CONF-861019--23

Retention of Hydrogen in Graphite*

R. A. Langley

Oak Ridge National Laboratory, Oak Ridge, TN 37831

CONF-861019--23

DE87 004266

Abstract

The retention of hydrogen in POCO AXF-5Q graphite has been measured at room temperature as a function of fluence and flux for H_2^+ ions at energies from 250 to 500 eV provided by a glow discharge. More than 2×10^{18} H/cm^2 has been retained, and no indication of saturation has been observed to a fluence of 5×10^{19} H/cm^2. In this experiment, retention was found to increase linearly with fluence for constant flux. A flux dependence was observed; that is, the retention rate was observed to decrease monotonically as the flux increased. A change-over experiment, deuterium to hydrogen, was conducted; the results show that significant change-over occurs (i.e., about 30% change-over for a fluence of 5×10^{17} D/cm^2).

DISCLAIMER

MASTER

I. Introduction

The present experiment was undertaken to measure the retention of hydrogen isotopes in POCO AXF-5Q graphite and to extend the database so that a better understanding of the interaction of deuterium and tritium with graphite could be obtained, thereby allowing a more reliable estimate of the tritium inventory in the Tokamak Fusion Test Reactor (TFTR).

The interaction of hydrogen and graphite has been studied for many decades. Probably the first notable investigation was reported by Bangham and Stafford [1] in 1925. They observed the disappearance of hydrogen from discharge tubes in which graphite was used as the cathode. Subsequent work performed by Montet [2] on the retention of protons by graphite showed significant uptake, again using a discharge tube with graphite as the cathode.

In the past several years, numerous studies on the retention of hydrogen in graphite have been made. Many of the results have been contradictory. The observed differences have been attributed to the state in which hydrogen was introduced (atomic or molecular, neutral or ionized), to the grade of graphite used, and to the hydrogen detection technique [3–15]. In addition, significant differences have been observed for the temperature dependence of the retention [2,9,13,14].

This paper presents the results of an experimental study of the retention of hydrogen and deuterium in POCO AXF-5Q graphite near room temperature. Measurements were performed for fluences to 5×10^{19} H/cm^2, for fluxes ranging from 0.05 to 1×10^{15} H/cm^2·s, and for ion energies ranging from 125 eV/H to 250 eV/H. Retention measurements were made for both hydrogen and deuterium, and a change-over experiment from deuterium to hydrogen was done. A method is presented to estimate the trap density for the 4.3-eV trap [13] based on the assumption that the trap is associated with the C–H covalent bond. From this trap density, the maximum tritium retention for that trap can be estimated; this estimate is considerably higher than most previous predictions for the total retention [16–20].

II. Experimental Procedure and Results

Causey et al. [13] have described the salient features of POCO AXF-5Q graphite. The pertinent characteristics that they give are repeated here: "BET surface area of approximately 1 m^2/g and composed of very uniform 10-μm grains, some of which may

have agglomerated to form larger grains. The density of the material is 1.84 g/cm^3." In addition, the manufacturer gives a porosity of 19% [21].

The graphite used for this experiment was cut from a large block [22] into plates about 3 mm thick. These plates were cut to shape and polished to remove cutting troughs and to provide relatively smooth surfaces. The cleaning procedure [23] consisted of washing the plates with water, acetone, and alcohol and then subjecting them to three successive ultrasonic cleanings. This procedure provided dust-free surfaces as determined by a cellophane tape test. The graphite plates were annealed at 2000°C for 30 min in a flowing argon atmosphere before the initial experiment. They were exposed to air for approximately two days between the annealing procedure and insertion into the discharge chamber.

