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Short communication

Thermal decomposition of cesium-ethylene-ternary graphite intercalation compounds

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ABSTRACT

In this paper, the thermal decomposition of air-stable Cs-ethylene-ternary graphite intercalation compounds (GICs) is discussed. The air stability of Cs-GICs is improved remarkably after the absorption of ethylene into their interlayer nanospace, because the ethylene molecules oligomerize and block the movement of Cs atoms. In addition, the evaporation of Cs atoms from the Cs-ethylene-ternary GICs is observed above 400 °C under a N_2 atmosphere of 100 Pa by ion attachment mass spectrometry. Although the results indicate that Cs-ethylene-ternary GICs remain stable up to approximately 400 °C, their thermal stability is not very high as compared to that of Cs-GICs.

1. Introduction

Graphite intercalation compounds (GICs) are graphite derivatives that contain other chemical species (intercalates) in their interlayer spaces. More than 100 intercalate species such as alkali metals, halogens, and metal chlorides have been found thus far. As charge transfer occurs between graphite planes and intercalates, the in-plane electrical conductivity of GICs becomes approximately 10 times higher than that of the host graphite. However, because GICs are generally unstable and tend to decompose easily in air, their practical application (e.g., as light conductive materials) is difficult.

We have studied Cs-graphite intercalation compounds (Cs-GICs) in order to obtain air-stable GICs. Cs-GICs are one of the most unstable GICs. When Cs-GICs are exposed to air, Cs atoms are easily released from the graphite interlayer. On the other hand, Cs-ethylene-ternary GICs, which are synthesized by the absorption of ethylene into the interlayer nanospace of Cs-GICs (Fig. 1), are relatively stable in air [1–4]. The high stability of Cs-ethylene-ternary GICs is considered to be a result of oligomerization of ethylene molecules in the interlayer nanospace of the Cs-GICs; the resulting ethylene oligomers block the movement of the Cs atoms and hold them in the graphite interlayer. In a previous study, using TG/GC–MS, we successfully demonstrated that ethylene oligomers were released from Cs-ethylene-ternary GICs and confirmed their formation in the interlayer nanospace of the Cs-GICs [5].

We believe that one of the promising applications of GICs is its use as a thermoelectric conversion material [6,7]. A thermoelectric conversion system must possess thermal stability in addition to air stability. However, thus far, methods to confirm the decomposition point of Cs-ethylene-ternary GICs, that is, the point at which Cs atoms are released, have not been developed.

In this study, we showed that ethylene absorption led to a considerable improvement in the stability of Cs-GICs in air. Further, we investigated the thermal stability of Cs-ethylene-ternary GICs. By carrying out ion attachment mass spectrometry (IAMS) analysis [8], we observed that Cs atoms were released from the Cs-ethylene-ternary GICs.

2. Experimental

Exfoliated graphite sheets (GRAFOIL, Ucar Carbon Company Inc.) manufactured from natural graphite and well-oriented pyrolytic graphite sheets (PGS, Panasonic Co.) were used as the host graphite materials. Prior to use, the GRAFOIL sheets were heat treated at 900 °C under vacuum. Cs-GICs were prepared by allowing the graphite to react with Cs vapor at around 200 °C under vacuum (two-bulb method); the composition of the GICs was CsC_{24}. Ethylene (C_2H_4) was then absorbed into the vacant space (nanospace) in the interlayer of CsC_{24} at around room temperature; this resulted in the formation of Cs-ethylene-ternary GICs having the composition $CsC_{24}(C_2H_4)_{1.0–1.1}$.

A microscopic Raman spectrometer, Renishaw Raman Microscope System 2000, was used with 632.8 nm He–Ne laser line, which focused the incident laser beam to a 20 μm diameter spot on the surface of samples.

