Feasibility of Intercalated Graphite Railgun Armatures

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Abstract

Graphite intercalation compounds may provide an excellent material for the fabrication of electro-magnetic railgun armatures. As a pulse of power is fed into the armature the intercalate could be excited into the plasma state around the edges of the armature, while the bulk of the current would be carried through the graphite block. Such an armature would have desirable characteristics of both diffuse plasma armatures and bulk conduction armatures. In addition, the highly anisotropic nature of these materials could enable the electrical and thermal conductivity to be tailored to meet the specific requirements of electromagnetic railgun armatures. Preliminary investigations have been performed in an attempt to determine the feasibility of using graphite intercalation compounds as railgun armatures. Issues of fabrication, resistivity, stability, and electrical current spreading have been addressed for the case of highly oriented pyrolytic graphite. This research was initiated and conducted as part of AFATL's Electromagnetic Launcher Technology Program, Site A-15, Eglin AFB Fl.

Introduction

Electromagnetic launchers have been suggested as an economical way to propel some payloads into space (especially from the lunar surface) and as launchers for antiballistic missile projectiles. Advancing the technology of electromagnetic launchers has proved to be a continuous research and developmental challenge. This challenge, in part, reflects the complexities encountered when attempting to extract and apply the physics of railgun armatures. Armatures, aside from having to be compatible with projectiles and launchers, must maintain electrical contact with the rails, conduct megaampere currents during millisecond time frames, absorb and dissipate ohmic heat, withstand kiloatmospheric pressures, and minimize in-bore damage. Understanding of such fundamental issues such as arc initiation, armature separation, current distribution, and arc length with regard to the behavior and performance of armatures remains ambiguous. Discussions of the four classical armature types (solids, plasmas, hybrids, and transitioning) along with their stringent requirements for developing hypervelocity railguns are provided at length in numerous electromagnetic launcher reports and publications.[1]

It may prove fruitful to explore the feasibility of fabricating armatures from graphite intercalation compounds (GIC's). GIC's are layered compounds with alternating layers of aromatic carbon sheets (graphene planes) and guest atoms or molecules (intercalates). The axial resistivity of GIC's can be lower by an order of magnitude over pristine graphite with little change in the mechanical properties. Of interest to the development of armatures is their potential for transmitting high and uniform electric currents from plasma armatures diffused in the solid graphite host armature. In this way rail to solid armature electrical contacts would be enhanced by the addition of diffused plasma contacts.

With graphite as the host, elements such as lithium (Li) or bromine (Br$_2$) are diffused between the graphene planes which creates a pattern of alternating layers with distinct electrical and thermal properties. This pattern can be tailored because of a phenomenon called staging. A fully intercalated (stage 1) compound has alternating graphene and intercalate layers. If half of the intercalate is removed, the lattice collapses into a stage 2 compound, in which one intercalate layer alternates with two graphene layers. Further dilution can produce stage 3, 4 and even higher stages. Other tailorable parameters include the crystallinity of the host graphite, and the choice of intercalate molecule.

The feasibility of intercalated graphite railgun armatures will depend upon the meeting of a hierarchy of objectives. The first is the fabrication of GIC's of sufficient size and quality to make a practical armature. The choice of intercalate must be guided by its chemical stability and its capacity to transmit and maintain high and uniform electrical currents. In addition, the GIC armature must have sufficient elastic and tensile strength to withstand the high pressures emanating from plasmas and J x B forces, and to thermally dissipate hot plasma constituents without losing the mechanical and thermal integrity of the armature.

This study is the initial phase of determining the feasibility of GIC's as armature materials. Relatively large pieces of graphite were intercalated with one of two candidate host materials, Br$_2$ or cadmium chloride (CdCl$_2$). The dynamics of the intercalation process were analyzed as a function of sample size, and the intercalation compounds were characterized structurally and electrically.
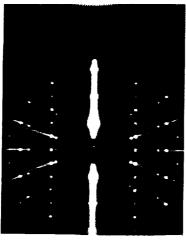
Methods and Materials