The retention experiments were performed in a glass bell jar system, shown schematically in Fig. 1. The system is pumped by a turbopump-forepump combination; the base pressure after a mild bakeout at ~100°C is 5×10^{-7} torr. A residual gas analyzer (RGA) is installed in the pump-out arm and connected to the discharge chamber with both a relatively large valve and a variable leak. The gas inlet system consists of a manifold with connections to H_2, D_2, O_2, and He gas bottles; a gas reservoir; a pressure manometer; and a pumping port connected to a mechanical pump. The manifold is connected to the bell jar system with two valves, a relatively large valve and a variable leak. The bell jar system has a sensitive pressure manometer to absolutely measure the pressure within the system. The discharge chamber, which is cylindrical in shape, is made of 304 stainless steel (SS). It is lined with a coaxial heater on the outer surface and equipped with three CrAl thermocouples. The graphite plates are arranged in a hexagon inside the SS chamber. Each side of the hexagon is approximately 15 cm high by 10 cm wide. The top and bottom are flat plates, and the graphite mass is 664 g. The area exposed to the discharge is 1464 cm^2, and the volume available to the glow discharge is 3915 cm^3. A 304 SS cylindrical anode enters the center of the chamber through a small hole in the base. The SS anode has an active length of 9.7 cm and an area of 29 cm^2. The volume of the bell jar system is 12.62 L.

The retention experiment consists of evacuating the bell jar system, filling it with hydrogen to a few tenths of a torr, and sealing the system from both supply and pump manifolds. A glow discharge is initiated by applying a voltage to the anode; sometimes a Tesla coil is required for glow initiation. The graphite cathode is grounded. Three experimental quantities are measured: the voltage applied to the anode, the current, and the bell jar pressure. The voltage is set by a power supply and is in the range from 300 to 550 V. The starting pressure for a particular measurement varied from 0.05 to 0.6 torr. Before the glow discharge was started, the pressure was monitored as a function of time; pressure was observed to increase with time at the same rate as the outgassing

3

rate determined before each measurement. This indicated that there was no significant hydrogen uptake due to exposure to gaseous hydrogen. The current is a function of both voltage and pressure and varies from 5 to 150 mA. Experiments were run in two modes: (1) constant voltage and (2) constant voltage and constant pressure (and, consequently, constant current).

Hydrogen retention is calculated from the pressure drop observed during operation of the glow discharge. This interpretation of the drop is justified by the results of time-dependent measurements of pressure and gas composition before and after completion of each implantation experiment (each discharge run). The rates of rise in pressure after discharges were only slightly higher than those obtained before discharges; both were in the range $(1-5) \times 10^{-5}$ torr/min. The outgassing rate decreased with time to the preimplantation values. The composition of the outgassing products was monitored with the RGA and found to consist mainly of masses 28, 18, 17, 16, and 12 after discharges run with H_2 and masses 28, 20, 19, 18, 17, 16, and 12 after discharges run with D_2. Based on the observed cracking pattern, these masses are thought to derive from CO and H_2O (D_2O). During some of the implant experiments, the gas composition was monitored by the RGA; the observed changes were very small and were associated with H_2O (D_2O) and CO. Based on these results, the amount of implanted hydrogen that leaves the graphite between implantation runs is very small compared with the retained hydrogen, and most of the hydrogen that leaves does so as H_2O (D_2O).

Initial retention experiments were run using mode 1. A typical "good" result is presented in Fig. 2. A "good" result is defined as one where little or no arcing occurs and where the discharge is confined to the discharge chamber and appears to be uniform; this aspect is discussed in detail later in the paper. The initial pressure was 0.256 torr, the applied voltage was 400 V, and the current decreased montonically with time from 65 to 29 mA. The initial current was 65 mA but dropped to near the final current within about 30 s. As noted above, the amount of hydrogen retained is determined by the pressure drop; the average fluence is determined from the current and the time interval. The relationship between current and flux is treated in detail in Ref. [24] and for this experiment is 100 mA $\simeq 10^{15}$ H/cm^2·s, assuming that the flux is uniform. Figure 3 presents the hydrogen retained versus fluence for the run of Fig. 2. This curve is almost linear and gives an average retention of 9.3%. Many similar results have been obtained for voltages ranging from 350 to 550 V, for currents ranging from 10 to 130 mA, and for pressures ranging from 0.05 to 0.6 torr. Mode 2 was used to measure retention more accurately because retention was observed to be flux dependent and in mode 1 the flux is not constant. Similar results for retention were obtained. The dependence of the retention rate (the ratio of the

