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Dynamics of Graphite Fiber Intercalation: In Situ Resistivity Measurements with a Four Point Probe

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DYNAMICS OF GRAPHITE FIBER INTERCALATION: IN SITU RESISTIVITY

MEASUREMENTS WITH A FOUR POINT PROBE

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SUMMARY

The dynamics of ferric chloride intercalation of single graphite fibers were studied, in situ, using a four point dc bridge. Measurements before, during, and after the intercalation showed that the intercalation occurred within minutes at 200 °C. Changes in fiber resistivity after exposure to air suggested hydration of the graphite intercalation compound. Deintercalation of the ferric chloride was initiated at temperatures in excess of 400 °C. Cycling the intercalant into and out of the graphite fiber gave no improvements in fiber resistivity. The activation energy of the ferric chloride intercalation reaction was found to be 17±4 kcal/mol, consistent with the concept of a preliminary nucleation step in the intercalation reaction.

INTRODUCTION

There has been considerable interest in preparing graphite intercalation compounds from commercially available graphite fibers, particularly in the fabrication of cables and composites (ref. 1). These conductive cables and composites may find extensive use in the aerospace industry due to their lightweight, high strength characteristics. Production of intercalated graphite cables and composites requires a thorough understanding of fiber intercalation and deintercalation dynamics. There have been a number of methods developed to study the intercalation process in situ; including changes in mass, sequential x-ray scans, Raman spectroscopy, and various electronic methods such as the four point dc bridge and the RF induction method (refs. 2 to 5). The four point dc bridge method was chosen over the others for its simplicity (ref. 6). With this method, one can easily observe the changes in fiber resistivity that occur upon intercalation and those that occur upon subsequent treatment, such as exposure to the atmosphere or repeated cycling of the intercalant.

This paper presents the results of in situ resistivity measurements on single Union Carbide P-100 graphite fibers during several different ferric chloride intercalation experiments. The P-100 fibers were chosen because of their commercial availability and their superior tensile strength and electrical conductivity (ref. 7). Ferric chloride was chosen as the intercalant because it has been used by many researchers in the field of intercalated graphite, and it has been reported to be stable in air for periods up to three years without destaging (ref. 8). Based on the results of this investigation, the paper was divided into three main topics: (1) stability of $FeCl_3$-intercalated fibers in moist air, (2) the effect of intercalant cycling on fiber resistivity, and (3) the interpretation of several fiber resistivity versus time curves.

APPARATUS AND PROCEDURE

The $FeCl_3$ intercalations were performed in an all-glass flow-through reaction vessel, shown schematically in figure 1. Four platinum wires, protruding through the glass, served as current and voltage leads in the conventional four point measuring arrangement. The fiber was attached to the four Pt leads via colloidal carbon paint (Structure Probe, Inc.). A Keithley model 225 current source supplied a constant current to the outer leads while a Keithley model 181 nanovolt meter monitored the voltage drop across the inner leads. The dimensions of the fiber were estimated from microscopic inspection at 300X. Scanning electron micrographs of certain fibers before and after some preliminary intercalations showed little to no expansion of the fibers (less than a 5 percent change in diameter). Expansion of the fiber upon intercalation was therefore neglected in the resistivity calculations. In all cases, the current in the fiber did not exceed 1 mA.

The three-way stopcocks connected to either end of the flow-through system allowed the direction of gas flow to be changed as needed. This arrangement was necessary for the intercalant cycling experiments. Either nitrogen or chlorine gas could be directed into the intercalation chamber.

The $FeCl_3$ used in these experiments (AESAR, anhydrous, 98 percent) was dried at 100 °C overnight, under a stream of dry nitrogen (obtained by passing compressed nitrogen through a drierite cartridge). To initiate the $FeCl_3$ intercalation, a small stream of chlorine (approximately 5 ml/min) was established in the reaction vessel and each zone of the furnace was incremented to the desired temperature. The graphite zone of the furnace was brought up to temperature before the intercalant zone so that changes in resistivity induced by changes in temperature would not interfere with the experiment. At these temperatures, the intercalation was completed within minutes. At the end of the experiment, the reaction tube was cooled to obtain the final room temperature resistivity.

RESULTS AND DISCUSSION

Stability of $FeCl_3$ - Intercalated Fibers in Moist Air

This section presents estimated resistivity values obtained before, during, and after a ferric chloride intercalation of P-100 fibers. In addition to the changes in resistivity observed during the intercalation step, changes were also recorded while the fiber was exposed to moist air, heated under dry nitrogen, or kept under ambient laboratory conditions for several months.