The graphite used for this study was "ZYH" grade of highly oriented pyrolytic graphite (HOPG). This is a high purity graphite with well oriented crystallographic "c" axis, and randomly oriented, or turbostratic, "a" axis. Precession x-ray diffraction photographs show the preferential ordering of the samples. In the crystallographic $h0l$ zone (Figure 1a) the structure is well ordered (except in the $h00$ direction). In the $hk0$ zone random ordering gives rise to Debye rings in the diffraction pattern.
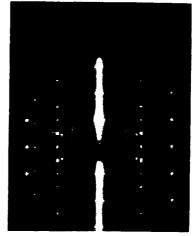
HOPG was intercalated with Br$_2$ using standard vapor-phase techniques which have been described elsewhere[2]. The procedure and apparatus used to intercalate HOPG with CdCl$_2$ has also be described in detail elsewhere[3].

In order to look at the scaling laws, pieces of HOPG with sizes ranging from 2 x 5 x 10 mm to 8 x 10 x 50 mm were intercalated with Br$_2$. (The smallest dimension is along the "c" axis and undergoes expansion during intercalation.) The intercalation and deintercalation rates were determined as well as the amount of Br$_2$ uptake. Deintercalation rates and densities were also determined for HOPG intercalated with CdCl$_2$.

(a) PRISTINE.   (b) BROMINE INTERCALATED.   (c) CADMIUM CHLORIDE INTERCALATED.

FIGURE 1. - X-RAY DIFFRACTION HOL PRECESSION PHOTOGRAPHS OF HOPG.

During the HOPG - Br_2 intercalation reactions, the "c" axis expansions were monitored and analysed as a function of sample size. When the expansion stopped, the reaction was assumed to be completed, but the reaction chamber remained sealed for an additional 60 - 84 hours. The samples were then removed from the reaction chamber, and their weight loss was monitored. The expansion was not reversible so this was not monitored.

It is difficult to characterize the electrical properties (such as resistivity) of highly crystalline graphite because of the large anisotropy between the "a" and "c" axes. Typically the resistivity along the "a" axis of graphite is three orders of magnitude less than the resistivity along the "c" axis.[4] Thus, when making measurements it is often difficult to determine whether the current has spread throughout the bulk of the sample, or whether only the top few layers are being measured. Intercalation actually increases the anisotropy, and makes the measurements even more difficult.[5]

The classical resistivity measurement technique utilizes a four-point probe. The outer two contacts provide a constant current to the sample, while the inner two sense the voltage drop. If the in-plane ("a" axis) resistivity is to be measured, current must be spread throughout the bulk of the material. Silver paint is painted across the entire end of the sample. This provides a current path to each of the graphene planes. The voltage probe can then be placed on the surface. The current spreading is enhanced if a rather long and thin piece of graphite is used. Painting on a series of voltage contacts allows the construction of a voltage-distance plot, and the least squares fit line will be a more accurate value than that obtained from a single pair of points.

If the voltage probes are mounted, not along the top of the sample, but along the side, the same value for the resistivity should be obtained. A comparison between these two values will reveal how successfully the current has been spread throughout the sample.

The transverse resistivity (along the "c" axis) is also an important value. Since no current flow is desired in that direction, a large transverse resistivity has advantages. To measure the transverse resistivity the voltage probes are first attached to the top and bottom faces of the sample. To facilitate even current spreading throughout, the top and bottom faces are painted with silver paint, except for the areas where the voltage leads are attached. The current leads are then attached to the painted faces.

The problem of anisotropy can be side-stepped if the contactless rf eddy current technique is used. A radio frequency field (in our case 55.55 kHz) set up across the sample induces eddy currents. The additional current which must be added to maintain the amplitude of the rf field is proportional to the resistivity and the thickness of the sample. No contacts need to be made, and only the component perpendicular to the magnetic field (the "a" axis) is affected. One drawback to this technique is that rather wide samples (at least a 2 cm square) are required to minimize edge effects. The rf resistivity of the individual samples could not be measured due to this constraint, but it was measured on some rather large pristine samples.

In some respects the absolute resistivity is not important in a railgun armature application. What is important is the "effective resistivity" in the railgun configuration. This includes resistivity along the axis between the rails, and the contact resistance between the armature and the rail. Thus, a two-point resistance railgun test apparatus was constructed which duplicates the electrical environment the sample will be subjected to.

