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Highly electrically conductive and air-stable metal chloride ternary graphite intercalation compounds with $AlCl_3$-$FeCl_3$ and $AlCl_3$-$CuCl_2$ prepared from flexible graphite sheets

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ABSTRACT

Ternary graphite intercalation compounds (GICs) incorporating two kinds of metal chlorides, namely, $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC, were synthesized from two types of graphite sheets, PGS and GRAFOIL. Their electrical conductivities and air-stabilities were evaluated in an attempt to identify highly electrically conductive and air-stable GICs. Their electrical conductivities were found to be higher than those of binary GICs such as $FeCl_3$- and $CuCl_2$-GICs. Especially, the $AlCl_3$-$CuCl_2$-GIC prepared from a PGS graphite sheet was found to have a high conductivity and high air-stability; the highest electrical conductivity was in excess of $1.0 \times 10^5\ Scm^{-1}$. Most $AlCl_3$-$CuCl_2$-GICs have a mixed structure of $AlCl_3$-$CuCl_2$-ternary GIC domains and/or $AlCl_3$-GIC domains. The proportion of each domain was dependent on the reaction time and the type of the host graphite. $AlCl_3$-$FeCl_3$-GICs prepared from PGS were found to consist only of $FeCl_3$-GICs, and their electrical conductivity and air-stability were slightly inferior to those of $AlCl_3$-$CuCl_2$-GICs. We concluded that an $AlCl_3$-$CuCl_2$-ternary GIC prepared from a PGS graphite sheet is highly electrically conductive and highly air-stable. Therefore, this is a promising candidate as a highly conductive and air-stable GIC for use in practical applications as a conducting material.

1. Introduction

Graphite intercalation compounds (GICs) have been investigated as a promising highly conductive material since the 1980s. GICs are synthesized by the intercalation of chemical species such as alkali metals, halogens, or metal chlorides with interlayers of host graphite. The in-plane electrical conductivity of GICs is higher than that of the host graphite because of the charge transfer between the intercalated species and the graphene planes. Unfortunately, GICs are usually unstable and rapidly decompose in air [1]. Therefore, the practical application of GICs as a conducting material has not yet been realized. We have been investigating GICs with the ultimate goal of developing air-stable and highly electrically conductive GICs [2–6].

In our previous report [2], we precisely compared four metal chloride GICs, namely, $FeCl_3$-, $CuCl_2$-, $MoCl_5$-, and $SbCl_5$-GICs, prepared from two types of graphite sheet (GRAFOIL® and PGS®), in terms of their air-stability and electrical conductivity. We found that the $CuCl_2$-GICs prepared from GRAFOIL ($CuCl_2$-GRAFOIL, herein), $CuCl_2$-PGS, and $MoCl_5$-PGS were highly air-stable. Moreover, $MoCl_5$-PGS was also highly electrically conductive. These four GICs have become the most popular metal chloride GICs because they can be prepared relatively easily. The characteristics of GICs are strongly affected by those of their host graphite. For example, in general, the electrical conductivities of GICs are approximately 10 times greater than that of the host graphite [1]. The air-stability of GICs is seen to be dependent on the structure and size of the host graphite crystalline structure [3–6]. Therefore, we investigated the effect on the air-stability of GICs of two different types of commercially available flexible graphite sheets. GRAFOIL sheets are manufactured by chemically treating natural graphite powder such that its volume increases 80-fold, relative to the raw material. On the other hand, PGS sheets are manufactured by the pyrolysis of polyimide films such that they have more highly oriented graphite relative to GRAFOIL [12–14]. Furthermore, the electrical conductivity of PGS is higher than that of GRAFOIL [2–6,10].

In this study, two types of metal chloride ternary GICs, $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC, were investigated with the goal of identifying GICs that are more electrically conductive and

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air-stable than $MoCl_5$-PGS. Ternary GICs are so called because they have two different intercalate materials in their interlayer, while GICs with only one intercalate, such as $FeCl_3$-GICs, are called binary GICs. Ternary GICs are classified into two structural types, that is, mixed and bi-intercalation types. In the mixed type, the two kinds of intercalated materials are stored in the same interlayer, while in the bi-intercalation type, the two materials are stored in different interlayers. The $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC that were prepared in this study were mixed-type GICs [11]. It should be possible to develop ternary GICs with excellent properties, given the extremely large number of possible combinations of intercalate materials and structures. Therefore, ternary GICs, especially ternary metal chloride GICs, have been the subject of considerable research [11,12].

Although many other binary metal chloride GICs are known besides $FeCl_3$-, $CuCl_2$-, $MoCl_5$-, and $SbCl_5$-GIC, we decided to investigate these ternary GICs. Our decision was based on the fact that these ternary GICs can be easily synthesized, as are $FeCl_3$-, $CuCl_2$-, $MoCl_5$-, and $SbCl_5$-GICs, with only metal chlorides, while the formation of the other binary GICs requires the addition of Cl_2 gas. Furthermore, although the formation of $FeCl_3$-GIC and $CuCl_2$-GIC requires that the temperature be maintained at 300 °C for 3 days and 480 °C for 45 days, respectively [2], $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC can be prepared at 150 °C in 1 h [11]. This easy preparation is a major advantage for practical applications.

