Applications of graphite intercalation compounds

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The properties of graphite intercalation compounds (GIC's) are discussed with respect to possible applications. Five families of intercalates give high electrical conductivity to GIC's: pentafluorides leading to high conductivity, 10^8 S/m (higher than metallic copper); metal chlorides; fluorine and alkali metals with bismuth giving relatively high conductivity of the order of 10^7 S/m plus stability in air; and residual halogens showing extremely high stability under severe conditions, though the conductivity is only of the order of 10^6 S/m. Electrodes of different GIC's have been tried in primary and secondary batteries, where their characteristics are high electrical conductivity and easy diffusion of electrochemically active species between the graphite layers. Primary lithium batteries of a covalent graphite fluoride are now widely used commercially. Secondary batteries using different host graphites and intercalates give interesting results. Large amounts of hydrogen can be stored in the functional space in alkali metal-GIC's. The same GIC's show high coefficients of isotope separation of hydrogen at liquid nitrogen temperature. The structure and texture of the host graphite play a decisive role in the absorption and separation behaviors of GIC's. Exfoliated graphite prepared by rapid heating of GIC's or their residue compounds leads to flexible graphite sheets which have great industrial applications. Some problems connected with the production and use of these sheets are discussed.

I. INTRODUCTION

With respect to their applications, the functionality of graphite intercalation compounds (GIC's) may be divided into five categories,[1] as summarized in Table I with representative intercalates and the main origin of each function.[2] In order to get high electrical conductivity of GIC's, the combination between host graphite and intercalate has to be selected properly, as will be discussed later. Even if electrochemical and catalytic activities, on the other hand, are mostly due to the functionality of intercalates themselves, their efficiency and selectivity are often enhanced by their intercalation into graphite.[3] Absorption of hydrogen gas occurs in the space between graphite layer planes and intercalated alkali metals, which area can be called functional space. The other functions mentioned in Table I chiefly involve intercalation and deintercalation processes.

The history of GIC's dates back to 1841, when the first paper on H_2SO_4–GIC's was published. The history may be divided into three periods: before 1974, from 1974 to 1987, and after 1987. Table II gives a very incomplete list of some important dates and topics in the history of GIC's. I apologize for a number of important topics and reports that are omitted from the table in order to simplify the long history.

A lithium primary battery using a covalent graphite compound, graphite fluoride, was commercialized in 1974 and high electrical conductivity of SbF_5–GIC, higher than

TABLE I. Functions of graphite intercalation compounds with respect to their applications.

1. Highly conductive materials	
HNO_3, SbF_5, AsF_5, $CuCl_2$, $FeCl_3$, F_2, K–Bi, residual Br_2	Combinations between host graphite and intercalates
2. Electrode materials in batteries	
Primary battery	
$(CF)_n$, $(C_2F)_n$, graphite oxide, F_2, $CoCl_2$, TiF_4, etc.	Efficiency enhancement of function of intercalates
Secondary battery	
H_2SO_4, $Ni(OH)_2$, $Mn(OH)_2$, HF	
Thermocell	Intercalation and deintercalation processes
Br_2, HNO_3	
3. Catalyzers for organic synthesis	
Li, K, K–Hg, K–$FeCl_3$, SbF_5, Br_2, H_2SO_4, HNO_3, etc.	Efficiency enhancement of function of intercalates
4. Materials for storage and isotope-separation of hydrogen	
K, Cs, Rb	Creation of functional space in intercalation compounds
5. Others	
Exfoliation of graphite	
H_2SO_4, HNO_3, $FeCl_3$, K–THF, Na–THF	Intercalation and deintercalation processes
Thermal energy storage	
$MnCl_2$–NH_3	
Electrochromic	
Li-dimethyl sulfoxide (DMSO)	

TABLE II. Short history of graphite intercalation compounds.

Year	Topics	Period
1841	H_2SO_4–GIC (Schafhautl)	First period: new GIC's
1859	Graphite oxide (Brodie)	
1926	K–GIC (Cadenbach)	
1930	Graphite fluorides (Ruff, Keim)	
1932	$FeCl_3$–GIC (Thiele)	
1933	Br_2–GIC (Frenzel)	
1954	Ternary M–NH_3–GIC's (Rüdorff, Schulze)	
1965	K–H–GIC (Saeher)	
1969	Daumas-Hérold model (Daumas)	
1971	Hydrogen absorption by alkali-metal-GIC's (Tamaru)	
1972	High conductivity of GIC's (Ubbelohde)	
1974	Li/$(CF)_n$ primary battery (Fukuda)	Second period: new physics and engineering
1976	High conductivity of MF_5–GIC's (Vogel)	
1980	Phase diagram for alkali metal-GIC's (Safran) Intercalation of amalgams (Hérold, El Makrini)	
1981	$Ni(OH)_2$–GIC secondary cell (Flandrois) Ionic fluorine-GIC's (Nakajima)	
1982	High conductivity of metal chlorides-GIC's (Oshima, Chieu)	
1983	Verification of high conductivity of AsF_5–GIC (Murakami)	
1985	Bi-intercalation (Furdin, Hérold)	
1987	Metal chloride-GIC's by molten salts (Inagaki)	Third period: applications