Data for the estimated resistivity of a single P-100 fiber over three different experimental conditions, are presented in figure 2. The first time interval represents the intercalation process. According to the in situ resistivity measurements, the intercalation of the P-100 fiber ceased in less than 5 min. These results are similar to results obtained by Endo et al. (ref. 9) for nitric acid intercalation of benzene derived fibers. A surprising feature of figure 2 is the near linear response during the intercalation process. During intercalation, one might expect various plateaus in the resistivity curve each corresponding to different stages; however, this was not the case. The initial linear response shown in figure 2 may be indicating

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rapid intercalation of the perimeter of the fiber (to some mixed stage), with little penetration of the intercalant to the center of the fiber. Hazrati, Olk, and Eklund (ref. 10) have observed such spatial distribution of $SbCl_5$ in pitch-based fibers heat treated to 2500 °C. X-ray analysis of $FeCl_3$-intercalated GM-3000 fibers, prepared in a similar fashion, has indicated regions of pristine graphite within the fibers (ref. 11). Little fiber expansion, as seen in preliminary experiments, is consistent with this argument. On the other hand, the abrupt stop in resistivity, as shown in figure 2, may be indicating complete intercalation of the fiber. The exceptionally low final resistivity value is consistent with this argument. In any case, upon cooling to room temperature, the resistivity of the fiber was 5.8 percent of the initial room temperature value.

The second time interval of figure 2 illustrates the stability of the $FeCl_3$-intercalated fiber over a period of several hours. Note that the fiber was kept under dry nitrogen during this step. There was not detectable change in fiber resistivity over this time period.

The third time interval of figure 2 shows the changes in fiber resistivity immediately after the reaction vessel was opened to the laboratory atmosphere. Over a period of 80 min, the resistivity of the fiber increased from 5.8 to 32 percent of its original value. One possible explanation for the observed increase in fiber resistivity is deintercalation. However, the nonexponential shape of the resistivity versus time curve and the absence of deintercalation during the much longer dry nitrogen step, suggest a different explanation. Upon exposure to air, the $FeCl_3$ in the $FeCl_3$-intercalated fiber must have acquired some waters of hydration. This is contrary to the observations made by Millman (ref. 8). The water of hydration may supply electrons to the embedded $FeCl_3$, reducing the effect of $FeCl_3$ on the graphite host material.

To test this idea, a $FeCl_3$-intercalated fiber, which had been exposed to moist laboratory air for several days after intercalation, was heated incrementally under dry nitrogen to drive off the waters of hydration (t = 20 min per increment). The results from this experiment are summarized in figure 3. There are two noteworthy features in figure 3. The first is a marked drop in fiber resistivity in the vicinity of 150 °C. This drop signals the loss of water from the graphite intercalation compound. Once all of the water has been driven out (at about 200 °C), the intercalated fiber regains its metallic-like behavior and the resistivity increases linearly with temperature. The second noteworthy feature is the deviation from linearity in the vicinity of 425 °C. This deviation is most likely due to a true loss of $FeCl_3$ from the graphite intercalation compound.

Figure 4 presents some long-term stability data for $FeCl_3$-intercalated P-100 fibers. The initial resistivity values in this figure were obtained after several hours of exposure to the air, so they represent the resistivity of the hydrated graphite intercalation compound. The data clearly show an upward trend in fiber resistivity with time. However, it is not clear at this point whether the upward trend is due to a true loss of intercalant or to continued hydration of the graphite intercalation compound.

Intercalant Cycling

One of the problems of intercalating these pitch-based fibers is that the intercalant does not always penetrate to the core of the fiber. Eklund (ref. 10) has shown this problem in $SbCl_5$-intercalated pitch-based fibers initially heat treated to 2500 °C. If there are regions of pristine graphite, then the degree of intercalation may be improved through intercalant cycling. Hooley (ref. 12) has shown that cycling $FeCl_3$ into and out of "large" graphite flakes improved the penetration of the $FeCl_3$ until a maximum expansion was achieved. This maximum expansion was similar in magnitude to the expansion observed in a single $FeCl_3$ intercalation using "small" flakes. Unfortunately, no data were available to show the trends in resistivity as a function of intercalant cycling. To address this hypothesis, the resistivity of a P-100 fiber was monitored during a complete $FeCl_3$ intercalation/deintercalation cycle, without exposure to moist air.