Results and Discussion

One measure of the quality of the HOPG is its density. Graphite has a crystallographic density of 2.2556 g/cm^3. The density of real samples, however, is lowered by an amount which is dependent upon the number of defects. Hence, the more perfect the crystallinity of the sample, higher is its density. The density was determined by measuring the linear dimensions with a digital caliper, and weighing the samples on an analytical balance. Although this method is not particularly accurate, it has the advantage of being non-destructive and non-contaminating. The average density of the pristine graphite was measured to be 2.22 ± .03 g/cm^3. The rather large scatter (1.4 percent) is due principally to the fact that the surface was not smooth but exhibited "bubble" structures. There may also have been errors in measuring the linear dimensions, and in the squareness of the corners of the sample.

Bromine Intercalation

The progress of the Br_2 intercalation reaction was monitored via expansion along the "c" axis direction. The thickness of the largest sample was measured at regular intervals throughout the reaction until it was constant. An example of the

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first two hours of a reaction is shown in Figure 2. Note that there is no change in the thickness during the first five minutes. During this time the vapor pressure of the Br_2 is increasing as it evaporates from the reservoir. Once a threshold pressure of Br_2 is built up, the reaction begins. The majority of the expansion occurs within the first two hours, but it continues at a low rate for several hours afterwards. Eventually, large cracks appear between the graphene planes within the sample, and bending distortions appear. This casts doubt on the value of using expansion to monitor the reaction in its later stages. After about 80 hours the reaction was assumed to be complete.

This points to a diffusion controlled intercalation reaction also. The larger pieces (perhaps even the smallest pieces) probably did not have sufficient time to fully react. The macroscopic cracks in the sample may have masked microscopic expansion. It is possible that large pieces cannot be intercalated within a reasonable reaction time. There are cases in the literature of intercalation reactions which took months to go to completion. In-situ weight measurements, which are being undertaken at this time, are needed to answer these questions.
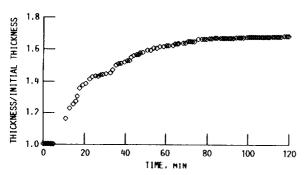

FIGURE 2. - EXPANSION IN THE CRYSTALLOGRAPHIC "C" DIRECTION OF HOPG UPON EXPOSURE TO 165 TORR OF BROMINE VAPOR.

FIGURE 3. - WEIGHT LOSS OF VARIOUS SIZE SAMPLES OF SAMPLES OF BROMINE INTERCALATED HOPG OVER TIME.

It has been shown by several authors that Br_2 rapidly diffuses out of graphite when the sample is removed from the Br_2 atmosphere. In order to obtain the maximum amount of Br_2 intercalated into the graphite, samples were rushed from the reaction chamber to tared weighing bottled and quickly sealed. The weight uptake of Br_2 by samples of various sizes is shown in Table I. From the weight uptake the nominal stoichiometric formula and nominal stage of the intercalation compound can be determined. These are also shown in Table I.

The data depicted in Table I reveal that there was a large effect of sample size on the uptake of Br_2 by the graphite. There are two possible interpretations for this effect. The Br_2 might be taken up more quickly by smaller pieces of graphite, especially if it is a diffusion controlled reaction. Alternately, the Br_2 may be lost more quickly by larger pieces, perhaps because larger stresses cause larger cracks and so more avenues of escape. The weighing bottles were opened and the Br_2 allowed to escape. At periodic intervals the sample vials were again weighed. In this way the deintercalation reaction was monitored. As can be clearly seen in Figure 3, smaller pieces, not larger, deintercalate more rapidly. This is consistent with a diffusion controlled deintercalation reaction.
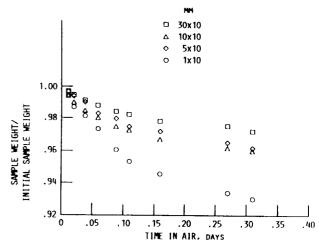
X-ray diffraction precession photographs confirmed that there are regions of Br_2 graphite intercalation compounds even in samples that had been allowed to desorb for several weeks (Figure 1b).

