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17 I-26373 DR-1728-0

UCID- 20489

UCID--20489

DE86 011011

TRITIUM GETTERING FROM AIR WITH HYDROGEN URANYL PHOSPHATE

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August, 1985

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price Code	Page Range
A01	Microfiche
Papercopy Prices	
A02	001 - 050
A03	051 - 100
A04	101 - 200
A05	201 - 300
A06	301 - 400
A07	401 - 500
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The managers of all tritium facilities now worry about their emissions into the atmosphere. The only method for cleaning tritium out of air is to catalyze the formation of tritiated water which is adsorbed, along with the overwhelming bulk of naturally occurring water vapor, on a zeolite molecular sieve. This method generally costs several million dollars for a small system, because of the necessary steel ducting, compressors and holding tanks.

We have long had the dream of finding another getter that might be cheaper to use and would, hopefully, not make tritiated water (HTO). In a previous paper, we discovered that hydrogen uranyl phosphate (HUP, with the formula $HUO_2PO_4 \cdot 4H_2O$) getters 1 ppm of tritium gas out of moist air.[1] This makes HUP the first known "direct" tritium getter to work in air. However, the tritium enters a hydroxyl network within the HUP, so that it is effectively still in "water" form within the HUP. Worse yet, we found up to 10% tritiated water formed during the previous gettering experiments.

The HUP is a canary yellow ionic conductor, which passes electric current as protons instead of electrons. It preferentially passes hydrogen gas, which ionizes at 0 V, rather than water vapor, which ionizes at almost 2 V. Tritium enters the HUP at the anode and hydrogen from the HUP comes off at the cathode. HUP is unusual in possessing the exceptionally low vapor pressure of 0.6 torr water vapor at 298 K.[2] This allows HUP to be used in fairly dry environments.

I. PROCEDURE

The making of the HUP discs with their porous stainless steel electrodes has been described.[1] We recall the important point that palladium black is required on the anode face of the HUP, probably to cause dissociation of the tritium gas. The HUP made as described will be called "high" density, because it is close to the theoretical density of 3.43 g/cc.[3] These samples are run in a 1.2 liter bulb, which is mainly a gold-plated ionization chamber. Because of the formation of background HTO, the system became more elaborate. A -117°C cold trap was added to the inlet line to trap out impurities. The zeolite molecular sieve was operated at room temperature to catch the HTO produced in the gettering. We then began to bake out the system at 200°C for 16 to 24 hours before each run. The zeolite was taken to 500°C to recover and evaluate the HTO after the run. Finally, the zeolite was found to be a maker of HTO at 500°C and we replaced it with a liquid nitrogen cold trap. The resulting HTO is counted as before.

The HUP discs used in bulb runs have a diameter of either 1.25 or 2.5 cm. The thickness is 1.1 mm for the high density material and 1.4 mm for the low density.

We next turned to a working air-tight glove box made of lucite with a steel skeleton. The box has a 5.5 m^3 volume and is served by a conventional catalyst/zeolite clean-up system. The box is used for the regular handling of large tritiated equipment.

In order to obtain a large surface area, a "low" density HUP of 2.1 g/cc is made as follows. A square foot of stainless steel porous electrode is lightly smeared with palladium black, and the powdered HUP is uniformly spread on top. The other electrode is put on top and the assembly bolted together with plastic screws. Pressure plates are put on either side, and the assembly is pressed at 465 tons (6,460 psi) for 24 hours. The thickness of the resulting HUP layer is 1.7 mm.

The box is fitted with a tritium injection system, an ionization chamber, a cold trap input cleaner, a liquid nitrogen trap for HTO collection and a water meter. Fans are used to circulate the air.

II. BULB RESULTS

We first consider the "cleanest" set of bulb runs. These use the liquid nitrogen trap instead of the zeolite molecular sieve to getter the HTO. The blank runs (with no HUP) are listed at the top of Table 1. A tritium concentration of 1 ppm is used and "moist" means about 6000 ppm of water vapor. We see that the presence of water vapor does produce more observed tritiated water. The identity of the "unaccounted for" tritium is unknown. We see, too, that the 600 V ionization chamber appears also to be catalytic. With the ionization chamber off, the background HTO formed is less than 1%.

Table 1 also shows the results of both high and low density HUP pills in both moist and dry air with 1 and 20 ppm initial tritium. After 24 hours at 4 V, we have 98% average gettering into the HUP with 1.6% HTO formed. The time to 90% gettering is 1 1/2 hours at 20 ppm and 2 to 6 hours at 1 ppm. These bulb runs demonstrate that the HUP is capable of gettering quickly up to a high total % which is set here by the inherent water production capability of the bulb itself. The HUP area of 5 cm^2 and the bulb volume of 1200 cc's gives us a ratio of 0.0042 cm^{-1}.

