Electromechanical and Electrical Behavior of Intercalated Graphite

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The exfoliation of intercalated graphite gives rise to a tensile stress along the c-axis. Although exfoliation is commonly performed by furnace heating, it can also be achieved by the passage of an electric current.

To study this electromechanical effect, highly oriented pyrolytic graphite (HOPG) intercalated with bromine was constrained from expansion by the application of a controlled amount of compressive stress along the c-axis while electric power was applied along the c-axis. Although expansion along the c-axis was inhibited, the amount of compressive stress required to constrain the sample (area perpendicular to c-axis = 0.232 cm^2; thickness along c-axis = 0.058 cm) increased sharply at a certain power as the power was gradually increased. In the first power cycle (i.e., first increase and decrease in power), the stress jumped from 0 to 1.24 X 10^6 Pa at a power of 0.01 W. In the second cycle, the stress gradually increased from 0 to 1.23 X 10^6 Pa and then jumped to 2.16 X 10^6 Pa at 4.0 W. The changes in stress in subsequent cycles (up to the 10th cycle) were similar to those of Cycle 2. However, the power at which the jump in stress occurred increased with cycle No., so that in Cycle 10 the jump in stress occurred at 9.9 W.

Although the sample was constrained from expansion the c-axis electrical resistivity (measured by the four-probe method) first increased and then decreased as the power was increased and the same effect was observed as the power was decreased. This effect was observed in all cycles. For example, in Cycle 10, the resistivity (i) increased from 0.26 to 0.50 Ω.cm when the power was increased from 0 to 4.5 W, (ii) decreased from 0.50 to 0.30 Ω.cm as the power was further increased from 4.5 to 9.4 W, and (iii) stayed at 0.30 Ω.cm up to 11.3 W. Upon decreasing the power subsequently, the resistivity (i) stayed at 0.30 Ω.cm down to 7.9 W, (ii) increased from 0.30 to 0.51 Ω.cm as the power was decreased from 7.9 to 3.9 W, (iii) decreased from 0.51 to 0.26 Ω.cm as the power was further decreased from 3.9 to 2.0 W, and (iv) stayed at 0.26 Ω.cm as the power was decreased to zero. The initial resistivity at the beginning of a cycle as well as the maximum resistivity of a cycle decreased with increasing Cycle No. The decreased was large in Cycles 1 and 2, but was small or zero in subsequent cycles. In particular, the maximum resistivity in Cycle 1 upon decreasing the power was the same as the maximum resistivity in Cycle 2 upon increasing the power.

Irreversible exfoliation of graphite-bromine (HOPG) under no constraint was found to decrease the c-axis resistivity from 6.3 X 10^{-1} to 3.0 X 10^{-2} Ω.cm and to increase the a-axis resistivity from 2.4 X 10^{-6} to 5.4 X 10^{-4} Ω.cm.

The observed jump in stress upon increasing the power is attributed to the initiation of bubble formation. (The expansion of the bubbles causes exfoliation.) This initiation occurred in two steps. The first step occurred in Cycle 1 and required only 0.01 W; the second step occurred reversibly in subsequent cycles at 4.0 to 9.9 W. The jump in stress was probably due to the change from bromine liquid to compressed bromine vapor in the graphite. The increase and then decrease in resistivity upon increasing or decreasing the power are attributed to the combined effect of microcrack formation (which tends to increase the c-axis resistivity) and the slight distortion of the graphite layers (which tends to decrease the c-axis resistivity).

When an electric current was passed along the axis of a Thornel P-100-4 graphite fiber intercalated with ICl, the electrical resistance per unit length was found to increase with increasing power and then decrease with decreasing power. In the first two power cycles, the change was partially reversible. In subsequent cycles, it was completely reversible, though with hysteresis. For example, in Cycle 3, the resistance increased from 140 to 260 Ω/cm as the power was increased from 0 to 7 X 10^{-2} W/cm and decreased back to 140 Ω/cm as the power was decreased back to zero. Exfoliation did not occur because of the low power used and the relative difficulty of exfoliating graphite fibers. (If exfoliation occurred, the resistance reached 600 Ω/cm.) The increase in resistance is attributed to the initiation of bubble formation, which caused the a-axis resistivity to increase. The formation of microcracks between the graphite layers also occurred, but it has little effect on the a-axis resistance.

This work revealed that the initiation of bubble formation is a partially reversible process in the first two cycles and is completely reversible in subsequent cycles. This process gives rise to a tensile stress along the c-axis of 10^6 Pa. Moreover, it causes the c-axis electrical resistivity to decrease and the a-axis resistivity to increase, even when exfoliation is constrained from occuring.

The initiation of bubble formation can be driven by electrical power, which is converted to heat and mechanical energy. Of practical significance is the high tensile stress produced. This paper has provided the first observation of this electromechanical effect, which may be exploited in electromechanical devices.