metallic copper, was reported in 1976. Prior to 1974, i.e., in the first period, research on GIC's was centered mostly on the synthesis of new compounds and the study of fundamental processes involved in intercalation. However, the commercialization of the lithium battery with graphite fluoride, coupled with the prospect of high conductivity of SbF_5– and AsF_5–GIC's, spurred both physicists and engineers: the former sought to elucidate problems associated with this unexpected high conductivity, while the latter tried to find new applications and ways to exploit the physical and chemical properties of GIC's. In the second period of GIC's history, there was remarkable progress in the physics of the GIC's theoretically and also experimentally, but practical applications, except for the development of the lithium battery with graphite fluoride and exfoliation of graphite, did not materialize, though a number of ideas and possibilities were suggested.

The discovery of high-temperature superconductive ceramics in 1987 created a new situation: GIC's seemed to lose their fascination for many scientists, and many of them switched to research on high T_c superconductors. Therefore, we are now in the third period of the history of GIC's, where the emphasis is directed toward the study of engineering and technological problems related to GIC's. Industrial interest in GIC's is rapidly increasing since the end of the second period of the history, particularly in Japan, as shown by Setton.[3] In view of the enormous volume of experimental data and knowledge already available, a substantial development of practical applications of various GIC's may be expected. Because GIC's are one of the candidates of new materials for advanced technology, more engineering and technological studies on GIC's must be done. It needs to be emphasized, however, that fundamental research is still essential to develop further the engineering and technology of GIC's.

In the present review, the functions of GIC's are discussed in relation to possible applications as highly conductive materials, electrodes in different batteries, materials for storage and isotope-separation of hydrogen, and other uses. Reviews on applications as catalysts for organic synthesis may be found in the literature.[4,5]

II. HIGHLY CONDUCTIVE MATERIALS

From the standpoint of applications, the intercalates which give high electrical conductivity to GIC's are principally of five families: pentafluorides, metal chlorides, fluorine, alkali metals with bismuth, and residual halogens. These families not only have high conductivity values, but they are also stable compounds, a technological necessity. The highest values of electrical conductivity for the five families of intercalates are summarized in Table III.

Pentafluorides, such as SbF_5 and AsF_5, can give very high room temperature electrical conductivity up to 10^8 S/m for GIC's,[6] much higher than metallic copper. In order to attain such high conductivity, the host graphite has to have very high crystallinity. Highly oriented pyrolytic graphite (HOPG) has been frequently used as the host, but has not always led to conductivity values as high as 10^8 S/m,[7] probably because of fluctuations in the crystallinity of HOPG samples. Vapor-grown carbon fibers (VGCF) and vapor-deposited carbon films heat-treated at temperatures higher than 3000 °C were successfully used as host graphite, resulting in conductivity as high as 10^8 S/m.[8,9]

The corrosive and poisonous nature of pentafluorides as well as the lack of air-stability of the compounds constitute serious obstacles to practical applications. Copper and teflon tubes were successfully used as protective sheaths.[6,10] Shioya *et al.*[8] pointed out that the conductivity of the AsF_5–GIC's prepared from graphitized VGCF was stabilized at a value around 10^7 S/m after exposure to air, and the sample remained for more than 2 years at the same value. For compounds based on vapor-deposited graphite films, the same stabilization effect was observed.[8]

Although the absolute values of the conductivity of GIC's with metal chlorides are not very high, they may yield creditable values comparable to that of copper,[11,12] when their low specific weight is taken into consideration. The data in the literature on the conductivity of metal chloride GIC's are plotted in Fig. 1 as a function of that of the host graphite material. In spite of a fairly large scatter, even by using the same intercalates, an increase of conductivity by a factor of 10 seems to be an average.

TABLE III. Highly conductive graphite intercalation compounds.

Material	Conductivity	Comments
Pentafluorides		
AsF_5/HOPG and VGCF	$1 \cdot 10^8$ S/m	Higher than metallic copper
Metal chlorides		
$CuCl_2$/MPCF $FeCl_3$/VGCF	$7.8 \cdot 10^6$ S/m $1.4 \cdot 10^7$ S/m	Creditable values, comparable with Cu
Fluorine		
F_2/HOPG and various CF's	$2 \cdot 10^7$ S/m	Stable in air
Donor couple		
K + Bi/HOPG	$2 \cdot 10^7$ S/m	Stable in air
Residue halogens		
Br_2 or ICl/MPCF's	$1 \cdot 10^6$ S/m	Very stable under severe conditions

The stability of these compounds under various circumstances has been studied by different authors. Flandrois *et al.*[13] reported high stability of $NiCl_2$–GIC's in air and also in a number of organic solvents, and Inagaki *et al.*[14] pointed out that no decomposition was detected in the x-ray powder pattern of $NiCl_2$–$FeCl_3$–GIC's after boiling in water for 1 h. For $CuCl_2$–GIC's, Ansart *et al.*[15] found no change in conductivity below 100 °C even after 3 months, but Gaier and Jaworske[16] detected a rapid decrease of conductivity in an atmosphere with 100% relative humidity. In spite of the contradiction in these experimental results, the metal chloride-GIC's have, or can have, stability higher than pentafluoride-GIC's, which is a definite advantage for the development of practical applications. Nevertheless, full understanding of the reasons behind the stability of some of these GIC's in the presence of such aggressive reagents as boiling water is still needed. In addition, standard testing procedures, including the testing atmosphere and detecting technique, are also required.