The flow-through arrangement described previously was used to perform the cycling experiments. Intercalant vapor (at 230 °C) was directed into the chamber holding the graphite fiber (at 230 °C) by a flow of chlorine gas. When intercalation had ceased, the chlorine gas was replaced with nitrogen gas, and the direction of flow was reversed to remove the intercalant vapor. A continuous flow of nitrogen throughout the rest of the experiment prevented contamination by moist air. After cooling to room temperature, the deintercalation was initiated by heating the fiber to 425 °C. When no further increases in fiber resistance were observed, the fiber was cooled again to room temperature and the intercalation procedure was repeated. The results from the cycling experiment are summarized in table I.

The room temperature resistivity values in table I clearly show that the resistivity of the fiber dropped after the first intercalation (from 250 to 60 $\mu\Omega$-cm). The first deintercalation, however, resulted in a net increase in fiber resistivity (from 60 $\mu\Omega$-cm to 470 $\mu\Omega$-cm). During the second intercalation, the resistivity got even worse. These results suggest that either the process of intercalation or deintercalation (or both) caused irrepairable damage to the graphite lattice. The added defects caused an increase in resistivity greater that the decrease in resistivity obtained by intercalation. It is difficult to say which of the two processes is responsible for the added defects. Forsman (ref. 13) has indicated that the deintercalation step (in HNO_3 intercalated fibers) is accompanied by the evolution of carbon monoxide and carbon dioxide. The only source of carbon for these species would be the graphite lattice. To obtain maximum performance from a GIC, the intercalation process should proceed at a rate that produces the minimum number of defects in the graphite lattice. (Presumably, the slower the rate, the fewer the defects.) This is an area for future study. In any case, the results from this experiment suggest that one loses more than one gains by intercalant cycling.

Fiber Resistivity Versus Time

The use of the four point method to monitor the progress of intercalation in graphite fibers as a function of time is not new. Forsman (ref. 14) has studied the HNO_3 intercalation of P-100 and GY-70 fibers. Endo (ref. 9) has used the four point method to study the HNO_3 and Br_2 intercalation of benzene derived fibers. Kalin and Goldberg (ref. 15) used a two point method

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to study bundles of PAN fibers during AsF_5 and SbF_5 intercalation. One thing is evident from the data reported in the literature; there are considerable variations in the rates of fiber intercalation, from one kind of fiber to another, and particularly from one intercalant to another. Hence, it is important to understand the dynamics of the particular system being investigated. To this end, a suite of experiments were performed with two purposes in mind: (1) to vary the experimental conditions of intercalation in order to "slow" the $FeCl_3$ intercalation to a point where the details of the resistance versus time curve could be seen, and (2) to gather enough kinetic information to construct an Arrhenius plot and calculate the activation energy of the intercalation reaction.

In this section, the resistance versus time results of one zone experiments performed at different temperatures will be discussed. The temperature range of interest was from 160° to 200 °C. As shown in figure 5, the lower the temperature, the slower the rate of intercalation. This was expected. By slowing the rate of intercalation, it was thought that incremental changes in resistivity due to staging would be seen. However, this was not the case. Rather, the initial changes in resistivity were basically linear until the equilibrium resistivity value was attained. The perturbation in the 160 °C data was attributed to fluctuations in the furnace temperature during that particular experiment.

Not only did the rate of intercalation increase with increasing temperature, the degree of intercalation (either penetration or stage or both) also increased with increasing temperature. The final room temperature resistivity ratios from a number of one zone experiments were plotted as a function of intercalation temperature in figure 6. Note that the maximum degree of intercalation occurred at a temperature of about 200 °C. Further increases in intercalation temperature gave no further decreases in resistivity.

To calculate the activation energy for the $FeCl_3$ intercalation of P-100 fibers, a two zone method was used in which the temperature of the intercalant (and therefore its vapor pressure) was held constant and the temperature of the graphite fiber was varied from one experiment to the next. The log of the slope of the initial rapid decrease in resistivity (normalized to the room temperature resistivity value) was plotted against 1/T to yield an Arrhenius plot. From this diagram an activation energy for the rapid initial reaction phase was obtained. The results are summarized in figure 7. Although the data are somewhat scattered because they are derived from multiple fibers, the activation energy for the rapid initial phase was approximately 17 kcal/mol.