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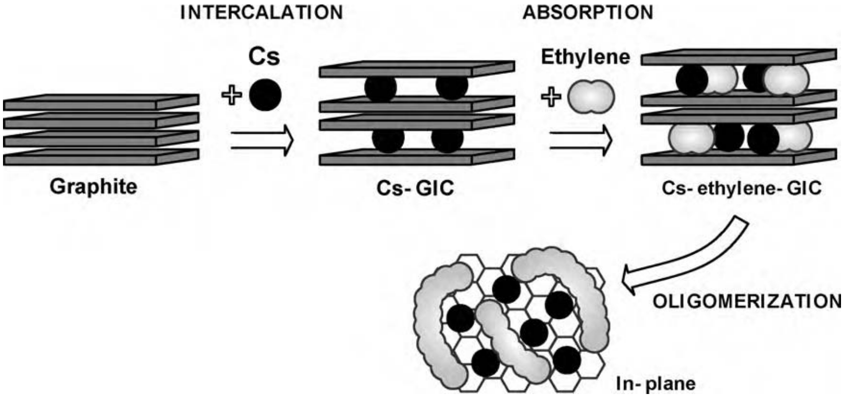

Fig. 1. Formation of Cs-ethylene-ternary GICs and oligomerization of ethylene molecules.

Ion attachment mass spectrometer (IAMS) was performed by Canon ANELVA Technix Co. Measurements were performed in a N_2 atmosphere of 100 Pa at a heating rate of 10 °C/min and at temperatures ranging from room temperature to 500 °C. Approximately 1.5 mg of sample was used, and the m/z values ranged from 5 to 410. In IAMS analysis, a gas molecule is ionized by attaching it to an alkali metal ion (Li^+).

3. Results and discussion

3.1. Stabilization of Cs-GICs by ethylene absorption

Fig. 2 shows Raman spectra of CsC_{24} and $CsC_{24}(C_2H_4)_{1.1}$ prepared using the GRAFOIL sheets after exposure to air for a week. The spectra of these two samples showed two major bands. The band with a peak at around 1580 cm^{-1} is termed the G band. This band could be attributed to the interior graphite layers (Fig. 3) that were not adjacent to the intercalate layers. On the other hand, the band with a peak at around 1600 cm^{-1} could be attributed to the bounding graphite layers that were adjacent to the intercalate layers, and this band is termed as the G′ band [9,10]. The appearance of the G′ band confirmed the existence of intercalates in the graphite interlayer.

In the case of CsC_{24}, the G band (1582 cm^{-1}) was the primary band and the G′ band (1608 cm^{-1}) was the secondary band. This observation indicates that the CsC_{24} sample decomposed in air; in other words, majority of the Cs atoms were released from the graphite interlayer. The band with a peak at 1649 cm^{-1} could not be identified. It is clear that the decomposition of the sample strongly affected its Raman spectrum, because Raman spectroscopy is a surface analysis technique [2]. However, the Raman spectrum of $CsC_{24}(C_2H_4)_{1.1}$ showed only the G′ band (1604 cm^{-1}); this indicates that the structure of the GIC was retained in the $CsC_{24}(C_2H_4)_{1.1}$ sample. In other words, most of the Cs atoms remained in the graphite interlayer.

The remarkable air stability of the Cs-ethylene-ternary GICs was proved to be attributable to the oligomerization of ethylene molecules in the interlayer nanospace of the Cs-GICs. The formation of ethylene molecules was confirmed by TG/GC–MS [5], and the oligomerization mechanism was elucidated by performing density functional theory calculations [11].

3.2. Thermal decomposition of Cs-ethylene-ternary GICs

Fig. 4 shows IAMS results for $CsC_{24}(C_2H_4)_{1.0}$ prepared using the PGS. The GICs prepared using PGS were suitable for this analysis because their decomposition was moderate as compared to that of the GICs prepared using GRAFOIL [12]. Moreover, although the IAMS analysis of $CsC_{24}(C_2H_4)_{1.0}$ was performed after exposure to air for 3 months, it was considered that the results were not affected because the air stability of $CsC_{24}(C_2H_4)_{1.0}$ was high, as mentioned in Section 3.1.