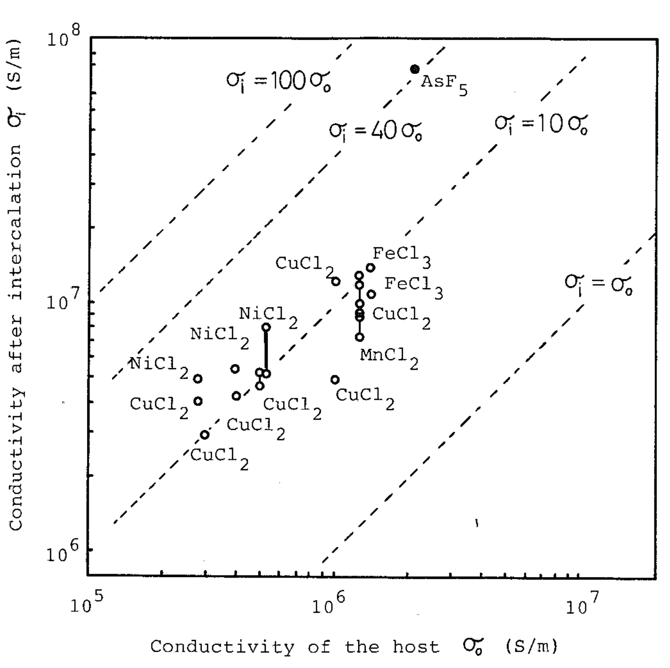

FIG. 1. Electrical conductivity after intercalation of metal chlorides as a function of that of the host graphite.

A simple process for the synthesis of GIC's under mild conditions and in large quantity also needs to be established. Sugiura *et al.*[17] developed a fast process for the intercalation of metal chlorides into carbon fibers and obtained a lightweight wire with a resistivity of about 5 $\mu\Omega$cm. The possibility of synthesis of these GIC's from molten salts of various chlorides is under study by Inagaki and his collaborators.[14,18–21]

GIC's with fluorine, in which most of the fluorine atoms were considered to exist as ions, were found to be synthesized under the coexistence of certain metal fluorides at relatively low temperatures, much lower than that for the synthesis of the covalent compounds, graphite fluorides $(CF)_n$ and $(C_2F)_n$.[22] These 'ionic' compounds with fluorine have relatively high electrical conductivity, which greatly depends on the host graphite and also slightly on the coexisting metal fluoride during preparation; the compounds prepared from HOPG and graphitized VGCF yield values as high as 2×10^7 S/m.[23,24] The conductivity also depends on the content of fluorine, and is a maximum for the stage-3 or -4, as in many other GIC's. Stability of the compounds in air is also closely related to the host graphite and the content of fluorine. The compounds prepared from graphitized mesophase pitch-based and PAN-based carbon fibers (MPCF and PANCF, respectively) showed a slight decrease in conductivity during the first 20 days after exposure to air, but are stabilized at values around 1.5×10^6 and 5×10^5 S/m, respectively. On the other hand, the compound from graphitized VGCF which gave as high a conductivity as 1.5×10^7 S/m showed a rapid decrease down to 10^6 S/m within 50 days.[24,25] The stability of these compounds was supposed to be due to fluorine atoms covalently bonded at the edge of the graphite layers.[24]

Most donor-type GIC's, such as KC_8, also have high electrical conductivity, but their marked reactivity with water interferes with their practical applications. Ternary GIC's containing an alkali metal and bismuth, however, were found to be fairly stable and to have relatively high conductivity.[26,27] The process for their synthesis is simple by using their alloy, but the separation of unreacted alloys from the GIC's formed is not easy, and in addition it is difficult to obtain single phases for each stage of these compounds. The ternary compounds, K–Bi–GIC's, belong to a family of GIC's containing an alkali metal and another element such as hydrogen, mercury, thallium, or lead, and so triple layers of potassium-bismuth-potassium are supposed to lie between graphite layers.

Excellent stability under severe conditions, high humidity or high vacuum, was shown by the residue compounds with bromine and iodine chloride, [16,28] though their conductivity values are one order of magnitude smaller than the GIC's mentioned above: the well-graphitized VGCF yields a conductivity value of 10^5 S/m.[29]

In Fig. 2 the conductivity after intercalation is plotted against that of the host material for different combinations between the host graphite and the five families of intercalates. Carbon fibers heat-treated at high temperatures [VGCF, MPCF, PANCF, and isotropic pitch-based (IPCF)] and HOPG are selected. In the case of the AsF_5 derivatives, only the lines representing the relations between these two conductivities are reproduced in Fig. 2, because they are reported on the basis of a large number of different carbon fibers with various heat-treatment temperatures.[8]