There have been a number of models proposed to explain the kinetics of intercalation. Barker and Croft (ref. 16) proposed a kinetic model based on simple diffusion of the intercalant. For the $FeCl_3$-graphite flake system, they found the activation energy for diffusion to be 2 to 3 kcal/mol. Metz and Siemsglüss (ref. 17) proposed a kinetic model for the $FeCl_3$ intercalation of graphite flakes in which nucleation at the edges of the graphite crystal occurred first and then islands of intercalant grew into the layered structure. The apparent activation energy for nucleation was 25 kcal/mol. Dziemianowicz and Forsman (ref. 14) recently proposed a model incorporating both nucleation and and diffusion. The apparent activation energy of 17±4 kcal/mol observed

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in the current set of experiments may be suggesting that the FeCl$_3$ intercalation of P-100 fibers follows a model incorporating nucleation followed, perhaps, by diffusion. The observed activation energy approaches the value measured by Metz and Siemsgluss. Unfortunately, the lower activation energy required for the secondary diffusion step, as suggested by Barker and Croft, would be obscured by the larger activation energy of the nucleation step.

CONCLUSIONS

The four-point dc bridge method was used to study the FeCl$_3$ intercalation and deintercalation dynamics of Union Carbide P-100 fibers. Intercalation of the fiber was rapid, with the reaction reaching completion within minutes. The rapid linear drop in fiber resistivity may reflect rapid intercalation of the perimeter of the fiber, while the interior of the fiber remained unchanged. Exposing a FeCl$_3$-intercalated fiber to moist air caused a noticeable increase in fiber resistivity. This increase was not interpreted as deintercalation, but was attributed to hydration of the FeCl$_3$ in the graphite intercalation compound. Apparently, the waters of hydration interfere with the extraction of electrons from the graphite lattice. Heating a hydrated FeCl$_3$-intercalated fiber to 150 °C effectively removed the waters of hydration, and continued heating to 425 °C caused true loss of FeCl$_3$ intercalant. Increases in intercalated fiber resistivity over the long term are somewhat ambiguous, reflecting either true deintercalation, or further hydration, or both. Moisture from the atmosphere may be a necessary prerequisite for the room temperature loss of FeCl$_3$ from a FeCl$_3$ graphite intercalation compound.

Cycling the intercalant into and out of the graphite lattice caused more losses than gains with respect to fiber resistivity. Apparently, the intercalation process or more likely the deintercalation process caused an increase in fiber defect resistivity which superseded the improvements in resistivity obtained by intercalation.

Finally, fiber resistivity versus time data from a number of FeCl$_3$ intercalation experiments has shown that initial resistivity changes occur in a linear fashion. The apparent activation energy, estimated from a Arrhenius plot, was found to be 17±4 kcal/mol. The observed changes in resistivity suggest that the intercalation reaction proceeds via a model incorporating nucleation, and perhaps, diffusion. The apparent activation energy was consistent with the literature values reported for the activation energy of nucleation. The apparent activation energy for the diffusion step, however, was obscured. From the suite of temperature data, it could also be seen that the optimum temperature for FeCl$_3$ intercalation of a single P-100 fiber was in the vicinity of 200 °C. Higher reaction temperatures gave no further decreases in fiber resistivity at room temperature.

Although the changes in room temperature resistivity upon intercalation are rather substantial (an improvement of about 20 fold) the practical applications of FeCl$_3$-intercalated P-100 fibers would probably be limited to non-humid environments. Preparation of the fibers in a single intercalation step would be preferred over intercalant cycling. To obtain the greatest changes in resistivity, the FeCl$_3$-intercalation reaction should be performed slightly in excess of 200 °C.

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TABLE I. - ESTIMATED RESISTIVITY VALUES FOR A P-100 FIBER
SUBJECTED TO AN INTERCALATION/DEINTERCALATION CYCLE
WITH $FeCl_3$

Conditions	Estimated[a] resistivity	
Before first intercalation, at 25 °C	250 μΩ-cm	
Before first intercalation, at 230 °C		160 μΩ-cm
After first intercalation, at 230 °C		60 μΩ-cm
After first intercalation, at 25 °C	60 μΩ-cm	
Before first deintercalation, at 425 °C		90 μΩ-cm
After first deintercalation, at 425 °C		210 μΩ-cm
After first deintercalation, at 25 °C	470 μΩ-cm	
Before second intercalation, at 230 °C		1100 μΩ-cm
After second intercalation, at 230 °C		740 μΩ-cm
After second intercalation, at 25 °C	1200 μΩ-cm	