Sample #104 with low-density HUP shows some interesting features regarding moisture. The sample was run 20 successive times cumulatively with a new atmosphere of 1 ppm tritium in moist air. The first run is the high efficiency result shown in Table 1. Five of the runs are shows in Fig. 1. The first run reaches 90% gettering in 2 hours, the second run in 1 hour and the 20th run in 3/4 hour. The gettering speed becomes faster. However the residual tritium increases in each run, and this background turns out to be HTO. This level increases in each run, although the starting moist air atmosphere is fresh in each case. The HTO is coming back out of the HUP, presumably by exchange with water vapor. This confirms that the gettering is almost a surface effect and once the surface is tritiated, the HUP returns to producing unwanted HTO. there are two interpretations. One is that the tritium passes all the way through the HUP and comes off the cathode. It is supposed to come off as tritium gas, but perhaps it is oxidized. The second possibility is that the tritium never goes very deep into the HUP but is gettered onto the surface. The moisture in each run then exchanges out some of the tritium as water. In the discussion section, we shall present figures to support this idea. For most of the runs, the moisture level is 7000 ppm. In two, it was 15,000 ppm and the residual tritium rose by 7%. This helps the assumption that water vapor exchanges out the tritium from the HUP.

We next consider the older data, with the zeolite sieve for HTO collection. The HTO background with moisture was 3.4% in this case. At the top of Table 2, we see oxygen and argon blank (no HUP) runs, with and without moisture. Clearly, it is the moisture, not the oxygen that catalyzes HTO formation in the empty bulb.

The center data of Table 2 shows the effect of increased potential. We have no improvement at 6 V and 10 V definitely is harmful. A sudden increase in water vapor occurred, suggesting that the HUP is dehydrating or decomposing. It is possible to use a lower potential. We have seen that 2 V is slower than 4 V;[1] Fig. 2 shows the results at 0.5 to 0.7 V. Here, only tritium gas is ionized and the current is only 50 nA. At this potential, the water vapor should be left behind in the air and the HUP should be a near-perfect selector for hydrogen. Unfortunately, the gettering is very slow. A 4 V run is shown for comparison.

We tried various compounds but failed to obtain more than 3% gettering. These materials include: lithium and potassium-exchanged HUP,[4,5] $KH_2Sb_2O_7$,[6] KH_2PO_4,[7] and KHF_2.[8] The last pair are low mobility proton electrolytes with a mechanism different from the HUP.

The presence of palladium black on the anode face of the HUP is necessary for gettering but is a possible source of HTO formation. As seen in Table 2, platinum black is equally good. However, iridium, powdered nickel and gold, and Raney nickel and cobalt all failed, with no more than 2% gettering. Clearly, only the best catalysts for dissociating tritium can be used.

III. BOX RESULTS

The first run in the 5.5 m^3 box used moist air with 1 ppm tritium and 1 ft^2 of low density HUP panel. The area-to-volume ratio required of the panel was $1.8 \times 10^{-4} cm^{-1}$ or 5% that of the bulb runs. A large fan blew the box air hard against the panel. The results are shown in Fig. 3. In 160 hours of gettering, we find 81% of the tritium gone from the ionization chamber reading. The water vapor content decreases by 1500 ppm, which often happens in the bulb runs too. A potential of 4 V was used for 50 hours, and then it was slowly increased to 6 V. The porous frit temperature varied from 26 to 38°C. Heat spikes occurred when the potential was stepped up. The box temperature varied between 23°and 28°C.

We had previously run blanks in the box and obtained 1 to 2% HTO formed from 10 to 13 Ci. This amount was not apparently increased by the presence of fans and the ionization chamber. Following 7 days of HUP gettering, we found 14.0% HTO, which would account for most of the residual tritium. Thus, 12% or 1.7 Ci, we must attribute to the operation of the HUP system. The HUP panel was allowed to remain for one week in the box, with the fan blowing on it, before analysis. When counted, the HUP showed only 0.24% tritium, although 81% had been gettered. The missing tritium appears on the stack monitor for that time. This was our first example of the tritium loss effect after gettering.

