

ELECTRICAL RESISTIVITY OF GRAPHITE NITRATES
F. Lincoln Vogel, Claude Zeller* and W.C. Forsman
College of Engineering and Applied Science and
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Introduction

Intercalation of acid molecules into the graphite lattice produces a lamellar compound, which for the case of nitric acid has the formula C_6nHNO_3 where n =stage of the compound. The formation of the lamellar compound invariably results in a decrease in the "a" axis resistivity over that of pristine graphite. This change on intercalation of graphite has been examined in some detail by several groups all employing the same general method, that is, four point resistivity measurements on highly oriented pyrolytic graphite (HOPG) performed in situ. The generally accepted value for in-plane resistivity of pure graphite is $4 \times 10^{-5} \Omega \text{cm}$ (1) Ubbelohde (2) reported values of $4 \times 10^{-6} \Omega \text{cm}$ for 1st and 2nd stage graphite in one series of experiments, and the same for stages 1 to 3 in another set of experiments (3). Fuzellier and Herold (4) reported lower values of $2.1 \times 10^{-6} \Omega \text{cm}$ for stage 2 and $2.2 \times 10^{-6} \Omega \text{cm}$ for stage 1. Since these are lower than any reported in the literature there is some reason to question them. Thompson, (5) using essentially the same techniques as the others reports $4.9 \times 10^{-6} \Omega \text{cm}$ with stage 2 and 3 being indistinguishable.

Recent work on SbF_5 - and

*Visiting Scholar from University of Nancy, France.

AsF_5 -intercalated graphite (6) revealed that the anisotropy that develops in acid intercalated compounds and the difficulty in forming suitable electrical contacts leaves the four point resistivity method open to serious question. An adequate solution to this problem has been found in an r.f. induction method (7) of measuring in-plane resistivities and so it seems advisable to re-examine the graphite nitrates with this technique.

Intercalation and Deintercalation Procedures

Graphite samples $0.2'' \times 0.2'' \times 0.01''$ thick were cut and cleaved from HOPG kindly supplied by Dr. Arthur Moore of Union Carbide Corporation. These were intercalated in vapor from 100% nitric acid made by distilling a mixture of KNO_3 and concentrated sulfuric acid. The apparatus was similar to that used by Ubbelohde having a reaction chamber containing a quartz spring balance and a means of controlling its temperature. It is connected by a manifold to the trapped vacuum pump or the temperature controlled nitric acid source or the purified nitrogen source. In operation, the sample is put in place on the pan of the balance, warmed in vacuum (10^{-3} torr) overnight. Intercalation takes place by admitting HNO_3 vapor to a

pressure determined by the temperature of the source and following the reaction by weight gain. Deintercalation is made to occur by first admitting N₂ to atmospheric pressure and then evacuating. Stage as determined by weight gain and x-ray diffraction agreed. It was possible, by means of a glove bag surrounding the reaction chamber, to transfer a sample to measurement vial without exposure to air.

Electrical Resistivity Measurements

Details of the measurement technique are given elsewhere (7). It consists of a ferrite core as part of a resonant circuit operating at 100 KHz. Inserting the sample into an air gap in the ferrite core produces a change in the resonant frequency which is a measure of the resistance of the sample. From the known geometry of the sample the resistivity can be calculated.

Results

In the work reported here only stage 2 and stage 4 compounds will be dealt with. The stage 2 compounds were made by direct intercalation only whereas the stage 4 compounds were made either by deintercalation of a stage 2 compound or by direct intercalation. The stage 2 compounds had in-plane resistivity values $\rho_a = 3.0 \times 10^{-6} \Omega \text{cm}$ while the stage 4 compounds had in-plane resistivity values $\rho_a = 2.9 \times 10^{-6} \Omega \text{cm}$. The stage 4 compounds were lamellar regardless of whether formed by intercalation or deintercalation.

Acknowledgement

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References

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