percentage of hydrogen retained to the incident fluence) on flux was observed to decrease as the flux increased, see Fig. 4. The dashed lines indicate the limits of the measured values. In the future, experiments using a third mode, constant pressure and deliberate voltage variation to change the current, will be carried out to determine this dependence more accurately. All measurements to date have been performed near room temperature. A total of 55 torr·L of hydrogen and deuterium has been retained; this is equivalent to 2×10^{18} H(D)/cm^2 or 10 ppm H(D)/C.

In presenting these results, three assumptions have been made:

1. That the current per unit area, and therefore the flux to the wall, was uniform. Little previous work has been done to substantiate this assumption but considering the nature of the plasma and sheath, it is thought that, if nonuniformities occur, they would be most prominent at projections into the plasma region. These have been minimized by the method of construction. Except for one small protruding edge, no joints protruded into the glow volume.

2. That deposits which gradually build up on an anode and its insulating glass shield do not account for any significant amount of the total hydrogen retained. Some investigators have reported carbon debris as a major source of retention [2,15]. These deposits will be analyzed for their hydrogen (deuterium) content.

3. That debris observed on the graphite after an initial bombardment period had negligible effect on the results. It was stated earlier that the graphite had been cleaned so that no dust was detected on the surfaces before the experiment. However, loose particles (thought to be carbon but not analyzed) were found when the apparatus was disassembled for inspection after the initial bombardment period. These deposits are thought to be caused by arcing. They were easily removed with a cloth wipe. The deposits were completely removed with ultrasonic cleaning and were not observed to reoccur after subsequent bombardment. In the present experiments, the results obtained after midcourse cleaning were like those obtained before.

A change-over experiment was performed, also at room temperature, with graphite that had previously retained about 1.5×10^{18} H/cm^2. This experiment was run in mode 2; the starting gas was D_2, and D_2 was fed in during the experiment to maintain a constant pressure. The glass bell jar pressure was maintained near 0.175 torr, the initial amount of D_2 gas in the chamber was 2.20 torr·L, and the gas feed rate was 4.45×10^{-2} torr·L/min. Masses 2, 3, and 4 were monitored with the RGA by bleeding off a small amount of gas from the glass bell jar. The results are shown in Fig. 5. The experiment was actually run for 52 min, but only the first 35 min are shown in order to present the first few minutes in more detail. Significant exchange, deuterium to hydrogen, was observed. There was a

30% change-over in the gas composition in 12 min, at which time the fluence was about 5×10^{17} D/cm^2. The flux during this experiment remained nearly constant at about 6×10^{14} D/cm^2·s. More change-over experiments will be done for temperatures to 200°C and for different fluxes.

III. Discussion

The trapping of hydrogen in the near-surface region of graphite has been investigated extensively in experimental studies (see, for example, [8,10,14]) and has been modeled using the local mixing model [25]. The experimental observations show that implanted hydrogen is immobile at temperatures to about 1000 K until the saturation concentration is reached. As saturation is approached, the depth profile broadens, but only in the implant surface direction. Near room temperature, saturation is about 0.5 H/C. Retention of implanted hydrogen has been studied to depths slightly greater than the implantation depth as a function of temperature and implant energy [25]. These results [25] and others confirm this model for the surface region. For the present experiment, about 50 times the estimated surface retention has been retained. Saturation has not been observed, an observation in agreement with the results of Causey et al. [13].