The rapid deintercalation of the Br_2 from the HOPG points to a larger issue, that of stability. It appears as though large stockpiles of Br_2 intercalated graphite armatures could not be manufactured in advance and stored until use. Not only would a large portion of the intercalate diffuse out, returning the graphite to its near pristine state, but the constant outgassing of corrosive and toxic Br_2 would pose an environmental hazard. However, Br_2 intercalated graphite armatures could be stored in sealed containers, to be opened only just before loading. In the early stages of deintercalation, the reaction may even be sufficient to provide a local atmosphere of easily ionized gas which could aid the initiation stage of firing the railgun.

Table I – Sample Characteristics of Br_2 Intercalated ZYH Grade Highly Oriented Pyrolytic Graphite

Length cm	Width cm	Height cm	Volume cm^3	Mass gram	Density g/cm^3	S/V cm^{-1}	Mass Br gram	Nominal Formula	Nominal Stage
1.015	.146	.616	.912	.2068	2.2675	18.9	.3743	$C_{8.2}Br$	1.2
1.057	.519	.240	.132	.2890	2.1960	14.1	.4453	$C_{12.3}Br$	1.8
1.027	1.008	.268	.277	.6069	2.1910	11.4	.8936	$C_{14.1}Br$	2.0
2.727	1.091	.283	.841	1.8676	2.2204	9.64	2.4658	$C_{20.8}Br$	3.0
5.055	.971	.614	3.013	6.7100	2.2274	5.71	7.8917	$C_{37.8}Br$	5.4

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Cadmium Chloride Intercalation

There are enough safety and storage concerns with Br_2 intercalated HOPG to make it prudent to consider a more stable intercalate. $CdCl_2$ intercalated graphite fibers have been reported to be stable compounds.[6,3] Thus, several small pieces of $CdCl_2$ intercalated ZYH grade HOPG were produced as a possible alternative.

Table II shows the sample characteristics of the graphite intercalated with $CdCl_2$. The linear dimensions are not as well characterized as the Br_2 intercalation samples were, and that may be reflected in the pristine density measurements, which were quite low (2.17 ± .02 g/cm^3). The reaction conditions required to intercalate a sample with $CdCl_2$ are much more severe than those required for Br_2 intercalation, but the higher surface to volume ratios were thought to help ensure the reaction would go to completion. Unfortunately, from the mass uptake data it is evident that the reaction was far from completion even in the case of the smallest sample sizes. X-ray diffraction precession photographs of $CdCl_2$ product show that graphite intercalation compounds are formed (Figure 1c). The vertical streaks that appear between the graphite reflections are due to disordered $CdCl_2$ located between the graphene planes. These results indicate that there are areas of well staged graphite, so evidently the samples are not homogeneous.
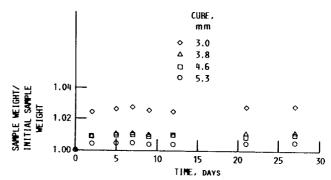

FIGURE 4. - DEGRADATION OF VARIOUS SIZE SAMPLES OF CADMIUM CHLORIDE INTERCALATED HOPG OVER TIME.

the best intercalate from a performance standpoint. It also, however, makes very unstable intercalation compounds, and so poses some possible problems.

Sodium hydride (NaH) may also offer low ionization potential and light weight. NaH also forms relatively stable GIC's, so this may be a compromise compound that combines low ionization potential with ambient condition chemical stability.

Table II -- Sample Characteristics of $CdCl_2$ Intercalated ZYH Grade Highly Oriented Pyrolytic Graphite

Length cm	Width cm	Height cm	Volume cm^3	Mass gram	Density g/cm^3	S/V cm^{-1}	Mass Cd gram	Nominal Formula
.305	.305	.305	.0283	.0614	2.1690	64.6	.0738	$C_{76}CdCl_2$
.381	.381	.381	.0553	.1210	2.1878	41.3	.1347	$C_{135}CdCl_2$
.457	.457	.457	.0956	.2104	2.2015	28.7	.2194	$C_{360}CdCl_2$
.533	.533	.533	.1518	.3318	2.1863	21.1	.3658	$C_{150}CdCl_2$
4.064	.305	.305	.3776	.8168	2.1634	24.8	.8689	$C_{240}CdCl_2$
4.064	.381	.381	.5899	1.269	2.1511	16.4	1.341	$C_{270}CdCl_2$
4.064	.457	.457	.8495	1.839	2.1648	11.7	1.955	$C_{240}CdCl_2$
4.064	.533	.533	1.1563	2.481	2.1457	8.9	2.636	$C_{240}CdCl_2$

