

POSTER

TEMPERATURE DEPENDENCE OF THE INTERCALATION OF BROMINE INTO PITCH-BASED FIBERS

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INTRODUCTION

Bromine intercalated pitch-based graphite fiber composites have been proposed as a substitute for aluminum in electromagnetic interference (EMI) shielding covers for weight critical applications.¹ Because of their exceptionally high strength and modulus, and their low density, a simple swap-out of covers could save in excess of 80 percent of the cover mass. Since covers comprise about 20 percent of the power system mass in a typical spacecraft, this reduction in the power system mass and corresponding increase in payload mass is significant.

Before a bulk use of intercalated graphite can be initiated, the reaction must be scaled from typical laboratory experiments, which range in scale from single filament to mg quantities, to kg quantities. Although there has been significant progress in this area², the basic intercalation reaction is not well understood, and that lack of understanding has hindered progress.

The bromine intercalation reaction has an unusual temperature dependence³. Bromination proceeds at low temperature more readily than at high. In fact, there exists a threshold temperature above which intercalation will not occur. This temperature is dependent upon the degree of graphitization of the fibers, with more highly graphitized fibers having higher threshold temperatures. Further, the temperature dependence is not simply due to vapor pressure effects. It was found that P-100 fibers will intercalate at -23 °C, where the vapor pressure of bromine is about 13 torr, but will not intercalate at room temperature with a 13 torr vapor pressure of bromine. Finally, pitch-based graphite fibers react only to form a single intercalation compound. Whether P-100 is intercalated with bromine at 45 °C or -23 °C, the result is always a stage 3 compound with a resistivity of about 50 $\mu\Omega$ -cm.

These unusual thermodynamic properties prompted this investigation into the temperature dependence of the dynamics of this reaction. The goal was twofold. An understanding of the reaction kinetics would shed light on the nature of the intercalation process of imperfectly ordered carbons, and perhaps on the nature of the bonding in bromine graphite intercalation compounds. Also, the determination of the optimum intercalation conditions would facilitate efficient mass production of this material.

EXPERIMENTAL

Thornel P-100 fibers (Amoco) were selected for this study because of their electrical properties, availability, and the extensive data base on their reaction with Br₂ vapor and the resultant intercalation compound. The progress on the intercalation reaction was monitored *in situ* using the four-point resistance of the fiber. This has shown to be a very sensitive indicator of the extent of reaction. The apparatus has been described in detail elsewhere⁴

Two different methods were employed in an attempt to garner reproducible data. In the first, a fiber was mounted on four platinum wires, brought to reaction temperature, and submerged in Br₂ vapor at the same reaction temperature. The vapor was maintained by a reservoir of Br₂ liquid. The *in situ* resistance of the P-100 fiber was measured continuously and recorded in intervals of a few seconds.

The reproducibility of these experiments was judged to be poor, however, and in an effort to improve it a second suite of experiments was performed. In this set of experiments, the fiber was periodically withdrawn from the Br₂ vapor and placed in a tube maintained at the reaction temperature until the resistance value stabilized, after which the measurement was recorded. The fiber was then resubmerged in the Br₂ vapor for the next time interval. Time recorded was the total time that the fiber was exposed to the Br₂ vapor.

It has been shown that when graphite is removed from the bromine environment that bromine quickly degasses from the surface.⁴ Thus, the second set of experiments was not entirely comparable to the first because there was a cycling in and out of the bromine from the surface layers of the fibers. Previous experiments have shown that the cycling of bromine in and out of P-100 fibers does not improve the extent of intercalation, and in fact, damage done to the fiber by this cycling results in a fiber with somewhat higher resistivity.⁵

The temperature was varied over most of the liquid range of Br₂ from 0 °C to 45 °C, in increments of 5 °C. Reaction at temperatures higher than 45 °C did not result in intercalation. Intercalation did occur at temperatures as low as -23 °C, but neither *in situ* nor interrupted measurements were carried out below 0 °C.

