

AQUEOUS ELECTROCHEMICAL INTERCALATION OF BROMINE INTO GRAPHITE FIBERS

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Introduction

Electrically conducting, high strength, high modulus composites are seen as having great potential, particularly in aerospace applications. One way to construct such composites uses highly graphitic fibers which have undergone intercalation, the insertion of guest atoms or molecules between the graphene planes of the fiber.

Graphite fibers have been intercalated by exposing the fibers to bromine vapor, liquid bromine, or in concentrated solutions of bromine in non-interacting solvents such as carbon tetrachloride. All of these methods involve direct contact with elemental bromine with all of the associated risk. Since the aqueous bromide ion ($\text{Br}^-_{(\text{aq})}$) is a stable and non-toxic species, it seems a logical starting point for a safer reaction route.

Electrochemical intercalation of bromine into graphite fibers starting from aqueous $\text{Br}^-_{(\text{aq})}$ was first demonstrated by Tillgner and Ruland [1] and Ho and Chung soon after reproduced the work [2]. Both studies showed strong evidence for at least partial intercalation, but the resistivity of even the best sample was 40 percent higher than typically obtained by vapor phase intercalation. Izumi *et al.*, studied the bromine intercalation of exfoliated graphite sheet and found that the most pronounced decrease in electrical resistivity occurred when the potential was high enough to promote the evolution of $\text{Br}_{2(\text{aq})}$, though the resistivity was still high[3]. But to meet the goal of a safer alternative bromine intercalation route, bromine intercalated graphite fibers with resistivity as low as that obtained by other methods but starting from aqueous $\text{Br}^-_{(\text{aq})}$ must be found.

Methods and Materials

The graphite fibers chosen as hosts for this study were highly graphitic pitch-based fibers produced by Cytec: ThorneI[®] K-1100, P-120, and P-100, with most of the work being done with the K-1100 fiber.

An initial body-centered cubic statistical design of experiments was used to optimize the reaction conditions [4]. For these experiments a 2.5 cm tow of fibers acted as the anode and a Pt wire as the cathode, with 1.00 M KBr as both the reactant and the supporting electrolyte. In the first iteration the time was varied from 15 sec to 15 min, the current from 200 mA to 2 A, and the temperature from 5 °C to 40 °C. A second set of experiments was designed around the low resistivity point of the first trial (15 min, 2 A, 5 °C). Final synthesis conditions from this set of experiments were to subject the fibers to 1.00 M KBr for 6.0 hr at 2 A current at 0 °C.

Success of intercalation was judged by x-ray diffraction and measurement of the four-point resistivity of the fibers. The stability of the intercalated fibers was tested by monitoring the resistance of the fibers at regular intervals over a period of several weeks.

Results

A comparison of the normal incidence x-ray diffraction photographs for pristine K-1100, K-1100 fibers that were intercalated using a vapor phase bromine method, and fibers that were subjected to the electrochemical conditions described above are shown in Figure 1. Note the presence of the diffraction rods in both the vapor phase intercalated and the electrochemically exposed fibers. This is unambiguous evidence for intercalation [1]. There are no differences between the two diffraction patterns, indicating not only that an intercalation compound was formed, but also that it is the same intercalation compound as is formed by the vapor phase reaction.

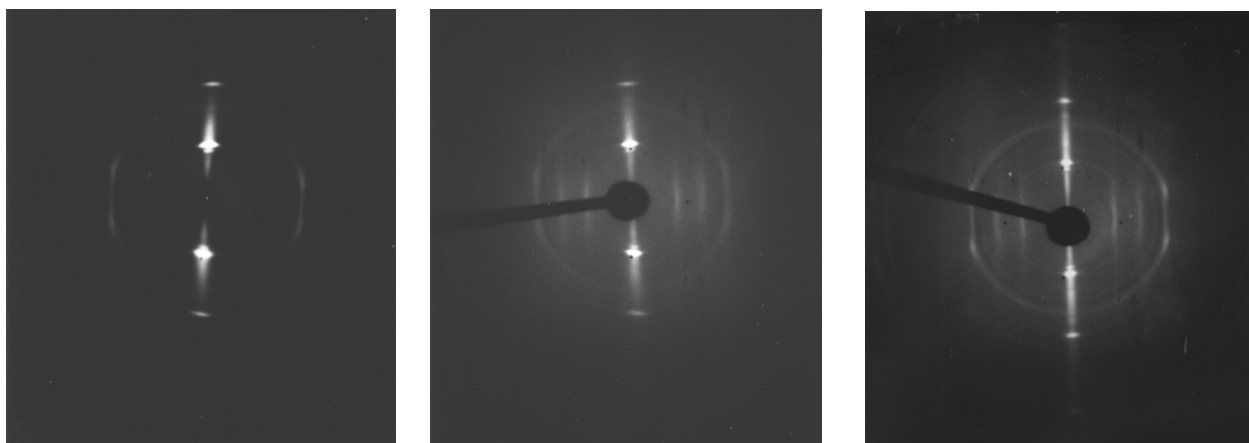


Figure 1-- Normal incidence photographs from (a) pristine P-100 fibers, (b) P-100 fibers treated with vapor phase bromine, and (c) P-100 fibers treated electrochemically. Note the presence of the diffraction rods in the pattern of bromine intercalated fibers.