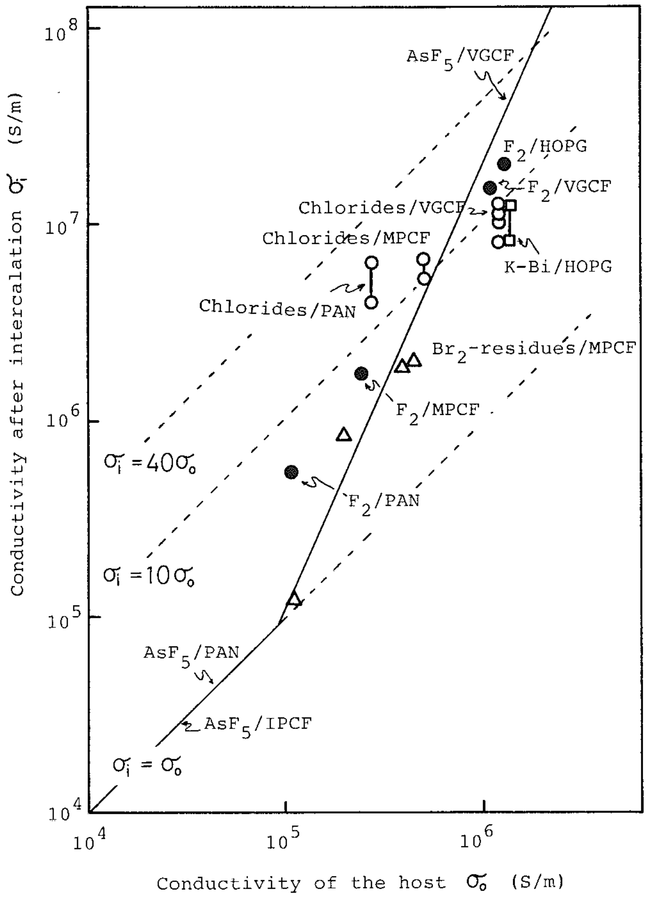

FIG. 2. Electrical conductivity after intercalation of different species as a function of that of the host fibers.

As shown in Fig. 2, conductivities as high as 10^8 S/m, higher than copper metal, can be obtained only by selecting a combination of highly crystallized host graphite with AsF_5. The conductivity of AsF_5–GIC's shows a very remarkable host dependency: if hosts with relatively low crystallinity are selected, only a small increase in conductivity, or even no increase, can be observed. Metal chlorides, fluorine and metal alloys, on the other hand, increase the conductivity by a factor of roughly 10, independent of the crystallinity of the hosts. It is worth noting that, after stabilization in air, the AsF_5–GIC's also give conductivity values on the order of 10^7 S/m.

Gaier[30] discussed technological hurdles to the application of intercalated fibers as electrical conductors from the standpoints of stability, homogeneity in properties, making electrical connections, and cost.

III. ELECTRODE MATERIALS IN BATTERIES

Various batteries have been developed which involve various electrochemical reactions of either graphite or GIC's with different intercalates. The common characteristics of these GIC electrodes are a high electrical conductivity and easy diffusion of electrochemically-active species between the graphite layers. The light weight of GIC's may be an advantage for electrodes, but in miniature batteries this might be offset if the volume required for a given capacity is large.

The power of these batteries, particularly their voltage, depends heavily on the combination of active materials and electrodes. Therefore, electrochemically active species have to be properly selected as intercalates. The electrochemical reactions occurring at the electrode are summarized in Table IV, by showing both the general scheme and a specific example for each type. The first five reactions in Table IV are the cases wherein the electrode is either a GIC or graphite itself and the intercalate ion is either a cation or anion. In most cases, intercalated ions are often solvated, although the solvating molecules are not shown in the formulae. Equations (6) and (7) in Table IV are redox reactions of metals intercalated as compounds. The redox reaction of nickel hydroxide has been used as a cathode reaction in commercial secondary batteries. In Eq. (7), nickel hydroxide is intercalated into graphite, which gives certain advantages, as will be discussed later. Some intercalates and their combinations with hosts for batteries are shown in Table V, together with a short description of the performance obtained.

Great success has been achieved by use of the covalent graphite fluoride $(CF)_n$ as the cathode material in a

TABLE IV. Electrochemical reactions at the electrodes in batteries with graphite intercalation compounds.

General formula	Examples	
$nC + A^+ + e^- \rightarrow C_nA$	$nC + Li^+ + e^- \rightarrow C_nLi$	(1)
$C_nA + B^+ + e^- \rightarrow C_nAB$	$(CF)_n + mLi^+ + e^- \rightarrow (CF)_n(Li)_m$	(2)
	$C_7CoCl_2 + mLi^+ + e^- \rightarrow C_7Li_mCoCl_2$	(3)
$nC + A^- \rightarrow C_nA + e^-$	$nC + mH_2SO_4 + HSO_4^- \rightarrow C_nHSO_4mH_2SO_4 + e^-$	(4)
	$nC + ClO_4^- \rightarrow C_nClO_4 + e^-$	(5)
$C_nA + B^- \rightarrow C_nAB + e^-$	$C_nFeCl_2 + Cl^- \rightarrow C_nFeCl_3 + e^-$	(6)
$C_nA \rightarrow C_nA' + H^+ + e^-$	$C_nNi(OH)_2 \rightarrow C_nNiOOH + e^- + H^+$	(7)

