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ELECTROLYTIC GETTERING OF TRITIUM FROM AIR

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We have removed 90% of 1 part-per-million tritium gas in air of 25% to 35% humidity by the d.c. electrical action of the solid proton electrolyte hydrogen uranyl phosphate (HUP). Gettering takes 5 to 24 hours for a 1 cm² HUP disc at 2 to 4 V in a static, 1200 cc gas volume. Hydrogen gas may be used to flush captured tritium through the HUP. Liquid water leaches out the tritium but water vapor is ineffective. This technique promises an alternative to the conventional catalyst/zeolite method.

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I. INTRODUCTION

Deuterium-tritium is the likely fuel for hydrogen fusion reactors. A possible but undesirable occurrence at such a reactor is the accidental release of tritium into the room air. The present method of cleaning tritium from air is to pass all the room air over a hot palladium or platinum catalyst, which turns the tritium gas to tritiated water, which is then adsorbed on a zeolite bed. There are two problems with this approach. The first is that tritiated water is about 25,000 times as dangerous

EMO

as tritium gas.¹ This ratio has increased through the years, not because water has been determined to be more dangerous, but because the gas appears to be less so.² With protective clothing and breathing apparatus, the ratio of hazard may be as great as 10^6 .³

The second problem with the catalyst/zeolite technique is cost. Sherwood has proposed the following equation for cost C:⁴

$$C(\$) \sim 3 \times 10^4 Q^{0.6} \ln D \quad (1)$$

where Q is the flow-rate in m^3/min and D is the ratio of tritium in to tritium out. Equation 1 is good to perhaps $\pm 50\%$. For a laboratory of $400 m^3$ and 99% clean-up, the cost is approximately \$5 million. Clearly, it would be desirable to have a cheaper technique.

Metal powders getter tritium in inert atmospheres but fail in air.⁵ We have previously experimented with solid acetylenes catalyzed with platinum or palladium at room temperature, but tritiated water was again the apparent product.⁶

We here use the solid proton electrolyte, hydrogen uranyl phosphate (HUP), which has the chemical formula $HUO_2PO_4 \cdot 4H_2O$ and one of the highest a.c. electrical conductivities known: about 0.01 to 0.5 S/m at room temperature.⁷⁻⁹ Most work has supplied the protons as ions from aqueous acidic solutions, but the HUP has been operated in gaseous hydrogen¹⁰ and is reported to have been used as well with solid

hydrides.¹¹ A.c. measurements are generally used to avoid polarization effects, but one d.c. study has been done.¹⁰ The HUP forms a sandwich-like structure with the $(\text{UO}_2\text{PO}_4)^-$ ion in one plane and a hydrogen-bonded -O-H- network in the other.¹² The proton passes through the -O-H- network by hopping from one oxygen atom to another whenever a hydrogen "hole" in the structure permits. It appears that all hydrogens are mobile, although only one in nine carries a charge. This results in a large proton density of 5×10^{27} charges/ m^3 ^{9,13} and a low proton mobility of about 10^{-9} $\text{m}^2/\text{V}\cdot\text{s}$. The electrical conductivity has been measured as being 100 times greater in the -O-H- plane than perpendicular to it.⁹ The ratio would probably be even larger in a single crystal. HUP is unusual among solid proton electrolytes in retaining its "water of hydration" in dry air. It is apparently stable at room temperature to as low as 2% humidity.¹⁴

II. EQUIPMENT AND PROCEDURE

The HUP is such an easy compound to make that a standard synthesis exists,^{15,16} which we shall briefly describe. Ten grams of uranyl nitrate hexahydrate is dissolved in 50 ml. distilled water and 8.4 ml. of 2.4 M phosphoric acid (Eastman or Mallinckrodt) is added. After one to two hours, the fine crystals formed are removed in a Büchner funnel. The crystals are washed with pH 2 aqueous phosphoric acid. The paper with the sample is air-dried to constant weight, and the canary yellow crystals are then stored in humid air.

The HUP samples are made as follows. We first punch two 316 stainless steel frit discs (Fall Trinity MicroCorp. Grade E with 35 μ m pores) of 12.7 mm diameter and 1.6 mm thick. These are crushed for 5 minutes at 6000 pounds force in a 1/2-inch diameter die to produce discs of 1.27 cm² area. Sharp extrusion points on the edges are removed. One frit is placed in the die and 5-8 mg. of palladium black is spread over the frit surface. The palladium black must be added to the anode face or the HUP unit will not work. We next add 0.23 g of carefully ground HUP. This is spread evenly and then is lightly compressed with a punch. The other frit is added onto the HUP, and the whole is pressed at 6000 lbs. force for 24 to 72 hours. The pressed HUP part of this sandwich is 0.5 mm thick and is a translucent greenish yellow. The final assembly is checked for electrical short circuits, wires are spot welded to the frits and the edges are epoxied.