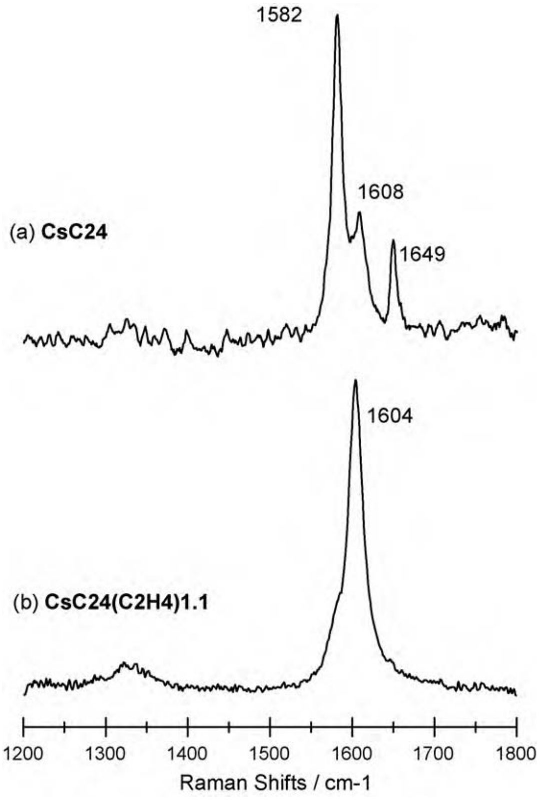

Fig. 2. Raman spectra of CsC_{24} and $CsC_{24}(C_2H_4)_{1.1}$ after exposure to air for 1 week.

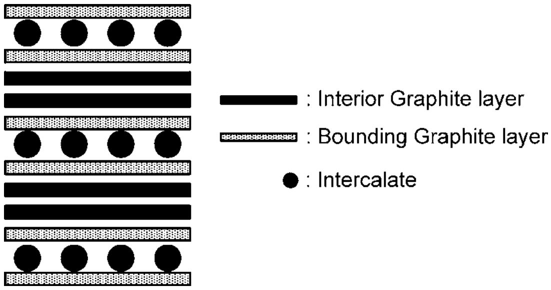

Fig. 3. Bounding and interior graphite layers in GICs.

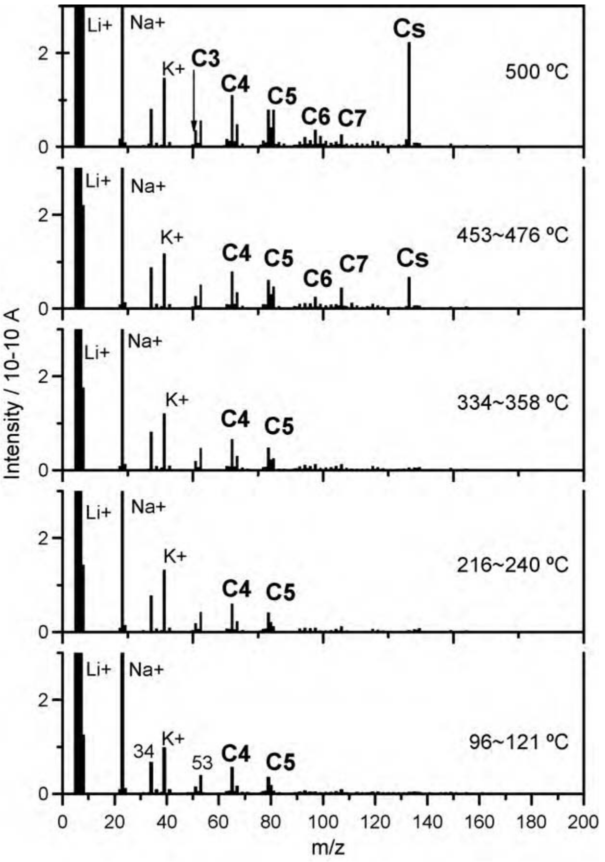

Fig. 4. IAMS results of $CsC_{24}(C_2H_4)_{1.0}$.

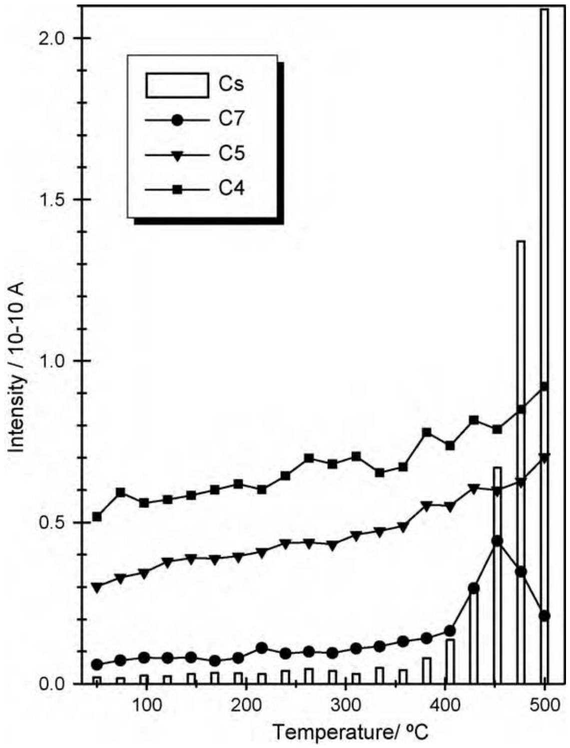

Fig. 5. Temperature dependence of release of gas from $CsC_{24}(C_2H_4)_{1.0}$.

