

The Effect of Intercalation Rate on Bromine Intercalated Graphite Fiber Quality

by

Donald A. Jaworske
NASA Lewis Research Center
Cleveland, Ohio 44135

Introduction

The demonstration of long term stability of bromine intercalated P-100 fibers has prompted additional investigation of this intercalated fiber material.¹ To find the optimum conditions for bromine intercalation, the progress of the intercalation reaction was monitored, in situ, with a four point probe. The partial pressure of bromine was varied from 93 to 208 torr and the resulting changes in fiber resistance were recorded over time.

Methods

The in situ resistance measurements were made on Union Carbide P-100 fibers, initially 250 $\mu\text{ohm-cm}$. Each was mounted on an oxidation resistant sample holder, which in turn, was placed in an all glass reaction vessel. Platinum wires connected the sample holder to the electronics in the conventional four point configuration. The vapor pressure of the bromine was controlled by the temperature of the bromine reservoir, and the chamber holding the graphite was held at room temperature. To initiate the intercalation, nitrogen was directed into the bromine chamber and the nitrogen-bromine mixture was then directed into the reaction chamber. After exiting, the gas mixture was directed into a gas scrubbing bottle for disposal. When the desired fiber resistance had been reached, the bromine vapor was flushed from the chamber with pure nitrogen.

Results and Discussion

The rate of intercalation, as measured by the four point method, depended on the vapor pressure of the bromine, providing the vapor pressure was above the threshold pressure.² Resistance vs. time curves for a "rapid," a "slow," and "no" intercalation (for bromine reservoir temperatures of 24.3, 12.2, and 7.8 $^{\circ}\text{C}$ respectively) are shown in figure 1. Experiments performed at intermediate temperatures showed no clear trends

between reaction rate and vapor pressure, suggesting that the flow rate of bromine or surface variations from fiber to fiber may be important in characterizing the rate of reaction. One surprising feature exhibited by this set of data was the downward trend in resistance (illustrated by the 12.2 $^{\circ}\text{C}$ data) that occurred after the initial rapid decline in resistance had taken place. This downward trend was observed in other bromine experiments, to various degrees. Such a downward trend was not observed in similar ferric chloride experiments, where the resistance value reached a plateau.³ As a result of this downward trend, most of the bromine intercalated P-100 fibers eventually reached the same degree of intercalation, as measured by the four point probe. Another surprising feature was the increase in resistance that occurred as the bromine was purged from the reaction vessel (as illustrated by the 24.3 $^{\circ}\text{C}$ data). This upward trend in resistance was observed in every case, to varying degrees; and was tentatively attributed to loss of bromine from the perimeter of the fiber.

Vapor pressure values were estimated from the bromine temperature, based on equation 1.⁴

$$\log_{10} p_{\text{Br}_2} = 5.82 - 638.25 / (T + 158) \quad (1)$$

Summarized in figure 2 are the final resistance ratios, obtained while the fiber was in equilibrium with either nitrogen (A) or bromine (B), as a function of bromine vapor pressure. The threshold pressure was about 102 torr. This value was somewhat larger than the value of 53 torr given by Hooley for pyrolytic graphite cylinders with similar numbers of exposed graphite layers.²

The increases in resistance, which occurred after the bromine vapor was swept from the reaction chamber, are summarized by figure 3. The data in this figure do not describe a linear relationship, rather, the fibers apparently regain a greater

fraction of their resistivity during the nitrogen purge step when they are not fully intercalated initially. To model this curvilinear behavior, the cross sectional area of a hypothetical fiber (with a radius of $5.5 \mu\text{m}$) was divided into three annular regions. The value of the resistivity for the inner region was varied from 0 to $250 \mu\text{ohm-cm}$; the value of the resistivity for the outer region was either the same as the inner region, for a surrounding bromine atmosphere, or $250 \mu\text{ohm-cm}$, for a surrounding nitrogen atmosphere; and the value of the resistivity for the intermediate region was between the value of the inner region and the outer region. The best fit of the experimental data (as shown by the solid line in figure 3) was obtained when the three annular regions were separated by interfacial radii of $2.5 \mu\text{m}$ and $3.5 \mu\text{m}$.

To confirm this model, the amount of bromine at several different locations across the diameter of a single bromine intercalated P-100 fiber was determined by energy dispersive spectroscopy (EDS). The results presented in figure 4 confirmed that some of the bromine in the outer skin was lost, however, the loss was not as severe as the model suggested.