We ran the experiment in two ways. In the single-bulb mode, the HUP unit sits in a gold-plated stainless steel container of 1200 cc with both sides open to the same tritium-air mixture. In the double-bulb mode, the HUP is glued to the end of a glass tube to form an air-tight seal between two chambers of 1200 cc volume each. The tritium-air mixture is placed on the anode side and argon of 10% humidity is placed on the cathode side. We expect the tritium to be oxidized at the anode forming tritons which are then attracted through the HUP to the cathode.

The gas-phase tritium is measured with an ionization chamber and the water vapor with a Panametric alumina-capacitance device. The d.c. potential and current across the HUP is monitored. When completed, the HUP-unit is taken apart and each part dissolved and counted in a scintillation counter. The HUP itself is dissolved in dilute nitric acid which is then mixed with United Technologies Packard Insta-Gel® counting fluid. At the end of the experiment, the closure for all tritium is usually $\pm 5\%$.

All samples are a nominal 1 part-per-million T_2 gas in "zero air", i.e., bottled air with a dew point of -77°C . This mixture is fairly stable when kept in stainless steel bottles, as there is an apparent drop in the T_2 gas concentration of perhaps 50% over a year. The desired amount of water vapor is added when the experiment begins. All experiments are at 0.1 MPa (1 atm) total pressure and diffusion at room temperature moves tritium through the air to the HUP.

111. EXPERIMENTAL RESULTS

Figure 1 shows the tritium gettering results for air of 35% humidity. Sample #48 was left for 24 hours with no potential and only 4% of the tritium was adsorbed. The application of 4 V d.c. started the gettering in this double-bulb run. Sample #51 shows the full potential of 4 V applied immediately in a single-bulb configuration. Sample #53 shows the slower gettering with 2 V applied at the start. Counting later showed the tritium to indeed be in the HUP.

Note that both 4 V runs above end with 10% of the tritium remaining. Never did we go below this level. By cold-trapping and counting, we found that this extra tritium is always HTO, which is exchanged off the unbaked vessel walls in the presence of water vapor. Despite pumping at room temperature, enough tritium remains on the gold to affect the next experiment. Because of this background effect, we are not able to ascertain the ultimate possible performance of the HUP or whether the HUP itself is partly responsible for the HTO formation.

Before running any samples, we routinely measured the a.c. properties with a Wayne-Kerr a.c. bridge at 1592 Hz. The samples of Fig. 1 all showed typical "good" initial values of 2 to $3 \times 10^{-3} \Omega^{-1}$ conductance and 1.4 to 1.6 μF capacitance. By the end of the 4 V runs, the conductance was still $2 \times 10^{-3} \Omega^{-1}$ but the capacitance had degraded to $1.2 \times 10^{-3} \mu F$. The 2 V sample, however, ended at 1.3 μF , which shows that the lower potential causes less damage. This "degradation" is reported as being caused by hydrogen reducing the phosphate groups of the HUP,¹⁷ although we know of no direct evidence for this process. It could also be loss of water of hydration or the pulling away of the electrodes from the HUP. Whatever it is, the decrease in a.c. capacitance appears to be a qualitative measure of the destruction of the HUP's tritium gettering capacity. The same degradation is seen also in the d.c. current.

We have noted that Pd black is needed, probably as an electrical contact, on the anode. We must ask, then, if the Pd is gettering the tritium. A sample of 0.27 g Pd black (40 times that on the HUP) was pumped to 10^{-6} Pa at 670 K, reacted with hydrogen for 24 hours and pumped again to high vacuum. The sample briefly sees air as it is put into the bulb, where it is pumped to 10^{-4} Pa at room temperature before starting the run. The results are shown in Fig. 2. Pd black will getter tritium in dry air, but water vapor (30% humidity) greatly diminishes its performance. The blank is the empty ionization chamber with moist tritium and air.

We also tried runs at 0.5 to 0.8 V d.c., potentials low enough to avoid ionization of water at the anode or formation of water at the cathode. We also wished to avoid possible electrochemical reactions in the HUP. As an example, run #56 gettered 23% of the tritium at 0.5 V in 67 hours, and only 0.8% appeared on the cathode side. But run #57, handled in an identical way, transferred 46% of the tritium to the cathode side in 72 hours, and only 6% remained in the HUP. The presence of air on the cathode side confirmed a leak through the HUP. The low voltage runs then merely highlighted the problem of small cracks and tritium gettering was proportionately reduced by the lower potential. No special behavior was seen.