IV. DISCUSSION

The Shilton and Howe model of HUP is as follows.[3] Only one proton of the nine in the formula carries a charge. Given HUP's full density of 3.43 g/cc, we have 5×10^{27} carriers/m^3. They then use

$$u = \frac{g}{Ne} \qquad (1)$$

where u is the carrier mobility, g the electrical conductivity (which is derived from the measured current and the dimensions), N is the carrier density and e is the electronic charge. Their best conductivity of 0.4 S/m leads to a mobility of 5×10^{-10} $m^2/V{\cdot}s$. We have seen this conductivity only in the case where 100 torr H_2 is used to provide the charge carriers. In this case, tritium can be flushed clear through the HUP disc.[1]

At low tritium gas concentrations and with water vapor present, charge carriers are not efficiently provided and the electrical conductivity is lower. For fully dense HUP, we find 4×10^{-3} S/m and 4×10^{-12} $m^2/V{\cdot}s$. We modify N to 70% for the low density HUP, where the measured electrical conductivity is 10^{-3} to 5×10^{-5} S/m. This gives mobilities of 2×10^{-12} to 10^{-13} $m^2/V{\cdot}s$. We next relate u to the diffusion coefficient. Then the times for these carriers to break through to the other side of the HUP is

$$t \sim \frac{4eL^2}{kTu} \qquad (2)$$

where L is the HUP thickness, k the Boltzmann constant and T the temperature. We find t to be 5000 hours to 100,000 hours for low density HUP. We have no reason to expect tritium to pass all the way through and exit at the cathode during our 24 hour runs. This is our reason for preferring the surface gettering model in our 20-run-experiment.

The Shilton and Howe model assumes that the electric field is constant everywhere in the HUP and, implicitly, that the HUP obeys Ohm's Law. We note, however, that the carrier density is so high that space-charging is expected.[8] This would limit the tritium to an anode surface layer and make the leakage current proportional to the 1.5 power of the potential.[10] Pure H_2 gas at 100 torr does obey Ohm's Law at 0 to 1 V. Water vapor does not because it furnishes carriers only above 1.8 V. Even at 6 V, the current changes as approximately the square of the potential.[11] This later case is what we see in our HUP, where the tritium concentration is so low that the water vapor furnishes 99% of the charge carriers at 4 V. We also recall the residual potential, which has the same polarity as the original applied potential.[1] This could be explained if a space charge crowded positive charge carriers into the anode region of the HUP. We cannot here resolve these model problems, and they both predict surface gettering in our case.

We have seen no diminishing of the HUP's gettering power after a six-month's wait before use. However, under a 4 V potential, the HUP rapidly degrades, possibly because of a electrolytic decomposition of the compound.[11] No extra water vapor is seen in the bulb runs, so that formation of dehydrated HUP[4] is apparently not the answer. It appears that water vapor should be formed in the conversion to any of the uranyl phosphates related to HUP.[12-14]

V. CONCLUSION

The HUP does getter tritium from air with nothing more than a room fan, but it does form some tritiated water. So, we suspect, does a zeolite sieve, but it is enclosed in a steel container and few systematic measurements are ever made on the exhaust. It would be desirable to run HUP at a potential low enough that only tritium gas ionizes and water vapor is left behind. This will probably await the discovery of a new proton electrolyte with a higher mobility. This magic material should also possess an even lower vapor pressure to lower the HTO-exchange effect. It should also be more resistant to degredation - a feature that will be helped by the use of a lower potential.

All but the last year was sponsored by Gene Nardella of the Office of Fusion Energy, Department of Energy. The last year was covered by the Chemistry Research Resource fund at LLNL. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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Blanks:

No.	Conditions	IC	% of Tritium HTO	 Unaccounted for
23	Dry; <1 h	on	0.06	-
24	Dry; 24 h	on	0.15	3.1
26	Moist; <1 h	on	0.22	-
25	Moist; 24 h	on	2.6	2.0
27	Moist; 24 h	off	0.81	1.2

HUP Runs:

No.	IC	Conditions	% of Tritium In HUP	 HTO	 Unaccounted for
101	off	dry, high density	96.4	1.4	2.2
102	on	dry, low	98.4	1.6	-
98	off	moist, high	97.0	2.4	0.6
99	off	moist, high	97.5	2.2	0.3
104	on	moist, low	98.2	1.6	0.2
105	on	moist, low	99.2	0.3	0.5
106	on	moist, low	97.9	2.1	-

Table 1. Data from the final set of experiments in the 1.2 liter bulb. The HUP runs are with 1-inch diameter for 20 hours at 4 V. "Moist" means about 6000 ppm water vapor. All runs are 1 ppm T_2 except 105 and 106, which have 20 ppm.