The first suite of experiments showed dramatic drop in the resistivity only when the temperature was low, and the current was high for relatively long times (Fig 2). The low temperature is consistent with what is known about the free energy of the vapor-phase intercalation. It was surprising that such high currents (2 A) were required to get significant intercalation, especially in light of the fact that the limiting voltage (about 7.5 V) occurred at an order of magnitude lower currents. The second body-centered suite of experiments was set up around the low fiber resistivity point from suite 1 found that further lowering the temperature had no appreciable effect, and more than 2 A could not be applied to the system with the equipment available. It was found that longer times (6 hr) improved the homogeneity of the intercalation.

When longer fiber tows were used it was found that intercalation only occurred within the few cm closest to the electrode connections. Increasing the reaction time had little effect on the lengths of the intercalation zones. Decreasing the KBr concentration to 0.30 M KBr in 1.0 M NaNO₃, in order to slow down and even out the reaction enlarged the intercalation region, resulting in uniformly intercalated, low resistivity tow of fibers (Fig 3).

The success of intercalation was found to be dependent on the current rather than voltage. This implies that the reaction is not controlled by the energy barrier, but by the availability of reactant. We thus came to the hypothesis that the fiber, acting as the anode, oxidized Br[⊖](aq) to Br₂(aq). Once the Br₂(aq) concentration at the surface of the fiber exceeds some threshold concentration the free energy difference would cause the Br₂(aq) to intercalate. To test this hypothesis samples of K-1100, P-120, and P-100 were soaked in a saturated solution of liquid Br₂ in distilled water. The reactions were chilled to near the freezing point and allowed about 24 hr to react. X-ray diffraction analysis revealed that the K-1100 fibers formed an

intercalation compound with a structure identical to that formed by either vapor-phase or electrochemical intercalation. Neither the P-120 nor the P-100 fibers appeared to react, though they did under the electrochemical conditions. Fiber resistivity measurements confirmed the diffraction result. This implies either that the charge on the fibers is important for the intercalation, or that the local Br₂(aq) concentration exceeds that of the bulk saturated solution.

One of the hallmarks of bromine intercalated fibers is that their residue compounds are stable under ambient conditions, high temperature, high vacuum, and high humidity. Although a full suite of stability experiments has not been carried out to date, the

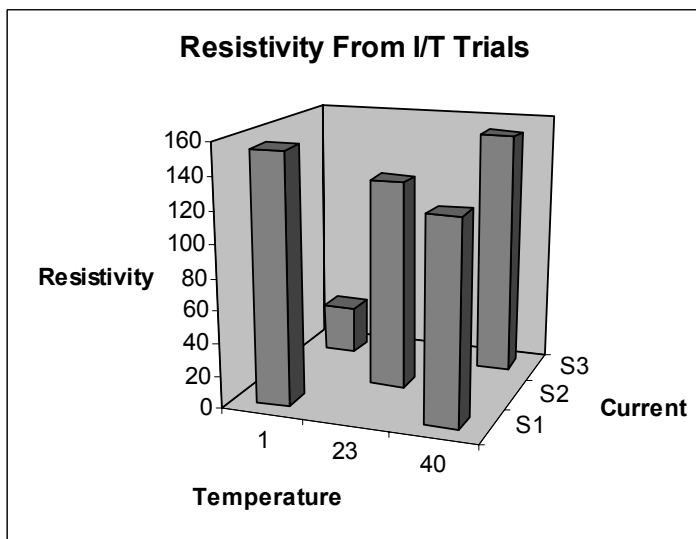


Figure 2 – Resistivity of K-1100 fibers subjected to a variety of intercalation conditions in the first suite of experiments.

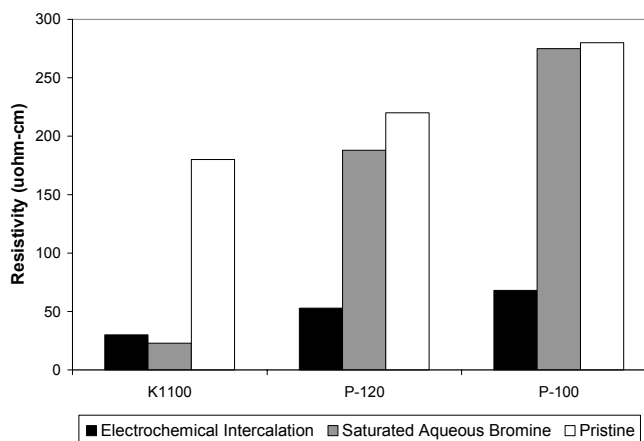


Figure 3 – Resistivity of K-1100, P-120, and P-100 fibers subjected to a aqueous bromine for 24 hours compared to pristine and electrochemically of intercalated fibers.

resistance of fibers exposed to ambient conditions was unvarying over several weeks, just as was seen with vapor phase intercalation methods [5].

References

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