Conclusions

Above a threshold pressure of 102 torr, the rate of bromine intercalation of single P-100 fibers varied from minutes to hours. Given enough time, the final resistivity value consistently reached

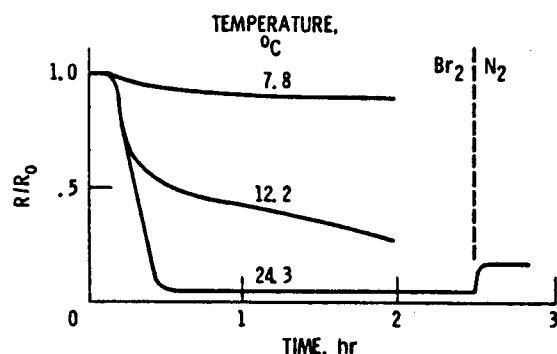


Figure 1. Resistance vs. time, at three bromine reservoir temperatures.

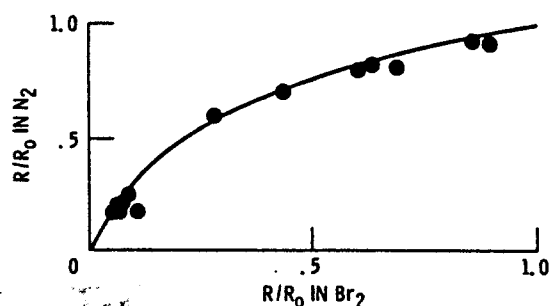


Figure 3. Increases in fiber resistance after the nitrogen purge.

about 7% of the pristine resistivity value. Minutes after the bromine gas was swept from the reaction chamber, the resistance ratio increased, suggesting a partial loss of bromine from the fiber. This increase resulted in a resistivity value approximately 18% of the pristine resistivity value. The increase in the resistance ratio was greater for fibers intercalated to a lesser degree. Mathematical modeling suggested that bromine was lost from the outer $2 \mu\text{m}$ of the fiber when the fiber was removed from the bromine environment. EDS analysis confirmed such a bromine gradient in the skin of the fiber, but the loss of bromine was not as great as the model suggested.

References

1. J. R. Gaier, "Stability of Bromine Intercalated Graphite Fibers," NASA TM-86859, Nov. 1984.
2. J. G. Hooley, W. P. Garby, and J. Valentin, "The Effect of Sample Shape on the Bromination of Graphite," *Carbon*, Vol. 3, pp. 7-16, 1965.
3. D. A. Jaworske, "Dynamics of Graphite Fiber Intercalation: In Situ Resistivity Measurements with a Four Point Probe," NASA TM-86858, Nov. 1984.
4. S. H. Anderson and D. D. L. Chung, "Thermodynamics of Intercalation of Bromine in Graphite," *Mat. Res. Soc. Symp. Proc.* Vol. 20, Elsevier Science Pub. Co., Inc., pp. 271-276, 1983.

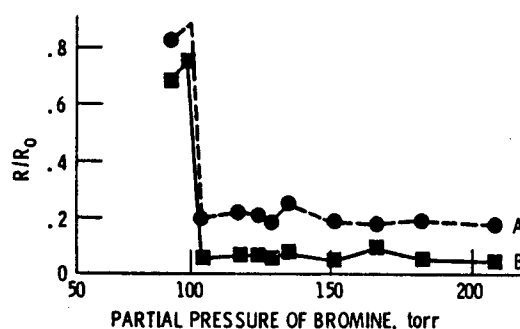


Figure 2. Final resistance ratios vs. bromine vapor pressure.

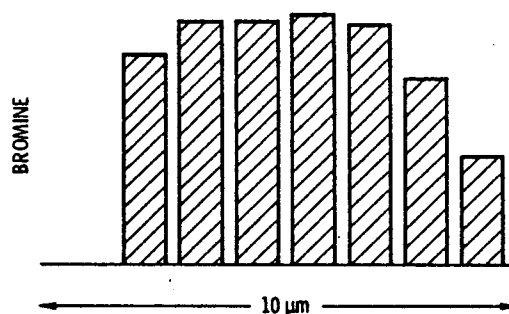


Figure 4. Bromine concentration across the diameter of a fiber.