Moisture

	HUP in *moist air*	HUP in *dry air*	HUP in *moist Ar*	HUP in *dry Ar*
T_2 in gas	1.5%	1.8%	0.9%	0.2%
HTO in gas	14.0	3.9	11.2	3.5
T in HUP	83.0	97.1	84.8	90.1
	98.5%	102.8%	95.9%	93.7%

Potential

	4 V	6 V	10 V
T_2 in gas	0.3%	1.9%; 2.9%	6.2
HTO in gas	3.8	3.1 ; 3.5	30.4
T in HUP	94.3	91.0 ; 93.5	58.2
	98.4%	96.0%; 99.9%	94.8%

Table 2. Other 24 hour bulb runs with the zeolite HTO system and a moist air HTO background of 3.4%.

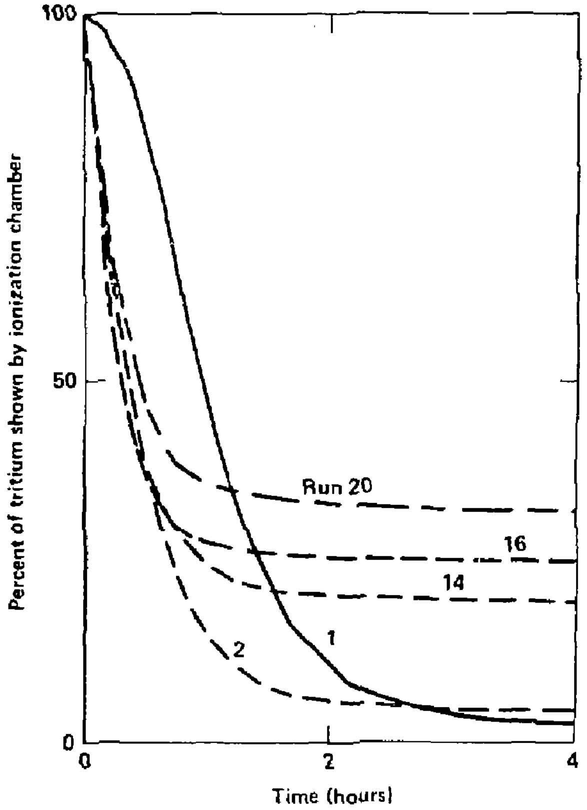

Fig. 1. Multiple-bulb run sequence with HUP #104. Each run has 1 ppm tritium in fresh moist air. Run No. 1 is a fine example of a fast getter.

Fig. 1

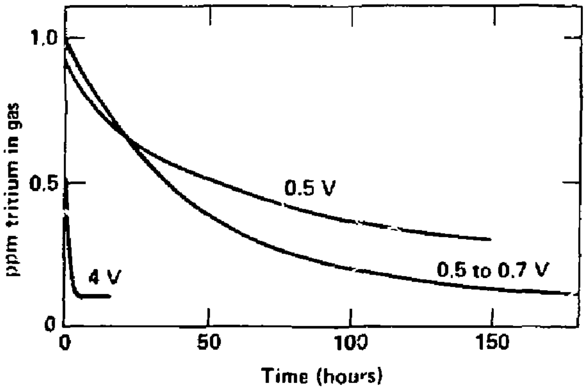

Fig. 2. Gettering is greatly slowed by the use of a 0.5 V potential, although only tritium is now processed by the HUP.

Fig. 2

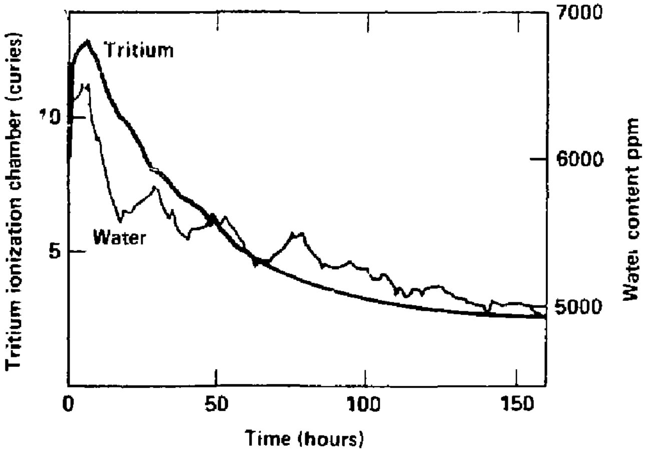

Fig. 3. Results of the first 5 m^3 box run with one square foot panel of HUP.

Fig.3