initial stage structure. Among the samples, $CsC_{24}(C_2H_4)_{1.4}$ which absorbed large amount of ethylene, was found to be exceptionally stable both in its stage structure and electric conductivity.

Keywords: Cs-GIC; XRD; Raman scattering; electric conductivity

INTRODUCTION

The binary stage 2 alkali metal - graphite intercalation compounds (AMC_{24}) are known to have very high electric conductivity, though they are unstable in air and easily decompose [1]. We have found that these compounds, in particular CsC_{24}, absorb several unsaturated organic molecules to form ternary GIC's, some of which maintain high electric conductivities and are considerably stable in air [2-4].

The most typical one among them is the ethylene - CsC_{24} ternary GIC. By XRD measurements its stage structure has been identified as stage 2 with I_C = 1.01 nm [2], and this structures was found to be retained, by successive XRD observations, even after several years in air. The electric conductivity was, however, not so stable and degrade gradually.

In the present study, we report the results of Raman spectroscopy on a few ternary GIC's including ethylene - CsC_{24} in order to elucidate the difference in the stability of the stage structure by XRD measurements and the electric conductivity during the long exposure to air.

EXPERIMENTAL

Three samples of the ternary GIC's, $CsC_{24}(C_2H_4)_{1.4}$, $CsC_{24}(C_2H_4)_{0.6}$ and $CsC_{24}(C_2H_3CN)_{1.2}$ were used in the present study. All these samples were prepared from CsC_{24} by being contacted with ethylene or acrylonitril vapor ; the details of the preparation were described elsewhere [3]. The host carbon material was Grafoil (Union Carbide, GTA grade).

Raman scattering measurements were made on these samples after exposure to air for 38 months for $CsC_{24}(C_2H_4)_{1.4}$, 13 months for $CsC_{24}(C_2H_4)_{0.6}$ and 17 months for $CsC_{24}(C_2H_3CN)_{1.2}$. A microscopic Raman spectrometer, Renishaw Raman Microscope System 2000, was used with 632.8 nm He-Ne laser line, which focuses the incident laser beam to a 20 μ m diameter spot on the surface of samples.

For only $CsC_{24}(C_2H_3CN)_{1.2}$, the Raman spectra were obtained on the interior surface of the sample after it was cleaved with a razor blade, because its upper surface was covered with something like oligomer of acrylonitril.

RESULTS AND DISCUSSION

The absorption - desorption isotherms and the stage structure from XRD patterns for $CsC_{24}(C_2H_4)_n$ and $CsC_{24}(C_2H_3CN)_n$ have been already reported in our previous works [3,5]. All these samples were confirmed to be stable at least under vacuum at room temperature. The XRD measurements were made periodically after exposure to air, and it was found that they have ternary stage 2 structure with I_C = 1.00 ± 0.02 nm. This structure was considerably stable showing nearly the same XRD patterns even after a year. Their electric conductivity, however, more or less decreased with time.

Raman Spectra

Raman spectra of $CsC_{24}(C_2H_4)_{1.4}$, $CsC_{24}(C_2H_4)_{0.6}$ and $CsC_{24}(C_2H_3CN)_{1.2}$ are shown in Fig.1 together with that of the pristine Grafoil. All spectra of these ternary compounds show the band with a peak at (1605 ± 1) cm^{-1} corresponding to the bounding graphite layer (adjacent to the intercalant layer) [6]. These results correspond reasonably to that of XRD, i.e., the main structure of these ternary compounds is stage 2 with I_C = 1.00±0.02 nm. Thus, the stage 2 structure is at least retained in these ternary compounds even after the exposure to air for a long time.

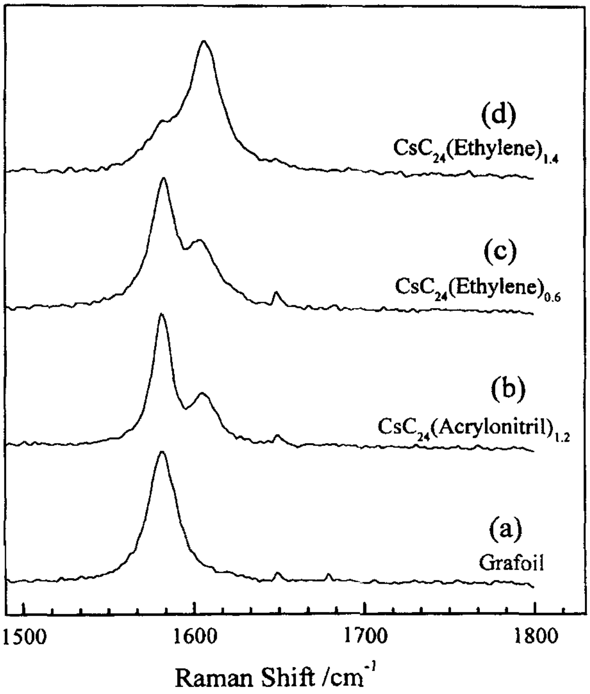

FIGURE 1 Raman spectra at room temperature of (a)Grafoil, (b)$CsC_{24}(C_2H_3CN)_{1.2}$, (c)$CsC_{24}(C_2H_4)_{0.6}$ and (d)$CsC_{24}(C_2H_4)_{1.4}$.

