

Alkali-metal-graphite intercalation compounds prepared from flexible graphite sheets exhibiting high air stability and electrical conductivity

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ABSTRACT

The practical use of graphite intercalation compounds (GICs) as industrial materials has been considered to be unfeasible because their air stability is fairly low, notwithstanding their high electrical conductivities and low densities. On the other hand, some air-stable GICs that exhibit p-type conduction have been reported. In this study, air-stable and electrically conductive GICs that exhibited n-type conduction were prepared from commercially available flexible graphite sheets (PGS graphite sheets). We observed that K-GIC and Cs-GIC were air-stable enough to be used in practical applications and were highly electrically conductive. The air stability of Cs-GIC was slightly higher than that of K-GIC. In addition, the stage-2 structure of Cs-GIC was more stable in that it maintained ten times higher electrical conductivity than that of the host graphite after 10 years of exposure to air. Moreover, Cs-ethylene-GIC was the most stable and exhibited a blue colored surface after 10 years of exposure to air. We assumed that the significantly improved air stability of the alkali-metal-GICs prepared from PGS graphite sheets is caused by the large crystalline size and the bending graphite layer structure of the host PGS graphite.

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1. Introduction

Graphite intercalation compounds (GICs) are formed by intercalating chemical species into graphite interlayers. The guest species are called “intercalates”. Alkali metals, alkali earth metals, halogens, and metal chlorides, among other species have been used as intercalates. Since charge transfer occurs between the intercalated species and the adjacent graphite layers (graphenes), the in-plane electrical conductivities of GICs become greater than that of the host graphite.

GICs can potentially be used in many different applications on the basis of the intercalation reaction and the interesting physical properties of GICs. At present, GICs are used in industries as electrode materials in Li ion secondary batteries and for manufacturing exfoliated graphite, applications that are based on the intercalation reaction. There have been expectations that GICs could be used in practical applications as highly electrically conductive and lightweight materials [1]. However, their practical use as functional materials has not been realized yet because of several limitations, the most serious among them being that they are normally instable in air.

Researchers have found, however, that this environmental instability can be overcome by an appropriate host graphite material and intercalates. For example, metal-chloride-GICs such as CuCl_2 -GIC [2,3] and MoCl_5 -GIC [4], as well as bromine residue compounds that are prepared through the de-intercalation of Br_2 from Br_2 -GIC [5,6], are well known as air-stable GICs and have been investigated in detail. However, these air-stable GICs exhibit p-type conduction; very little is known about air-stable n-type GICs [7–9]. Alkali-metal-GICs and alkali-earth-metal-GICs comprise the majority of n-type GICs, and some ternary-GICs can be formed by co-intercalation, such as Na-Hg-GIC [10] and K-NH₃-GIC [8]. Alkali-metal-GICs, which are representative of n-type GICs, are very sensitive to moisture in the air and decompose immediately upon exposure to ambient air.

It is well known that the characteristics of GICs are strongly affected by those of the host graphite, in particular their air stability. It has been reported that the air stability of GICs prepared from natural graphite flakes with relatively large diameters is much greater than that of GICs prepared from smaller flakes [4]. In addition, although some graphite films that are synthesized by pyrolysis of aromatic polymers are suitable for preparing air-stable GICs, it was primarily p-type GICs that were investigated in these studies [11,12]. A patent currently exists on the preparation of air-stable n-type GICs from graphite films synthesized by pyrolysis of polyphenylene oxadiazole (POD), but details on this process have not been provided [13]. It is known that the decomposition rate of GICs is fairly low. Therefore, the large grain size or crystalline size

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of the host graphite such as graphite films should improve the stability of the resulting GIC. The air stability of GICs is also possibly affected by the size of the host graphite and the stage index (the intercalate concentration, mentioned below) of the initial structure, as well as by the characteristics of the host graphite and the choice of intercalates.

In order to expand the potential practical application of GICs, we have been investigating on how to create novel n-type GICs that exhibit high electrical conductivity and air stabilities. For example, for thermoelectric device applications, both n-type and p-type GICs are necessary [14,15]. We found that the co-intercalation of ethylene into Cs-GIC prepared from natural graphite powder or exfoliated graphite sheets improves its air-stability [9,16,17]. In particular, for Cs-ethylene-GICs that contain large amounts of ethylene, the composition $\text{CsC}_{24}(\text{C}_2\text{H}_4)_x$ ($x > 1.0$) exhibited relatively high air stability in addition to high electrical conductivity.

In this study, we succeeded in creating more highly air-stable n-type GICs that exhibited high electrical conductivities by using commercially available flexible graphite sheets manufactured by pyrolyzing polyimide film, as the host graphite. Herein, we show the significantly high air stability and electrical conductivity of these n-type GICs and discuss the origin of the stability.

2. Experimental

Commercially available PGS (EYGS, Panasonic Co.) were used as the host graphite [18,19]. Grafoil (GTA grade, Graf Tech Co.) and HOPG (SPI-1 grade, SPI SUPPLIES Inc.) were also used for making comparisons. Grafoil is manufactured by expanding and compressing pure natural graphite flakes. The host graphite sheets were cut into strips that were 2–10 mm wide and 5–40 mm long. The thicknesses were 0.1 mm for PGS and Grafoil and 0.2 mm for HOPG. Grafoil was used after evaporating the impurities in it at 1173 K for 4 h. PGS and HOPG were used without further purification.