The present results confirm the importance of retention in the bulk of the graphite. Causey modeled his results using the DIFFUSE code, which is applicable to bulk diffusion, and obtained a trap concentration of 1.7×10^{-5}/C atom and a trap energy of 4.3 eV. In addition, he made a rough estimate of the surface diffusion coefficient for hydrogen on the grain surfaces and obtained $D = 1.2 \exp(-0.9 \text{ eV}/kT)$ cm^2/s, much larger than previous results [5]. The present retention and change-over results can be explained by assuming an open porosity for the graphite with a high surface diffusion coefficient at room temperature, in agreement with the estimate of Causey et al. [13]. The trap energy of 4.3 eV found by Causey is probably associated with the C–H covalent bond. To estimate the trap density and energy the following argument is made. Graphite is made up of carbon atoms arranged according to a two-dimensional hexagonal pattern. The layers of carbon atoms (i.e., the basal planes) are stacked with an abab scheme. Each carbon atom has four valence electrons: three σ electrons and one π electron. The σ electrons form strong covalent bonds with the nearest neighbors in the plane, and the π electron is loosely bound [26]. The planes are separated by 3.35 Å, and the nearest-neighbor spacing is 1.42 Å. Each carbon atom on the end of the plane has only two nearest-neighbor carbon atoms, so there is an available σ electron for bonding to atoms or molecules that come close to this "active" carbon atom. For the lattice parameters given here, the number of active

6

carbon atoms per unit area perpendicular to the basal plane is $1.3 \times 10^{19}/m^2$. Based on the strength of the C–H bond in benzene, a reasonable estimate for the trapping energy of hydrogen on the active carbon atom is 4.3 eV [27]. If one assumes that the graphite grain in AXF-5Q graphite is cubic and that only four sides of the cube have active carbon atoms on them, then for a 10-μm grain there are 5×10^9 active carbon atoms per grain, out of the total number of carbon atoms per grain, 10^{14}. Then, if the maximum number of trapped hydrogen atoms per active carbon atom is one, the saturation density for hydrogen with a trap energy of 4.3 eV is 5×10^{-5} H/C.

Additional traps with lower trap energy are probably available, so the saturation density determined above is probably a lower limit for the total saturation density. Aronowitz and Chang [29], using calculational methods, have determined a chemisorbed site for atomic hydrogen on the basal plane of graphite with a binding energy of 0.7 eV at an equilibrium distance of 2.25 Å above the plane. In addition, Meyer et al. reported a hydrogen content of 200 ppm for POCO AXF-QB [28]. In addition, atomic hydrogen could enter the grain and diffuse along planes, so that there may be a sizable solubility for hydrogen within each grain. It is thought that hydrogen does not readily diffuse through the basal planes [29], but this aspect needs further investigation.

These considerations indicate a high potential for trapping of tritium in the 2 Mg of graphite in TFTR. The saturation limit for tritium in the 4.3-eV traps is itself approximately 100 g. The actual retention will be strongly dependent on the history of tritium exposure and plasma operating characteristics and should be considerably less for any reasonable operation scenario.

The gas accountability in the change-over experiment is easily calculated. The results after 30 min show D retention in an amount equivalent to 2 torr·L of D_2 and H release equivalent to 1 torr·L of H_2. This quantity of H is only 2% of the total implanted hydrogen, and the rate at which H entered the gas phase decreased markedly after only a few minutes, mostly due to the fact that hydrogen is lost from the gas phase because of its reimplantation. These results suggest a technique for conditioning the graphite in fusion devices so that a near-constant ratio of deuterium to tritium can be maintained during a plasma discharge while minimizing the amount of tritium retained in the graphite. A conditioning scenario might consist of glow discharge implantation of deuterium into the graphite surface region, followed by use of this implanted deuterium as a source during a plasma discharge. At the completion of series of discharges, a substantial fraction of the implanted tritium could be removed by exchange with deuterium using a glow discharge, thereby minimizing the tritium inventory in the graphite.