Inagaki and Ohira investigated the formation process and reaction product in detail [11–14]. These ternary GICs form gaseous complexes such as $FeAlC_6$ and $CuAl_2Cl_6$. The reaction products consist of $AlCl_3$-GIC, $FeCl_3$-GIC, and $AlCl_3$-$FeCl_3$-GIC, or $AlCl_3$-GIC, $CuCl_2$-GIC, and $AlCl_3$-$CuCl_2$-GIC. It was thought that the gaseous complexes and $AlCl_3$ vapor first intercalate and form the stage-1 structure of the $AlCl_3$-$FeCl_3$-ternary GIC or $AlCl_3$-$CuCl_2$-ternary GIC, and then split to give the $AlCl_3$-GIC domain and $FeCl_3$ or $CuCl_2$-GIC domain [11,12].

The electrical properties of these ternary GICs have seldom been reported. Therefore, the electrical conductivity and air-stability of $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC prepared from flexible PGS and GRAFOIL sheets were evaluated. In this paper, we introduce highly electrically conductive and air-stable GICs prepared from PGS.

2. Materials and methods

As host graphite materials, PGS (Panasonic Co.; EYGS 182310; 0.1-mm thickness) and GRAFOIL (UCAR Co.; GTA grade; 0.3-mm thickness) were used. These are commercially available flexible graphite sheets. The GRAFOIL was purified at 900 °C in a vacuum before use, as it tends to carry some sulfur residue left over from the manufacturing process. Each of these sheets was cut into 3 mm × 20 mm strips. Anhydrous metal chlorides, that is, $FeCl_3$ (> 95.0% purity), $CuCl_2$ (98%), and $AlCl_3$ (99.9%) were used without any further purification.

First, graphite strips and two metal chloride powders were combined under Ar in a glass tube with a diameter of 6 mm, which was evacuated down to a pressure of around 10 Pa and then sealed off at a length of 11 cm. The molar ratio of graphite: $AlCl_3$:$FeCl_3$ or $CuCl_2$ was 3:1:1; the weight of PGS was approximately 0.05 g while that of the metal chlorides was 0.2 g. The weight of the GRAFOIL was approximately 0.1 g and that of the metal chloride was 0.4 g. Then, the reaction tubes were heated in an electric furnace to 150 °C. The reaction times were set to 1 or 3 days for the $AlCl_3$-$FeCl_3$-GICs and 10 min to 20 days for the $AlCl_3$-$CuCl_2$-GICs. The reaction conditions were adopted from previous studies [11].

After the specimens had been exposed to air, measurements of the in-plane electrical conductivity and X-ray diffraction (XRD) were performed repeatedly. We heated three reaction tubes simultaneously in the same electric furnace. Then, we measured the electrical conductivities and XRD patterns for three specimens extracted from each of the three reaction tubes. For the measurements of the air-stability, we stored all the measuring samples under the same conditions.

The four-terminal method was employed to measure the in-plane electrical conductivities at room temperature, while XRD with CuKα X-ray radiation (RIGAKU, RINT2000) was used to determine the structure. The electrical conductivity measurements were performed on three independently synthesized specimens of each GIC under the same reaction conditions to confirm their reproducibility. The air-stability of the GICs was assessed by repeating the measurements over time, using specimens set in the measurement holder and stored under stable ambient conditions (at a temperature of around 20 °C, and around 40% RH).

The electrical conductivities and the structures of these ternary GICs were observed after exposure to air over time in the same manner and under the same conditions in order to make a comparison with the results previously obtained for the four binary GICs and the two ternary GICs addressed in the present study [2].

Hereafter, the GICs prepared from PGS and GRAFOIL will be referred to as $AlCl_3$-I-PGS and $AlCl_3$-I-GRAFOIL (I = $FeCl_3$ or $CuCl_2$), respectively.

3. Results and discussion

3.1. Electrical conductivities

The electrical conductivities of the $AlCl_3$-$FeCl_3$-GIC and $AlCl_3$-$CuCl_2$-GIC, prepared from PGS and GRAFOIL, and immediately after exposure to air, are listed in Table 1. These values are higher than those for binary GICs such as the $FeCl_3$-GIC, $CuCl_2$-GIC, $MoCl_5$-GIC, and $SbCl_5$-GIC investigated in our previous work [2]. In our previous study, the highest value that we obtained was 6.1×10^4 Scm^{-1} for $MoCl_5$-PGS. However, in the present study, the highest value obtained was 7.0×10^4 Scm^{-1} for $AlCl_3$-$CuCl_2$-PGS, which was 16 times higher than that of the host PGS. Even the lowest value

Table 1
Electrical conductivities of ternary GICs prepared from PGS and GRAFOIL.

	PGS			GRAFOIL		
	Reaction time	σ_{GIC}/Scm^{-1}	$\sigma_{GIC}/\sigma_{host}$	Reaction time	σ_{GIC}/Scm^{-1}	$\sigma_{GIC}/\sigma_{host}$
$AlCl_3$-$FeCl_3$-GIC	3 d	4.9×10^4	11	3 d	5.4×10^3	4.9
		4.2×10^4	9.3		4.6×10^3	4.2
		4.0×10^4	8.9		4.5×10^3	4.1
$AlCl_3$-$CuCl_2$-GIC	30 min.	7.0×10^4	16	12 h	6.1×10^3	5.5
		6.7×10^4	15		5.9×10^3	5.4
		4.3×10^4	9.6		4.6×10^3	4.2
Host Graphite	–	4.5×10^3	1.0	–	1.1×10^3	1.0