RESULTS AND DISCUSSION

Initially, one fiber for each temperature was intercalated using the continuous method. The measurement was fraught with difficulties, especially when experiments below room temperature were attempted. *In situ* fiber resistances in many cases were either unchanged or increased. After the fiber was removed from the Br_2 , the fiber resistance would rapidly drop to values expected for Br_2 intercalated P-100. After a series of resistance as a function of time curves were generated which seemed reasonable, that is, the resistance fell over time and there was no large drop upon removing the fiber from the Br_2 , no obvious trend in the temperature dependence was observed.

At this point the issue of reproducibility was addressed by measuring the *in situ* resistance of several fibers at the same temperature. The resulting resistance curves showed more variation from fiber to fiber than from temperature to temperature. Figure 1 shows the mean time to intercalation $\pm \sigma$ (defined as $\rho = 0.3 \rho_0$) for several fibers at different temperatures.

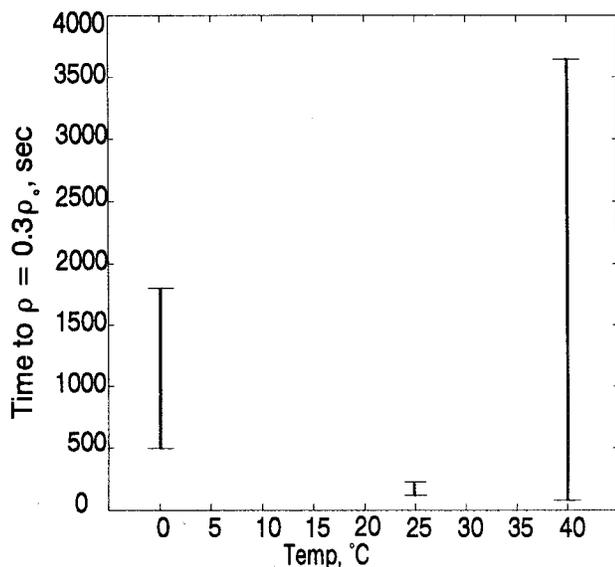


Figure 1 -- Time of intercalation in Br_2 vapor as a function of temperature in *in situ* experiments.

The interrupted intercalation reaction was tried in an attempt to generate more reproducible data. Since the resistance seemed to return to a reasonable value when the fiber was removed from the Br_2 , it was thought that perhaps the Br_2 was interacting with the measurement circuit in such a way as to generate spurious readings.

When a family of resistance as a function of time curves at varying temperatures was generated, there

seemed to be a random distribution. Once again, when several trials at the same temperature were measured, the variation was as great as among those with temperature differences (Figure 2).

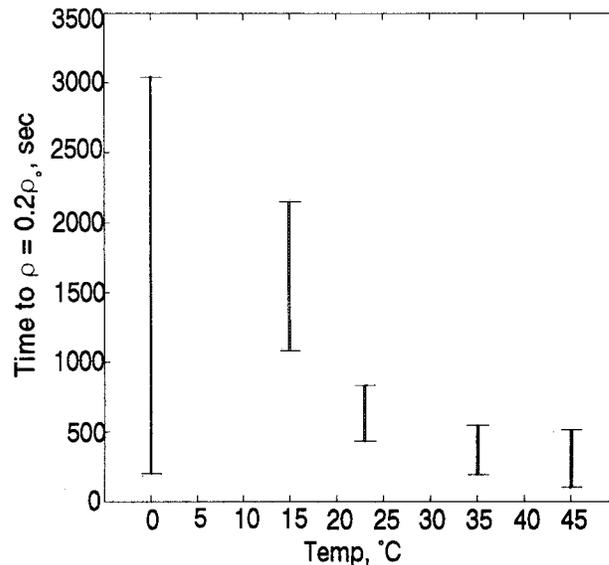


Figure 2 -- Time of intercalation in Br_2 vapor as a function of temperature in interrupted experiments

CONCLUSIONS

The Br_2 intercalation dynamics for P-100 graphite fibers was studied over a temperature range of 0 - 45 °C using *in situ* resistance measurements as an indicator of intercalation. It was found that the fiber to fiber variation was greater than the temperature dependent variation. There seems to be no kinetic advantage to using either a higher or a lower temperature intercalation in this system.

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