primary lithium battery.[31] Now this battery is commercially distributed all over the world. Similarly, the covalent compound of graphite fluoride $(C_2F)_n$, which may possibly be called a stage-2 compound, gives good performance for the cathode of a primary lithium battery.[32] The use of GIC's with different intercalates, such as $CoCl_2$, TiF_4, etc., has also been investigated for cathode materials.[33] In recent experiments the covalent compound, graphite oxide, has performed as well as graphite fluoride.[34] Also, ionic intercalation compounds with fluorine, which were synthesized in coexistence with metal fluorides, did well.[35] In all cases, the reaction responsible for the voltage of the cell is the intercalation reaction of Li^+ into the compounds, probably accompanied by solvating molecules, such as propyrene carbonate.[36]

The intercalation reactions of the perchlorate ion ClO_4^- and bisulfate ions HSO_4^- into graphite electrodes were attempted for use as electrode reactions,[37,38] but the repeated charge-discharge cycles were found to lead to the disintegration of the graphite electrode. However, a composite electrode of natural graphite NG (80 wt.%) with polypropyrene PP (20 wt.%) was reported to withstand over 2500 cycles of charge-discharge in sulfuric and hydrofluoric acids.[39] Stable intercalation-deintercalation repetition (charge-discharge cycles) of perchlorate ions ClO_4^- was shown, using graphitized VGCF for the anode.[40]

Secondary batteries of GIC's with nickel hydroxide, which were synthesized from $NiCl_2$–GIC's by electrolysis in aqueous KOH solution, were reported to show high performance.[41] In these electrodes, the change in the valence of nickel in the compound was of fundamental importance [see Eq. (7) in Table IV]. Similar electrodes of the compound with manganese hydroxide showed even better achievement.[42] High electrical conductivity of the GIC's and the ease of diffusion of the intercalate in the interlayer space are an advantage for the cathode material in secondary batteries. Batteries with metal-hydroxide-GIC's at both electrodes were also tried, but they did not give outstanding results.[42]

A secondary battery with carbon fibers at both electrodes was developed, showing no apparent decrease in capacity during charge-discharge cycles and in the open circuit voltage (OCV) of 1.8 V.[43] The intercalation and deintercalation of potassium in aqueous KBr solution were reported to be the fundamental reaction in this battery. A battery with nickel hydroxide at the cathode and activated carbon fibers at the anode was also constructed, and had a capacity exceeding 1000 C/g of CF.[44] Storage and release

TABLE V. Batteries using graphite intercalation compounds as electrodes.

Primary batteries with lithium anode	
$(CF)_n$	Light weight, high voltage, high energy density, low self discharge
$(C_2F)_n$	Higher voltage than with $(CF)_n$
F_2–GIC's	High capacity, flat discharge plateau
Graphite oxide	High energy density
Secondary battery	
KOH/$Ni(OH)_2$-, $Mn(OH)_2$–GIC's	High capacity, high efficiency
KOH/[$Ni(OH)_2$+$Fe(OH)_3$]–GIC's	Easy preparation of GIC
KOH/activated CF	Simple construction
HF, H_2SO_4/80% NG + 20% PP	Numerous charge-discharge cycles
Thermo cell	
Br_2, aq. KBr/NG	69 mV OCV, short life
Br_2, aq. KBr/VGCF	200 mV OCV, 10 mA/cm^2 SCC
NO_x, HNO_3/PANCF	100 mV OCV, long durability

NG: natural graphite, PP: polypropyrene, VGCF: vapor-grown carbon fiber, PANCF: PAN-based carbon fiber, OCV: open circuit voltage, and SCC: short-circuit current.

of hydrogen at the surface of the activated carbon fibers were believed to be a cause of this large capacity.

Although a battery using intercalation and deintercalation reactions at both electrodes, donor-type GIC formation at the cathode, and acceptor-type GIC at the anode seems feasible, none has been reported so far.

A thermocell is a kind of concentration cell, a device to convert a small temperature difference between two electrodes to electric power.[45–47] In this cell, an active material, such as bromine, circulates automatically as a vapor from the high- to the low-temperature electrodes and as an ion in the liquid electrolyte from the low- to the high-temperature electrodes, as shown schematically in Fig. 3. Long durability, up to 2 years, was experimentally demonstrated by a thermocell using HNO_3 as an electrolyte and the 2200 °C-treated PANCF as electrodes. Furthermore, no maintenance was required.[48]

A device converting thermal energy to electricity by using the GIC's as electrodes was proposed by Huffman and Haq.[49]

IV. MATERIALS FOR STORAGE AND ISOTOPE-SEPARATION OF HYDROGEN

Large amounts of molecular hydrogen can be absorbed in the space among alkali metal atoms intercalated in between graphite layers,[50,51] with the following advantages: (1) up to 13.7 l (NTP) of hydrogen can be absorbed per 100 g of GIC, close to the value 15.5 l obtained with $LaNi_5$; (2) small mass of the absorbant; (3) no appreciable change in size during absorption-desorption cycles—in other words, no disintegration after repetition of the absorption-desorption cycle; (4) perfect reversibility; (5) quick absorption; (6) desorption by simple heating or evacuation; (7) no contamination by impurity gas, e.g., oxygen—in other words, high stability at liquid nitrogen temperature.