[a] Based on a constant fiber diameter of 10 μm
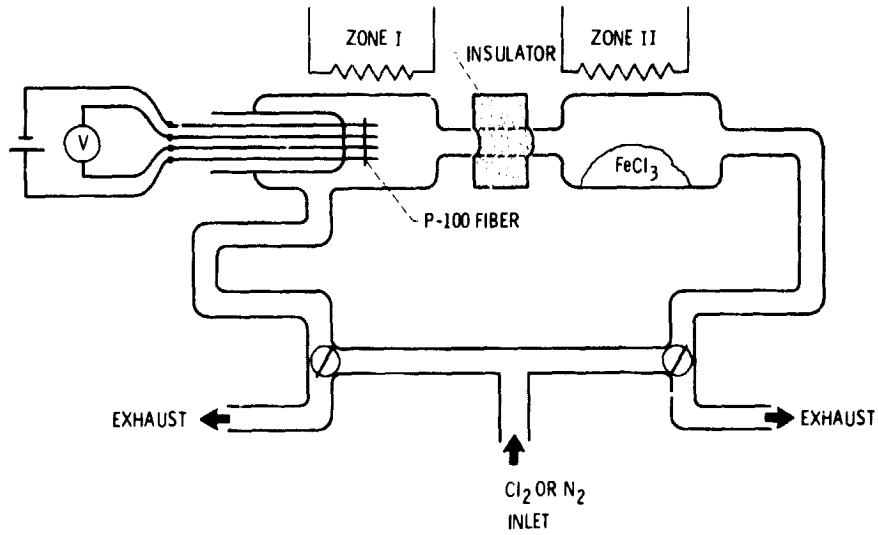
Figure 1. - Schematic diagram of the flow-through reaction vessel, with the in situ four point probe.
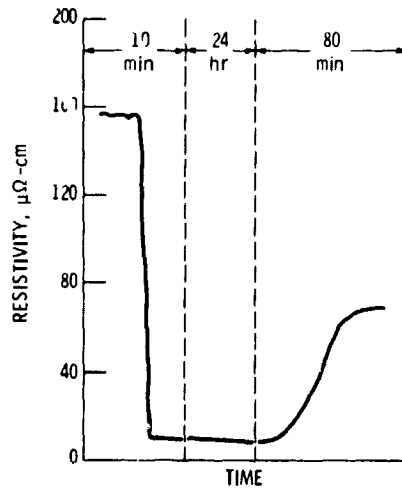
Figure 2. - Changes in resistivity of a P-100 fiber over three conditions: (1) during a 10 min intercalation with $FeCl_3$ at 200° C., (2) under dry nitrogen for 24 hr at 25° C, and (3) exposed to moist laboratory air for 80 min at 25° C.
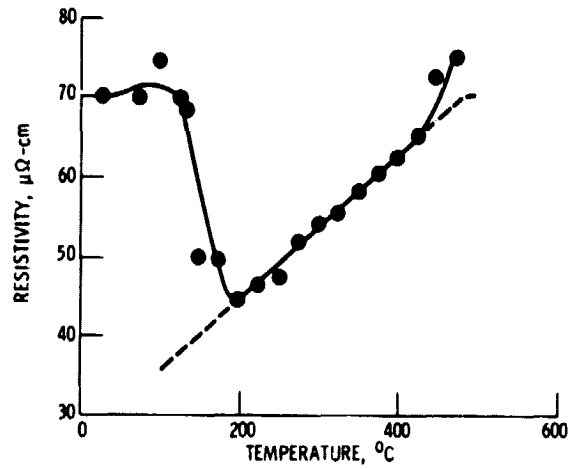
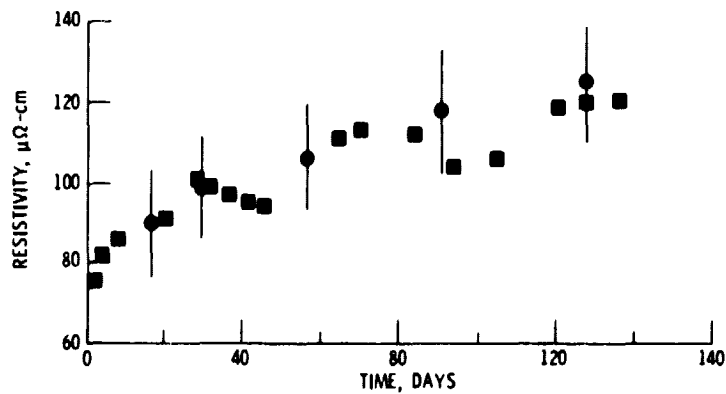Figure 3. - Variation in resistivity of a hydrated FeCl$_3$-graphite intercalation compound, as a function of increasing temperature.