IV. Summary

The retention of hydrogen and deuterium in POCO AXF-5Q graphite has been measured near room temperature. The retention was observed to increase linearly with fluence for constant flux. A flux dependence was observed: the retention rate was observed to decrease as the flux was increased. The present results are in basic agreement with the previous results of Causey et al. in demonstrating that hydrogen saturation is large and is dominated by retention in the bulk of the graphite.

The change-over experiment ($D \rightarrow H$) yielded significant exchange and proceeded on a time scale that suggests that suitable conditioning of the graphite in TFTR might be obtained by the glow discharge technique.

V. Acknowledgments

This work was undertaken as part of the ORNL collaboration on research on the TFTR project. The author would like to acknowledge Julian Dunlap, ORNL, and Fred Dylla, PPPL, for their help in initiating the experiment and Richard Dyer, ORNL, for his help in the electrical design and its implementation.
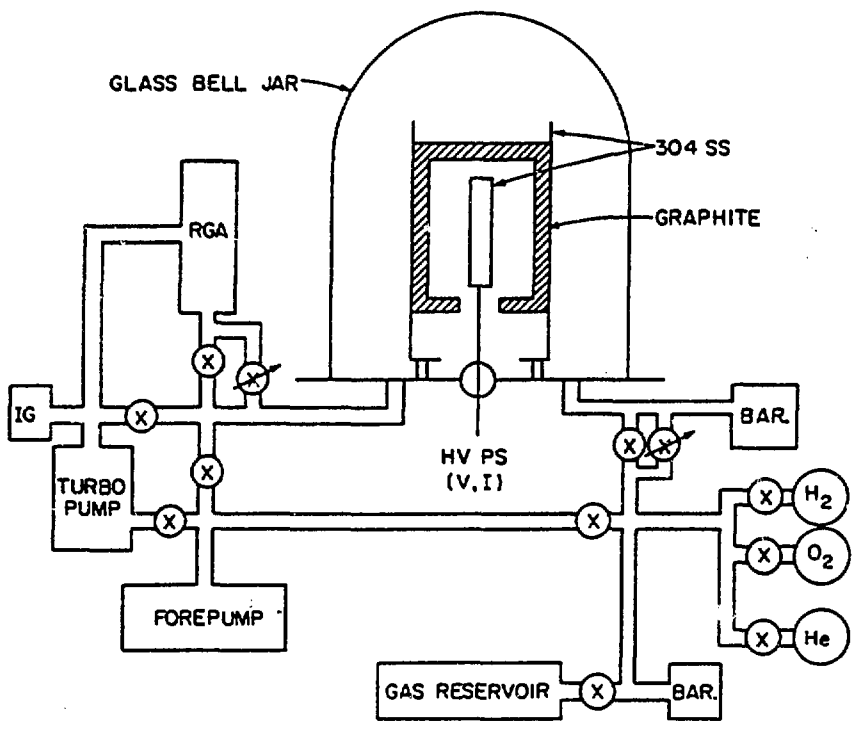
REFERENCES

1. D. H. Bangham and J. Stafford, J. Chem. Soc. **127** (1925) 1085.

2. G. L. Montet, Proc. 4th Conf. on Carbon, Buffalo (University of Buffalo, 1959) 159.

3. J. T. Clarke and B. R. Fox, J. Chem. Phys. **46** (1967) 827.

4. S. J. Steck, C. A. Pressley, Jr., S.-Sh. Lin, and F. E. Stafford, J. Chem. Phys. **50** (1969) 3196.

5. M. Balooch and D. R. Olander, J. Chem. Phys. **63** (1975) 4772.

6. R. K. Gould, J. Chem. Phys. **63** (1975) 1825.

7. K. Flaskamp, H. R. Ihle, G. Stöcklin, E. Vietzke, K. Vogelbruch, and C. H. Wu, Proc. Int. Symp. on Plasma-Wall Interaction, Jülich (Pergamon Press, 1976) 285.