The use of Cs– and Rb–GIC's as materials for cryosorption has been proposed.[52] In Fig. 4, isotherms of the equilibrium pressure P_{eq} vs the volume of gas absorbed per gram of GIC (prepared from graphite sheet) are shown.

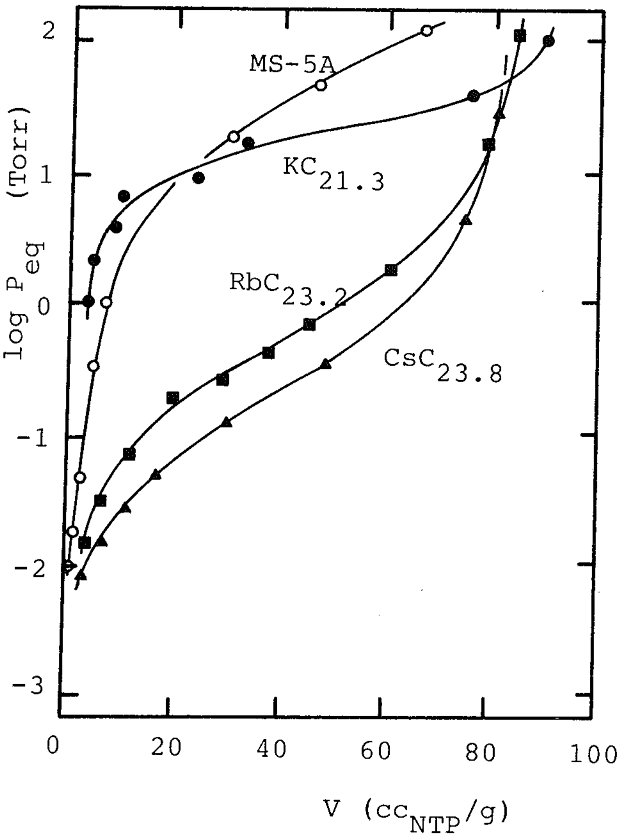

FIG. 4. Absorption isotherms of hydrogen at 77 K represented by a plot of the logarithm of the equilibrium pressure, P_{eq}, against the volume of gas absorbed per gram of GIC, V.[52]

In the same figure, the result on a molecular sieve MS-5A is also plotted for comparison. Even under pressures as low as 1 Torr, the volumes of hydrogen absorbed by the compounds with Cs and Rb are ten times greater than those by the K-GIC and the molecular sieve MS-5A. Table VI shows the equilibrium pressure P_{eq} of hydrogen and deuterium gases at small values of fractional absorption ϕ of 0.2 and 0.5 on the different GIC's and the molecular sieve. The Cs– and Rb–GIC's can absorb hydrogen gases at pressures as low as 0.1 Torr.

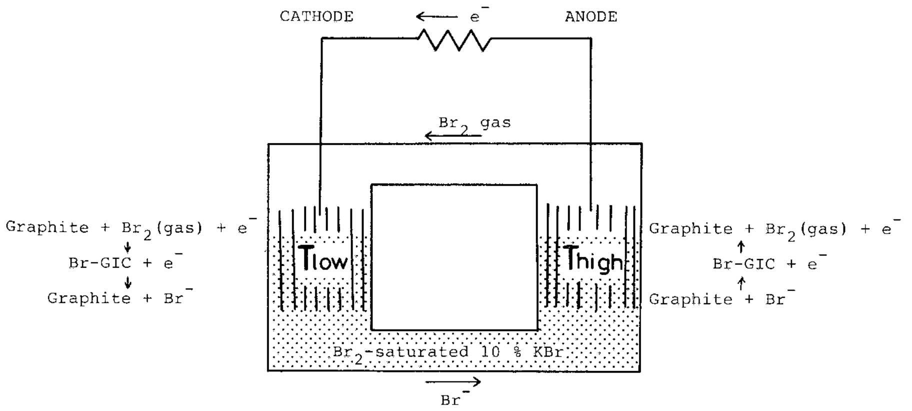

FIG. 3. Schematic diagram of the mechanism of the thermocell in which bromine circulates as the active species. The supposed reactions at the low-temperature and high-temperature electrodes are shown, the former being a cathode and the latter an anode in the case of active bromine material. The active material circulates as Br_2 gas in the upper bridge and as Br^- ion in the lower bridge of the cell.