At temperatures below 350 °C, almost only small *n*-alkanes C4 and C5 were detected at $m/z = 65$ and 79, respectively. At $m/z = 51$, a complex of C_3H_8 (m.w. = 44) and Li^+ (m.w. = 7) was obtained. These *n*-alkanes were formed by the oligomerization of ethylene molecules or the thermal decomposition of large oligomers. In previous work [5], we confirmed the presence of ethylene oligomers up to C20.

Above 450 °C, large *n*-alkanes, C6 ($m/z = 93$) and C7 ($m/z = 107$), and Cs^+ ($m/z = 133$) were detected. Li^+, Na^+, and K^+ ions were added to the system to ionize the gas molecules. The peaks at $m/z = 34$ and 53 could not be identified. The formation of Cs^+ could be attributed to two factors; however, these factors have not yet been clarified. One possible factor may have been the ionization of the Cs atoms caused by a Li^+ attack. The other factor may have been the direct evaporation of Cs^+ formed by the charge transfer between intercalated Cs atoms and graphite planes. Because metal atoms can be detected by IAMS, it was used for the investigation of the Cs-GICs.

Fig. 5 shows the temperature dependence of the amount of evaporated Cs atoms and released *n*-alkanes C4, C5, and C7 in the IAMS analysis. The release of small *n*-alkanes C4 and C5 was observed across the entire temperature range, and the amount of release increased gradually with the temperature. The amount of C4 was the largest among the released *n*-alkanes. This observation was consistent with the results of a previous TG/GC–MS analysis [5]. The amount of evaporated Cs atoms increased considerably at around 400 °C. It was observed that the evaporation of Cs atoms accelerated as the blocking effect of the ethylene oligomers subsided.

We briefly investigated the thermal decomposition of CsC_{24}. After the CsC_{24} sample was synthesized under vacuum at around 10 Pa, a piece of PGS was added to the reaction tube under an Ar atmosphere. Then, the reaction tube was evacuated again until around 10 Pa. The CsC_{24} sample was bright blue as a result of the charge transfer between the Cs atoms and the graphite planes. When the reaction tube was heated, the color changed slightly at around 400 °C; the blue color of CsC_{24} faded only slightly and the PGS piece became very pale blue in color. This observation suggests that the Cs atoms were not released from the interlayer of the Cs-GICs (CsC_{24}) up to 400 °C; almost same result was obtained for the Cs-ethylene-ternary GICs. It is considered that the absorption of ethylene into the Cs-GICs (CsC_{24}) was effective in improving their air stability; however, it was not very effective in improving their thermal stability.

During the TG measurements, weight loss was observed in $CsC_{24}(C_2H_4)_{1.0}$ prepared using PGS under a N_2 flow [5]. This weight loss was found to be 12% between 700 and 900 °C, and it could be partly attributed to the evaporation of the Cs atoms. The amount of weight loss of $CsC_{24}(C_2H_4)_{1.0}$ corresponded to evaporation of 40% of the Cs atoms from $CsC_{24}(C_2H_4)_{1.0}$. The difference in the evaporating temperatures observed during IAMS (under the N_2 atmosphere of 100 Pa) and TG (under the N_2 flow) measurements could be attributed to the difference in the atmospheres under which these measurements were performed.

4. Conclusions

In this study, we confirmed that ethylene absorption is an effective method for improving the air stability of Cs-GICs. Further, by carrying out IAMS analysis, we measured the amount of Cs atoms (Cs^+) evaporated from Cs-ethylene-ternary GICs at temperatures above 400 °C under a N_2 atmosphere of 100 Pa. For the first time, we were able to directly observe the evaporation of Cs atoms from the Cs-ethylene-ternary GICs. Although these results indicate that the Cs-ethylene-ternary GICs were stable at temperatures up to 400 °C under 100 Pa, their thermal stability was not very high as compared to that of Cs-GICs. We concluded that absorption of ethylene into the Cs-GICs (CsC_{24}) was effective in improving their air stability; however, it was not very effective in improving their thermal stability.

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