8. R. A. Langley, R. S. Blewer, and J. Roth, J. Nucl. Mater. **76 & 77** (1978) 313.

9. P. Hucks, K. Flaskamp, and E. Vietzke, J. Nucl. Mater. **93 & 94** (1980) 558.

10. G. Staudenmaier, J. Roth, R. Behrisch, J. Bohdansky, W. Eckstein, P. Staib, S. Matteson, and S. K. Erents, J. Nucl. Mater. **84** (1979) 149.

11. R. A. Causey, T. E. Elleman, and K. Verghese, Carbon **17** (1979) 323.

12. J. Roth and R. Schulz, J. Nucl. Mater. **94** (1982) 497.

13. R. A. Causey, M. I. Baskes, and K. L. Wilson, J. Vac. Sci. Technol. **A4** (1986) 1189.

14. M. Braun and B. Emmoth, J. Nucl. Mater. **128 & 129** (1984) 657.

15. W. K. Hsu and R. A. Causey, these proceedings.

16. B. L. Doyle, D. K. Brice, and W. R. Wampler, IEEE Trans. Nucl. Sci. **NS-28** (1981) 1300.

17. B. L. Doyle, SAND81-0622 (1981).

18. D. K. Brice, B. L. Doyle, W. R. Wampler, S. T. Picraux, and L. G. Haggmark, J. Nucl. Mater. **114** (1983) 277.

19. M. I. Baskes, D. K. Brice, D. B. Heifetz, H. F. Dylla, K. L. Wilson, B. L. Doyle, W. R. Wampler, and J. L. Cecchi, J. Nucl. Mater. **128 & 129** (1984) 629.

20. D. B. Heifetz, H. F. Dylla, M. Ulrickson, and M. I. Baskes, PPPL-2353 (1986).

21. Poco Graphite, Inc., product brochure (1983).

22. The AXF-5Q graphite block was obtained from M. Ulrickson, Princeton Plasma Physics Laboratory.

23. A. W. Mullendore, Sandia National Laboratories, personal communication, 1986.

24. R. A. Langley and H. Howe, J. Nucl. Mater. **121** (1984) 237.

25. D. K. Brice, B. L. Doyle, and W. R. Wampler, J. Nucl. Mater. **111 & 112** (1982) 598.

26. C. A. Klein, Rev. Mod. Phys. **34** (1962) 56.

27. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd ed. (Allyn and Bacon, Inc., 1975).

28. R. T. Meyer, A. W. Lynch, J. M. Freese, M. C. Smith, and R. J. Imprescia, Carbon **11** (1973) 258.

29. S. Aronowitz and S. Chang, Astrophys. J. **293** (1985) 243.

Figure Captions

Fig. 1.   Apparatus for measurement of hydrogen retention. Explanation of symbols and abbreviations: $\otimes$, valve; $\not{\otimes}$, variable gas leak; IG, ionization gauge; RGA, residual gas analyzer; SS, stainless steel; HV PS, high voltage power supply; and BAR, sensitive pressure manometer.

Fig. 2.   Pressure drop in bell jar during a glow discharge experiment versus time for an applied voltage of 400 V and a current range of 65–25 mA.

Fig. 3.   Total retained hydrogen versus hydrogen ion fluence. Data obtained from results of measurement given in Fig. 2.

Fig. 4.   Hydrogen retention versus incident hydrogen flux. The dashed lines indicate the upper and lower bounds of the measured values.