Figure 4. - Variation in fiber resistivity for over 120 days. Squares represent data collected from a single fiber. Circles represent the average of five fibers. Error bars reflect the standard deviation observed in the five fibers. Resistivity values for the suite of five fibers were obtained by J. Gaier, NASA Lewis Research Center.
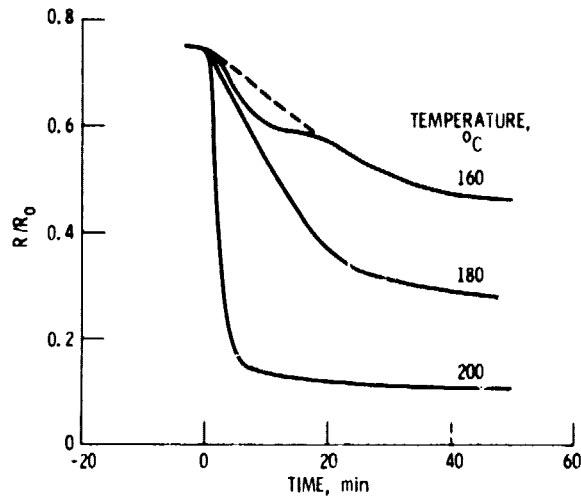
Figure 5. - Resistance ratio vs. time for several FeCl₃-intercalated P-100 fibers. Both the intercalant and the fiber were kept at the highlighted temperatures.
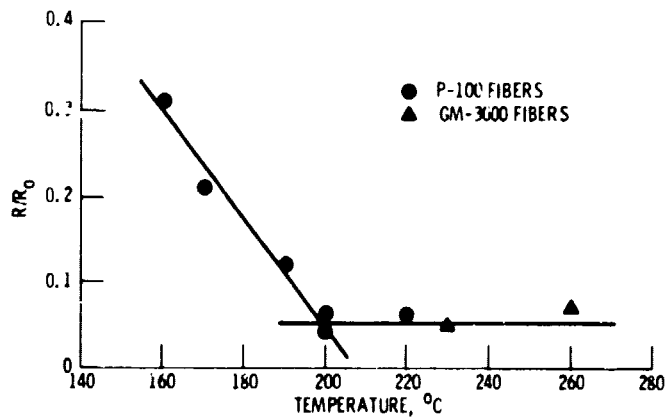

Figure 6. - Final room temperature resistance ratios of FeCl₃-intercalated fibers at a number of one zone reaction temperatures. Exposure time was in excess of 30 min.
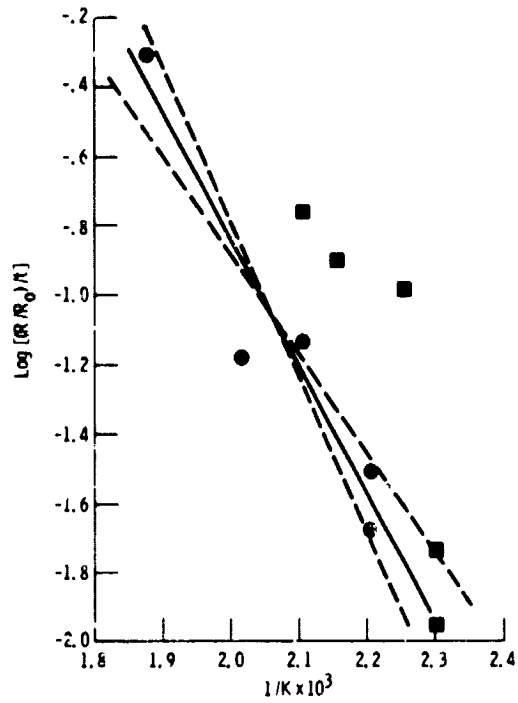
Figure 7. - Arrhenius plot of the initial rate of $FeCl_3$-intercalation of single P-100 fibers. (Circles represent two zone experiments with the $FeCl_3$ held at 180° C, squares represent one zone experiments where the intercalant and the fiber were kept at the same temperature.) Solid line is the least squares fit of the data represented by the circles.