GIC specimens were synthesized by the vapor method. The alkali metals, Li (>99.9% purity), K (99.95%), and Cs (99.95%) were also used without further purification. One at a time, the alkali metals were put into a reaction tube with the graphite strips under an Ar atmosphere. The reaction tube was made of Pyrex glass or stainless steel. After evacuating, the tubes were sealed and heated to 723 K for Li, and to 473 K for K and Cs. The reaction end points were confirmed by the colors of the specimens.

The characteristics of GICs are described by the term “stage,” which refers to the number of graphite layers that lay between adjacent intercalated layers. Generally, a higher-stage structure gradually changes to a lower-stage structure during the intercalation process, finally resulting in a saturated stage-1 structure. The composition of each stage for the alkali-metal-GICs is known. In the case of heavy-alkali-metal-GICs (K-GIC and Cs-GIC), for example, stage-1 is KC_8 , stage-2 is KC_{24} , stage-3 is KC_{36} , and so on. In the case of Li-GIC, stage-1 is LiC_6 and stage-2 is LiC_{12} or LiC_{18} . Although the stage structures can be identified exactly by the lattice constants along the *c*-axis (called the identity period, I_c) obtained by X-ray diffraction (XRD) analysis, in the case of heavy-alkali-metal-GICs, they can also be confirmed roughly by the specimen color: gold for stage-1 and blue for stage-2; the colors for higher stages gradually become darker.

Cs-ethylene-GIC was prepared by the absorption of ethylene into stage-2 Cs-GIC (CsC_{24}) at approximately room temperature. Ethylene gas was introduced into a vacuum in a reaction tube containing the CsC_{24} specimens and the amount of absorbed ethylene was measured by the change in pressure in the reaction tube. Stage-2, stage-3, and stage-4 K-GICs (KC_{24} , KC_{36} , and KC_{48} , respectively) were prepared by fractional thermal decomposition (the partial de-intercalation of K atoms) of the stage-1 GIC in a vacuum.

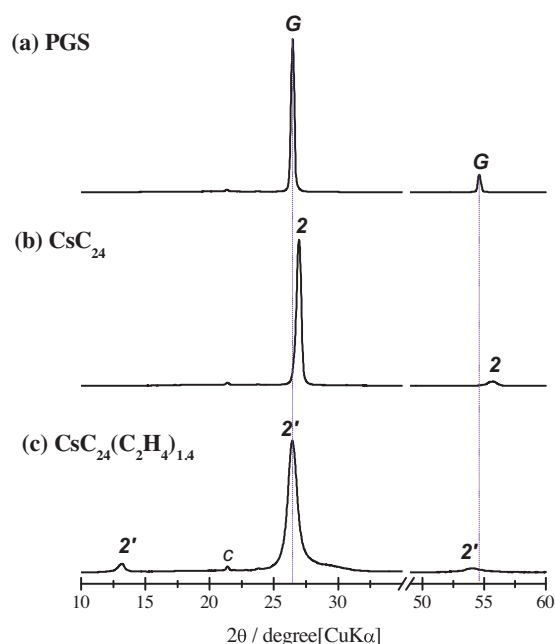


Fig. 1. XRD patterns after three years in air of CsC_{24} , and $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ prepared from PGS. **2**: CsC_{24} ($I_c = 0.99$ nm); **2'**: $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ ($I_c = 1.1$ nm); **G**: graphite ($I_c = 0.67$ nm); **C**: compound for mounting sample.

XRD patterns were obtained by using Cu $K\alpha$ X-rays and the in-plane electrical conductivities were determined by the four-terminal method at room temperature at regular intervals after the GIC specimens had come into contact with air in order to observe their decomposition behavior. The specimens were held in a desiccator (relative humidity: 20–30%, temperature: 293–298 K) in air.

3. Results and discussion

3.1. Significantly high air stability of CsC_{24} and $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ prepared from PGS

The XRD patterns after three years of exposure to air of the stage-2 Cs-GIC (CsC_{24}) and Cs-ethylene-GIC ($\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$) prepared from PGS are shown in Fig. 1, along with the XRD pattern for the host PGS for comparison. These two GIC specimens retained their stage-2 structures, which were almost the same as their initial structures. The most notable aspect of the present results is that the blue surface color of the $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ specimen could be seen with the naked eye. Usually, even for relatively stable GICs, the color of the specimen surface disappears immediately after it comes into contact with air and becomes dark. The retention of the surface color therefore indicates the significantly improved air stability of the GIC specimen that was formed.

Furthermore, after 10 years of exposure to air, the $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ specimen still exhibited a blue color, as shown in Fig. 2, meaning that the specimen retained a substantial amount of its stage-2 structure. The electrical conductivities of the CsC_{24} and $\text{CsC}_{24}(\text{C}_2\text{H}_4)_{1.4}$ specimens are shown in Table 1. It must be noted that for both of the specimens the electrical conductivities were around $5 \times 10^4 \text{ Scm}^{-1}$ and were about ten times higher than that of the host PGS ($4.5 \times 10^3 \text{ Scm}^{-1}$), even after 10 years of exposure to air.

In the case of the $\text{CsC}_{24}(\text{C}_2\text{H}_4)_x$ specimens that were prepared from Grafoil, the stage-2 structure was also retained during contact with air for long periods, judging from the XRD analysis results. However, the electrical conductivities decreased to 50–70% of their initial values, which were four to eight times higher than that

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