TABLE VI. Equilibrium pressure P_{eq} at fractional absorption ϕ of 0.2 and 0.5.[52]

GIC	Gas	Equilibrium pressure P_{eq} (Torr) $\phi = 0.2$	$\phi = 0.5$
Cs–GIC	H_2	0.05	0.32
	D_2	0.04	0.25
Rb–GIC	H_2	0.16	0.71
	D_2	0.05	0.20
K–GIC	H_2	8.9	32
MS–5A	H_2	11	83

The structure and texture of the host graphite were found to play a decisive role in the absorption behavior of the compounds. High values of separation coefficient of hydrogen isotopes by the GIC's with potassium were reported,[53,54] much higher than those found with the molecular sieve MS-5A, as summarized in Table VII. It can also be seen that the GIC's prepared from the 1500 °C-treated coke give higher values of separation coefficient than those prepared from 2300 °C-treated. For a given heat treatment temperature (HTT), the composition of the GIC's is an important parameter.

Excellent separation of hydrogen isotopes was obtained by using GIC's as a column filling in a gas chromatograph.[55] A 5 cm column of KC_{24} gave a much better separation of p-H_2, o-H_2, HD, o-D_2, and p-D_2 at 77 K than a 5 m column of alumina.

V. OTHER APPLICATIONS

Rapid heating of GIC's or of their residue compounds induces a notable exfoliation of the host graphite perpendicular to its layers, mostly due to rapid expulsion of the intercalated species. Flexible graphite sheets, prepared from this exfoliated graphite by roll-forming, are currently receiving increasing demand for use as gaskets, packing, and thermal insulators at high temperatures. Apart from the intrinsic properties of graphite, these graphite sheets show a high thermal resistivity, high anisotropy in thermal conductivity, stability to compressive strain, easy relaxation of induced stress, self-lubricity, etc.

TABLE VII. Isotope-separation coefficients and volume of hydrogen absorbed per gram of K–GIC's.[53]

GIC	Host	$a(H_2/D_2)$	$a(H_2/HT)$	v(mlH_2, NTP)
KC_{12}	Petroleum coke	8.7	5.0	92
KC_{24}	HTT = 1500 °C	5.7	3.7	111
KC_{12}	Petroleum coke	7.1	4.5	72
KC_{24}	HTT = 2300 °C	5.7	3.7	120
KC_{22}	Graphite sheet	5.9	···	119
	Molecular sieve MS-5A	2.6–2.8	1.7	102

Residue compounds with sulfuric and nitric acids are used in industrial production of graphite sheets, mostly because they retain large amounts of intercalates between their graphite layers in the residue compounds. Some problems connected with the production and use of graphite sheets prepared by this industrial process have been pointed out: the necessity of using concentrated sulfuric or nitric acids for the production, the formation of poisonous oxide gases SO_x and NO_x during exfoliation, and the possibility of erosion of metals by traces of acid remaining in the sheets of the exfoliated graphite.

Different intercalates have been used for exfoliation of graphite, mostly in order to solve the problems mentioned above. They are listed in Table VIII together with some comments on noteworthy points. The synthesis of $FeCl_3$–GIC's from hydrated salt and preparation of the exfoliated graphite from them[56] make practical applications attainable because of simplicity of the synthesis process. Preparation of the exfoliated graphite from Na or K-THF-GIC's is also interesting as a practical process because these GIC's can be synthesized at room temperature.[57] The Co-THF-GIC's lead to graphite sheets in which fine particles of metallic cobalt are dispersed.[58,59] From the GIC's of graphitized VGCF with $SbCl_5$[60] and also with K-THF,[61] an intriguing exfoliation behavior was observed. After complete exfoliation, VGCF changes to thin sheet, in which graphite layers are preferentially oriented perpendicular to the sheet surface, as shown in Fig. 5. The exfoliation process of this VGCF has been discussed in detail.[61] Exfoliation can even be obtained by exposing to air the GIC's prepared by electrolysis in polypropyrene carbonate solution of $LiClO_4$.[62]

A system for the storage of thermal energy has been proposed[63]: storing it during deintercalation of ammonia molecules from ternary GIC's with metal chloride and NH_3, and releasing it during reintercalation of ammonia. The thermal capacity of the system can be about 200 Wh/kg of GIC.

A reversible change in color (black to blue) due to intercalation and deintercalation of Li from its salts dissolved in organic electrolytes was tried for use as an

TABLE VIII. Intercalates for exfoliation of graphite.

$H_2SO_4 + HNO_3$	Industrial process; necessity of concentrated acids, formation of SO_x and NO_x
$FeCl_3$	Possibility of using the hydrated $FeCl_3$
Na–THF or K–THF	Dispersion of fine alkali metal particles; exfoliation of graphitized carbon fibers
Co–THF	Magnetic; dispersion of fine cobalt metal particles
$LiClO_4$-polypropyrene carbonate (PC)	Spontaneous exfoliation in air at room temperature
$SbCl_5$	Exfoliation of VGCF graphitized