The stability of the weight of these compounds was considerably higher that the Br_2 compounds as can be seen in Figure 4. Whereas the weight dropped in the case of Br_2 compounds as Br_2 diffused from the lattice, the weight increases over time for the $CdCl_2$ intercalated samples. If generalizations can be made from $CdCl_2$ intercalation compounds with fibers as the host, this is due to the uptake of water. In graphite fibers the weight increase can be accelerated by putting the samples in a high humidity environment, and can be reversed by heating.

Other Intercalates

There are, of course, considerations which may over-ride the stability issue. An important performance characteristic may well be a low ionization potential for the intercalate. We are initiating a program to study the dynamics of intercalation with Li. Li, with its light weight and low ionization potential may be

Electrical Properties

The principal reason to intercalate graphite for railgun armatures is to decrease the resistance of the armature. Perhaps the largest gain will be in the lowering of the contact resistance, but the bulk resistivity of the material is also lowered. Intercalation provides additional charge carriers (electrons in the case of Li and NaH, holes in the case of Br_2 and $CdCl_2$) in the conduction band. "A" axis resistivity can be lowered by several orders of magnitude over pristine graphite.[3]

The values of the axial resistivity (measured along the "a" axis) the transverse resistivity, the eddy current resistivity, and the resistivity in the railgun configuration are summarized in Table III. There are several clues in this table that the current spreading was not uniform in these samples, and that the resistivity values are indeed maximum values.

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Table III -- Resistivity of ZYH Grade HOPG

Resistivity mΩ-cm	Pristine ZYH	Br_2 Intercalated	$CdCl_2$ Intercalated
Axial	0.600	0.690	0.100
Transverse	13.	7.4	100.
RF Eddy Current	0.500	-----	-----
Railgun	180,000	1,400	-----

The "a" axis resistivity for the large samples we measured is about an order of magnitude higher than values reported in the literature[3]. When very thin samples of pristine ZYH were measured, values similar to those in the literature (40 $\mu\Omega$-cm) were found. The rf eddy current value, however, is quite close to the axial resistivity measured on the large samples. This is difficult to explain.

The transverse resistivity values are more consistent with literature values.[4] The path of the current in this direction, however, is much more resistive than in the perpendicular directions (along the "a" axes) so spreading of the current is not expected to be as much of a problem. Each plane will tend to be an equipotential surface. As was discussed earlier, intercalation causes an expansion along the transverse ("c" axis) direction. This results in poor crystallite-to-crystallite contacts in this direction and so a wide sample-to-sample spread in the transverse resistivity for intercalated ZYH.

The railgun resistivity is much higher, and that is to be expected. This is because it includes the sample to rail contact resistance in addition to the sample resistance. The contact resistance term totally dominates the measured resistivity. Herein lies the hope of this armature design. When the plasma is activated, it will make contact between the sample and the rail. The additional current path should substantially reduce the contact resistance which will substantially reduce the railgun resistivity.

Conclusions

Before railgun tests can proceed with an intercalated graphite armature, there are several parameters which must be optimized. If the Br_2 intercalation compound is to be used, then reaction rates must be increased, or reaction times must be lengthened. The rate might be increased by lowering the temperature of reaction. This technique has allowed poorly graphitized fibers, such as Amoco P-55, to be brominated, something which was not possible at room temperature. In-situ evaluation is required to know when the reaction has come to completion.

Both the intercalation and deintercalation reactions appear to be diffusion controlled. While this means that the intercalation reaction may be more time consuming when using larger samples, it also means that there will be a larger open air shelf life. The shelf life will still probably be short, and the armatures should remain sealed until just prior to use.

There are advantages to using $CdCl_2$ as the intercalate, but disadvantages also. The principal advantage is in its stability and ease of handling after manufacture. Disadvantages include a much more complex fabrication process, and perhaps somewhat lower performance in the railgun due to its higher ionization energy.

Other possible alternatives include using lithium or sodium hydride graphite intercalation compounds, which are expected to perform very well in the plasma state.

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