It should be noted, however, that there is significant difference among these spectra ; the spectra of $CsC_{24}(C_2H_4)_{1.4}$ show almost a single peak at 1606cm^{-1} corresponding to bounding graphite layer, and this single band is also observed in the spectra of the sample after the heat treatment up to 120℃ in air. On the other hand, those of $CsC_{24}(C_2H_4)_{0.6}$ and $CsC_{24}(C_2H_3CN)_{1.2}$ show intense band with a peak at 1582cm^{-1} corresponding to the interior graphite layer (not adjacent to the intercalant layer) [6], in addition to the bounding layer peak. It is considered that the stage structure of the latter two compounds was partly disintegrated, and the samples might have the mixed structure of the stage 2 and higher stages, although XRD results indicate the retention of the only stage 2 structure.

The fact that the Raman shift, 1582cm^{-1}, is almost the same as that of pristine Grafoil, might indicate the partial decomposition of the sample to graphite. This observation is, however, in conflict with the XRD results. We consider that the degradation of the ternary compounds occurs from the periphery of the grains, especially at the upper surfaces of the specimen. The short optical skin depth of these compounds (~100 nm) [7] as compared with the thickness of the specimens (~500 μ m) must be taken into account.

Stability of Structure and Electric Conductivity

The change of electric conductivity with time, as shown in Fig.2, is reasonably explained with the present Raman scattering results. The electric conductivity of the stage 2 structure is higher than those of higher stages or that of pristine Grafoil [8] ; thus the sample of $CsC_{24}(C_2H_4)_{1.4}$, which essentially retained the stage 2 structure, exhibits the rather high electric conductivity for a long time. The gradual decomposition at the periphery of the other two samples caused the decrease of the total electric conductivity, although the average bulk structure indicated by XRD measurement retained stage 2 structure.

The difference between $CsC_{24}(C_2H_4)_{1.4}$ and $CsC_{24}(C_2H_4)_{0.6}$ can be explained as follows. The sample of $CsC_{24}(C_2H_4)_{1.4}$ contains much larger amount of C_2H_4 molecules than $CsC_{24}(C_2H_4)_{0.6}$. And in the former, rough calculation shows that the almost all nano-space in the interlayer of CsC_{24} is occupied, thus the oligomerized C_2H_4 network would be enough strong to retain the stability of the ternary compound.

In the case of $CsC_{24}(C_2H_3CN)$, the amount of absorbed acrylonitril (C_2H_3CN) seems to be nearly saturation. The ability of oligomerization of acrylonitril, however, is considered to be too high to be absorbed into interior of CsC_{24} : some parts of C_2H_3CN in the interior region would be fairly lower

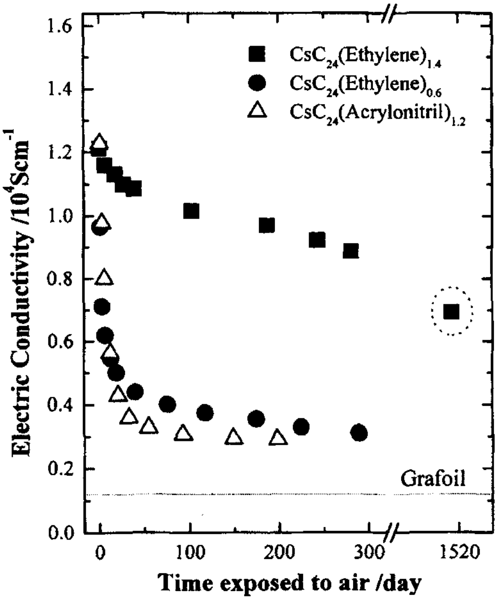

FIGURE 2 The time dependence of electric conductivity at 20℃ in air of (a)Grafoil, (b)$CsC_{24}(C_2H_3CN)_{1.2}$, (c)$CsC_{24}(C_2H_4)_{0.6}$ and (d)$CsC_{24}(C_2H_4)_{1.4}$.

than 1.2. Thus the network of C_2H_3CN molecules would be incomplete in this case also.

CONCLUSIONS

Raman scattering measurements on the ternary GIC, $CsC_{24}(C_2H_4)_{1.4}$ proved that the stage 2 structure had been retained in this compound even after the exposure to air for 38 months, corresponding to its high stability in electric conductivity.

The samples of $CsC_{24}(C_2H_4)_{0.6}$ and $CsC_{24}(C_2H_3CN)_{1.2}$ showed, on the other hand, some degradation of the stage 2 structure, in conflict to the XRD observations. It is suggested that these compounds formed incomplete network of oligomelized organic molecules as compared with that of $CsC_{24}(C_2H_4)_{1.4}$ and gradual decomposition from the periphery region of grains might occur, resulting the decrease of their electric conductivity.

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