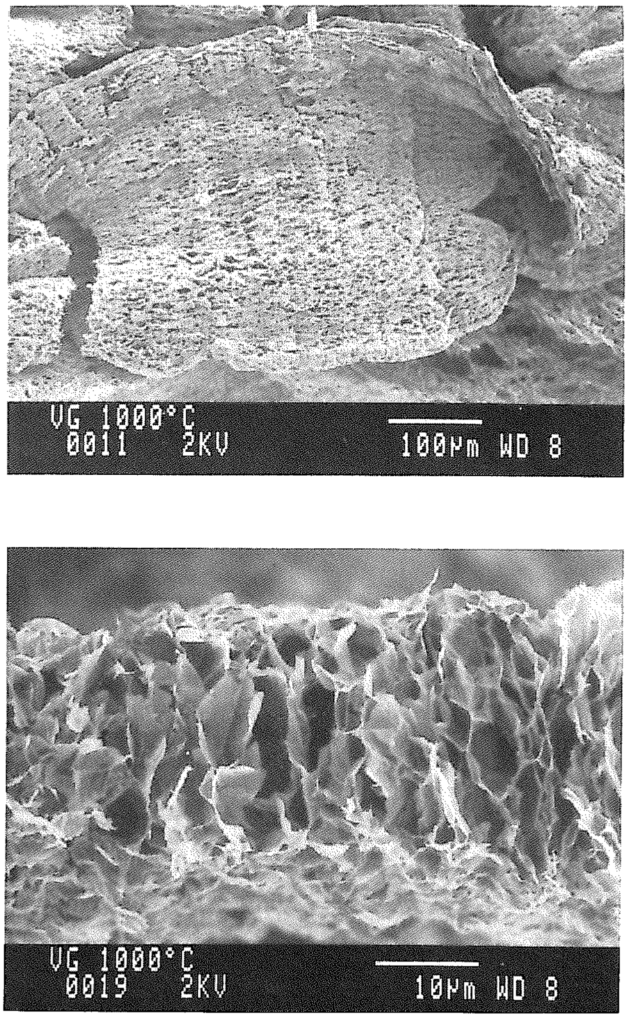

FIG. 5. Exfoliation of graphitized vapor-grown carbon fiber.[61]

electrochromic device.[64] Writing and erasing delays were reported to be on the order of 0.2 s. This electrochromic phenomenon was recently reproduced by using graphite films prepared from polymers.[65]

VI. CONCLUDING REMARKS

In order to develop the various applications of GIC's, different problems have to be discussed from the engineering point of view, such as host graphite, synthesis, stability, etc. Gaier[30] pointed out the problems associated with applications of highly conductive intercalated carbon fibers.

One characteristic of carbon and graphite materials is that they have various structures and textures,[66] yielding a wide range of properties. A number of experiments show that the host graphite has definite effects on the functions of the resultant GIC's, as mentioned before: the necessity of high crystallinity of the host graphite to obtain high electrical conductivity in AsF_5–GIC's, the determinative effect of the conductivity of the host materials on that of the resultant GIC's with metal chlorides, fluorine, and residual bromine, and a strong dependency on the heat treatment temperature of the host on the separation coefficients of hydrogen isotopes of the resultant K-GIC's. However, more detailed and systematic understanding of the effects of host materials on the structure and functions of GIC's is required. The selection of the structure and texture of the host is very inportant not only to obtain high functionality, but also to attain stability of GIC's in order to manipulate them in air.

Further development of host materials is also necessary. Highly oriented pyrolytic graphite (HOPG) has been used as the host in the past, but when produced in large quantities, lacks sufficient homogeneity in structure and properties, and is also expensive. Graphite films prepared from different organic polymers are promising as hosts for GIC's, though most of them have been studied only on a laboratory scale so far. Vapor-grown and mesophase-pitch-based carbon fibers are interesting, particularly the latter, which have a wide range of texture in the cross section of the fibers. Small flakes of natural graphite have been widely used as the host for GIC's, and flakes of so-called kish graphite, which are recovered from cast iron processing, are now going to be produced on an industrial scale.

The two-bulb method is an excellent process for the synthesis of well-defined homogeneous GIC's, but it usually requires a long time and relatively high temperatures to complete the intercalation reactions. The mixing of host graphite with intercalates results in fast intercalation. By using mixtures of intercalates which give molten salt systems, the temperature for intercalation reactions can even be lowered. In these mixing methods, isolation of the formed GIC's from the reaction system usually presents difficulties. In the case of metal chloride-GIC's, they can be washed out from the unreacted chlorides by water or hydrochloric acid because of their high stability. Synthesis of GIC's in organic solutions is interesting because of the reaction at room temperature and the ease of isolation of the GIC's formed, though disadvantages of long reaction times and co-intercalation of organic molecules exist.

Most GIC's are not stable in air, water, or different organic media, and so techniques to stabilize the GIC's have to be developed. Different ideas and proposals have been presented: shielding by the formation of graphite at the edge of the host particles, formation of stable hydroxides at the edge of the particles, and co-intercalation of the second intercalates such as organic molecules. However, none of these approaches has been verified experimentally or theoretically to date, and controlled stabilization of GIC's with sufficient reproducibility has never been realized. Successful stabilization of K-GIC's may result in new fields of applications exploiting their high electrical conductivity, high rate of electron transfer between intercalated potassium atoms and graphite layers, and even their colors. Physical ways to prevent decomposition of GIC's, embedding them or coating them by some organic polymers, for example, might be possible for some applications.

Looking to the future, many milestones are sure to be added to the post-1987 period in the history of experiments with graphite intercalation compounds.

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