Fig. 5.   Time evolution of H_2, HD, and D_2 during change-over experiment. Original composition is 100% D_2. D_2 gas is fed in at a rate of 4.45×10^{-2} torr·L/min to keep the current constant.
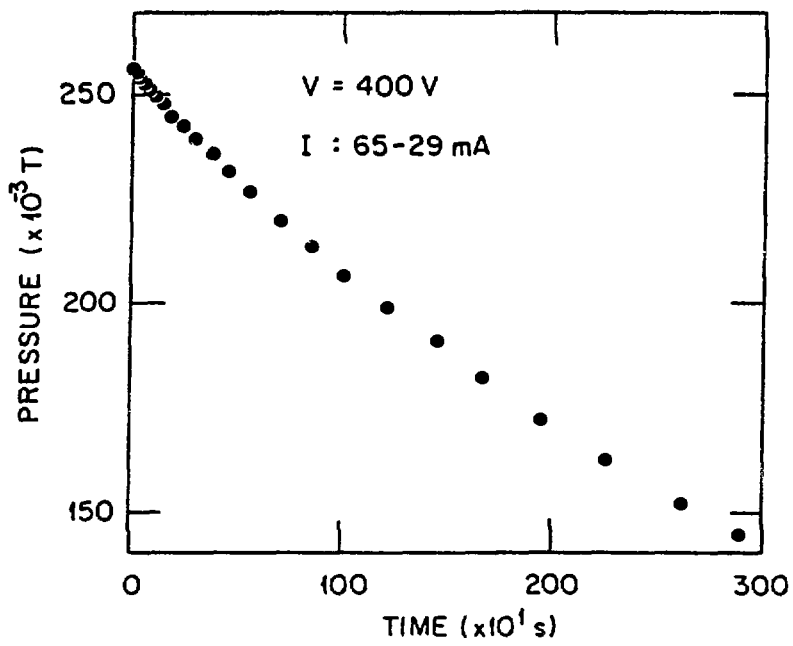
ORNL-DWG 86-2792   FED