Let us return to our "standard" HUP unit following a successful 4 V gettering. How can we get the tritium out again? In one case, we added 55% humidity to the argon on the cathode

side of a double bulb run and reversed the 4 V potential. Over 52 hours, only 9% of the tritium in the HUP emerged back into the air on the original anode side. In another case, the potential was increased to 10 V in the forward gettering direction, but the anode bulb tritium rose within minutes from 0.11 to 0.54 ppm. Possibly the HUP was dehydrating or decomposing, so that use of the lowest possible potential is clearly desirable. We twice placed gettered "HUP" discs in liquid water, and the tritium was leached out with a 1/e-time of about 5 to 10 hours, so that all tritium was effectively gone in 24 hours. Clearly, the HUP does not bind the tritium tightly.

After yet another gettering in the double-bulb mode, we flushed out the air-tritium on the anode side and added 27 kPa H_2 gas of 17% humidity as a hydrogen source. Figure 3 shows the flushing of the tritium through the HUP into the cathode bulb. By integrating the current plus following the cathode build-up of hydrogen gas, we find that we have replaced all the hydrogen in the HUP over 3 times in order to move 80% of the tritium across the 0.5 mm thickness of the HUP. In this run, 2% of the original tritium left the HUP and went back into the anode bulb air. In other hydrogen flushes, from 10 to 40% of original tritium reappeared in the anode gas. These experiments again confirm the view that the gettered tritium is close to the anode surface of the HUP and flushing it through requires moving much or all of the hydrogen in the HUP interior.

IV. DISCUSSION

We should next like to consider various HUP properties. Figure 4 shows the d.c. electrical conductivity versus potential for 1 mm HUP samples. We see that hydrogen gas is a more efficient source of protons than water (pH 4) or moist air. For the latter two, the upper curve is for fresh HUP and the lower curve for degraded HUP following a day's experiments.

The lowest curve in Fig. 4 is 1 mm HUP with solid gold blocking electrodes and the sample completely sealed in epoxy. This was a repeat of Shilton and Howe's similar experiment in which they derived an upper value of electronic conductivity of 10^{-6} S/m at 1 V at room temperature.⁸ We are not sure this is electronic or some sort of chemical reaction. We tried as well a "standard" HUP sample epoxied front and back to prevent hydrogen from entering or leaving. After 26 minutes at 4 V, the sample blew apart on the cathode side, which we take as evidence that hydrogen was trying to come off the porous cathode frit.

One of the most remarkable effects with the HUP is its residual voltage. For example, we gettered tritium for 167 hours at 2 V d.c. At the end of this time, we removed the power supply and rewired the HUP unit across a 1 M Ω resistor. We found a residual potential across the resistor of 1.82 V. Careful experiments showed that the polarity was the same as that originally applied with our external power supply. We next took out the resistor and put an ammeter in. The potential across the

1 K ammeter resistance dropped to near-zero in 3 minutes with a total discharge current of about 3×10^{18} charges. The 1 M Ω resistor was replaced and the residual potential gradually rose back to 0.87 V.

The HUP shows a large dielectric constant of about 3×10^5 at the start and 300 at the end of a run. This could be caused by space charging near the plates or at grain boundaries or possibly by residual ferroelectric ordering.⁹ The effect of space charging is to block the electric in the interior of the sample and allow conductivity only in a skin layer of thickness¹⁸

$$\lambda = (2k\epsilon_0 U/Ne)^{1/2} \quad (2)$$

where U is the d.c. potential, K the dielectric constant, $\epsilon_0 = 8.85 \times 10^{-12}$ C/V $\cdot$ m, N the charge density (taken to be 5×10^{27} charges/m³) and $e = 1.602 \times 10^{-19}$ C/charge.¹⁸ If this effect is present, it would allow tritium gettering only in a thin layer near the anode with a low leakage of current through the bulk of the HUP sample.

The interesting properties of HUP offer a hope that tritium gas can, indeed, be directly gettered from air. One can visualize flat panels of electrolytic getter fixed on the walls of laboratories and reactor rooms or massed in large dead-space tanks. It may be possible to carry out the gettering by passing the contaminated air over the panels with nothing more expensive than a low power blower. This offers the enticing possibility of the development of a cheaper tritium clean-up system.

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Fig. 1. Tritium gettering curves for 1 ppm T_2 gas in air of 3.4 humidity.

Fig. 2. Gettering of 1 ppm T_2 with 0.27 g palladium black. total gas pressure is 0.1 MPa at room temperature. A fast HUP gettering is shown for comparison. "Wet" air is 25% to 35% humidity.

Fig. 3. Flushthrough of tritium in HUP using H_2 gas. 100% tritium on the Y-axis corresponds to 72% gettered tritium initially by the HUP.

Fig. 4. D.c. electrical conductivity versus potential curves for HUP samples. The H_2 is at 13 to 26 kPa; the T_2 -in-air sample has 20% humidity. The gold blocking electrodes prevent hydrogen ions from entering or leaving the samples. The liquid water and air samples start high but degrade to the lower curves.