ORNL-DWG 86-2796   FED
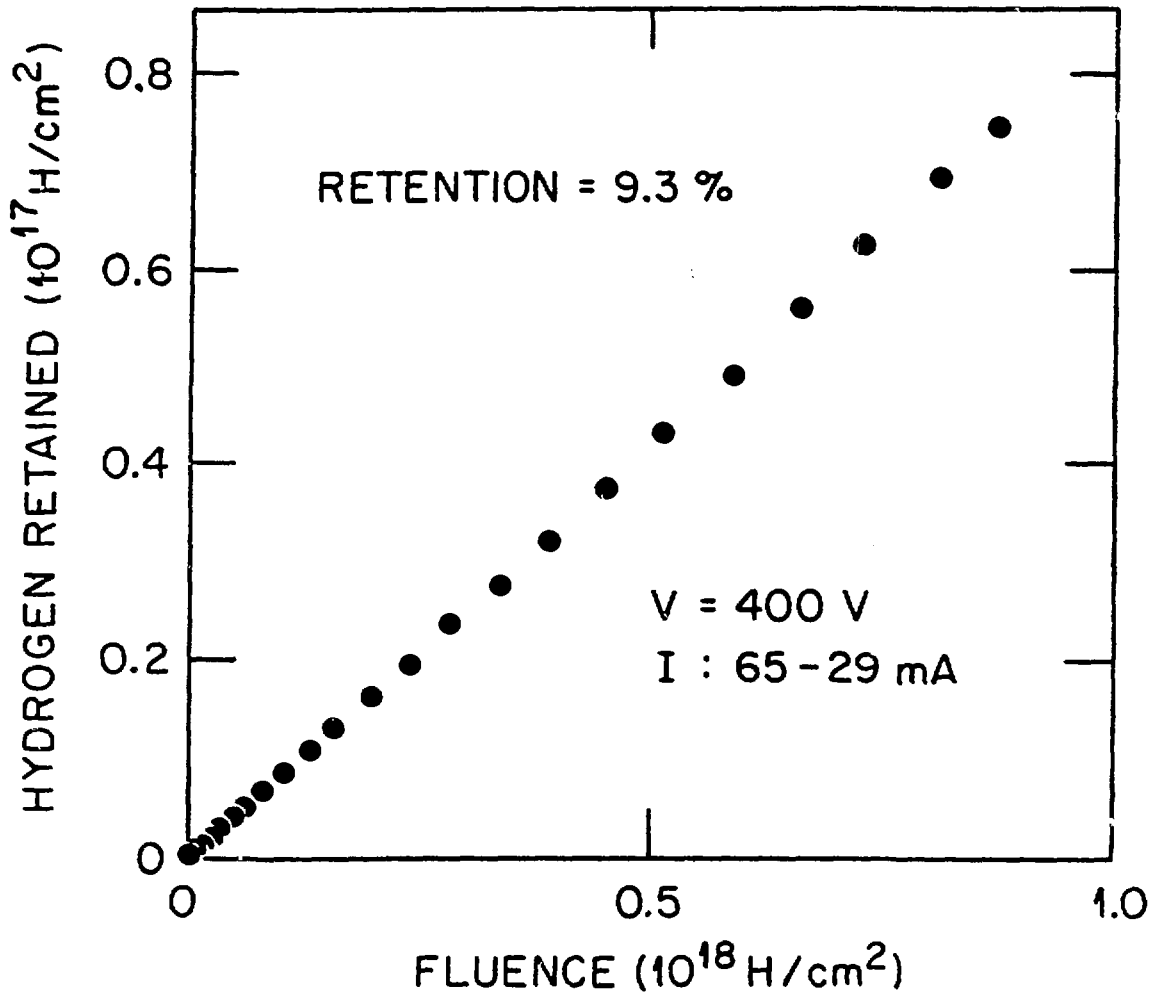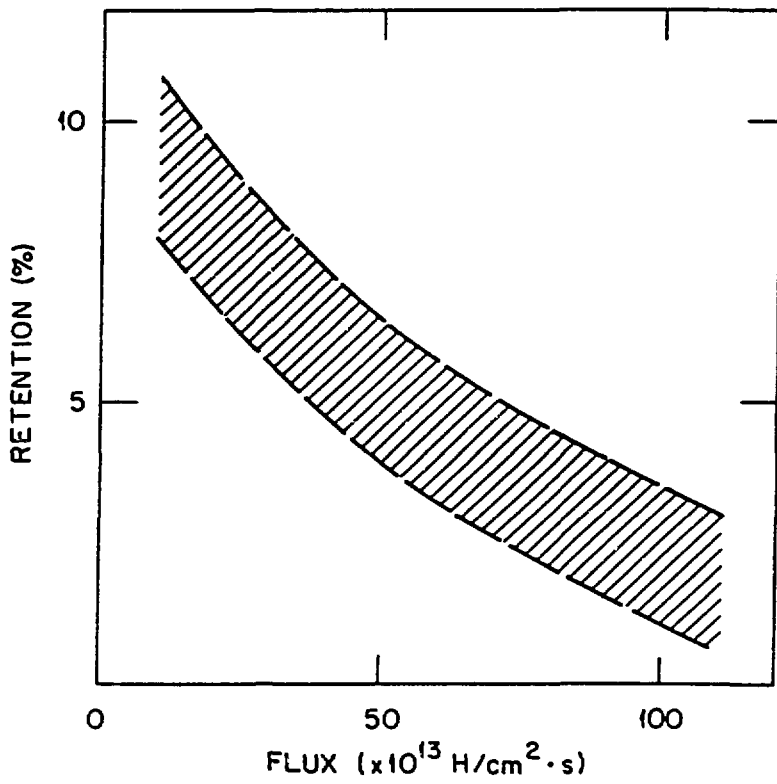
V = 400 V

I : 65-29 mA

FIG. 2

RETENTION = 9.3 %

V = 400 V

I : 65−29 mA

HYDROGEN RETAINED (10^{17} H/cm^2)

FLUENCE (10^{18} H/cm^2)

FIG. 3

ORNL-DWG 86-2794   FED

FIG. 4

ORNL-DWG 86-2793A FED

FIG. 5