H_2 Production in Polyethylene Irradiated with Heavy Particles

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Introduction

Self-irradiation of waste materials is constantly changing their composition and thereby complicating management decisions. One of the major problem products is gaseous molecular hydrogen, which can accumulate to explosive concentrations. Successful waste management of hydrogen producing materials requires on accurate radiation chemical yields under a variety of conditions.

Information on the radiolysis of polymeric materials with gamma rays is available. However, heavy ions such as the α-particles associated with transuranic elements have a high rate of linear energy transfer (LET= -dE/dx) and can produce the same products with very different yields. This work concentrates on the production of molecular hydrogen in the radiolysis of solid organic materials with heavy ions such as ^{1}H and ^{4}He.

Summary

The observed yields of H_2 in the radiolysis of polyethylene show a strong dependence on particle LET. This variation could have a noticeable consequence on prediction of hazardous gas production from bulk materials exposed to transuranic waste materials.

Hydrogen production appears to be complicated by diffusion processes out of the bulk material. More information is necessary to differentiate production yields from observable yields.

A apparatus has been successfully designed and used to measure H_2 production in situ from the radiolysis of solid organic materials with high LET heavy ions.

Particle Characteristics in Polyethylene

Particle	Energy (MeV)	Differential LET (eV/nm)	Average LET (eV/nm)	Range (mm)
^{1}H	2	17.0	37.2	0.070
	5	8.4	21.9	0.339
	10	4.8	14.0	1.17
	15	3.4	10.7	2.41
^{4}He	5	97.1	167	0.034
	10	58.8	121	0.102
	15	42.8	97.2	0.203
	20	33.8	82.4	0.336
^{12}C	10	748	843	0.012
	20	561	744	0.028
	30	450	663	0.048

$$\mathrm{LET} = -\,dE/dx$$

$$\overline{\mathrm{LET}} = \frac{1}{E_o}\int_o^{E_o} -\,dE/dx\; dE$$

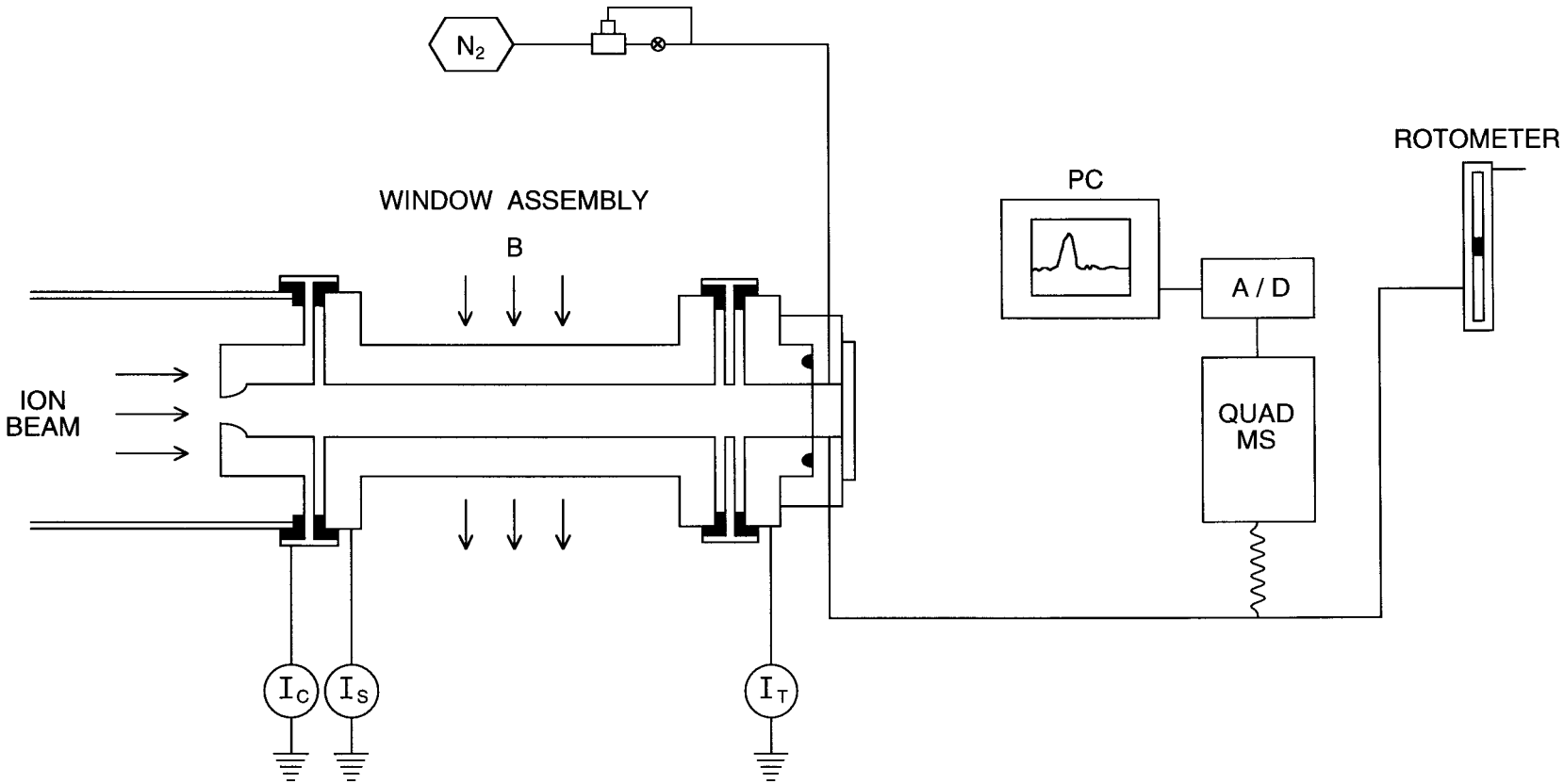
Experimental

High-density polyethylene (M_w ~ 125,000) was irradiated with protons and helium ions from the Notre Dame Nuclear Structure Laboratory. The particles pass through a window assembly that collimates the beam, suppresses scattered electrons, aligns the sample, and collects the total charge on the sample. Dosimetry is performed by integrating the collected charge in conjunction with knowledge of the particle charge and energy. The later two quantities were obtained by magnetic analysis.

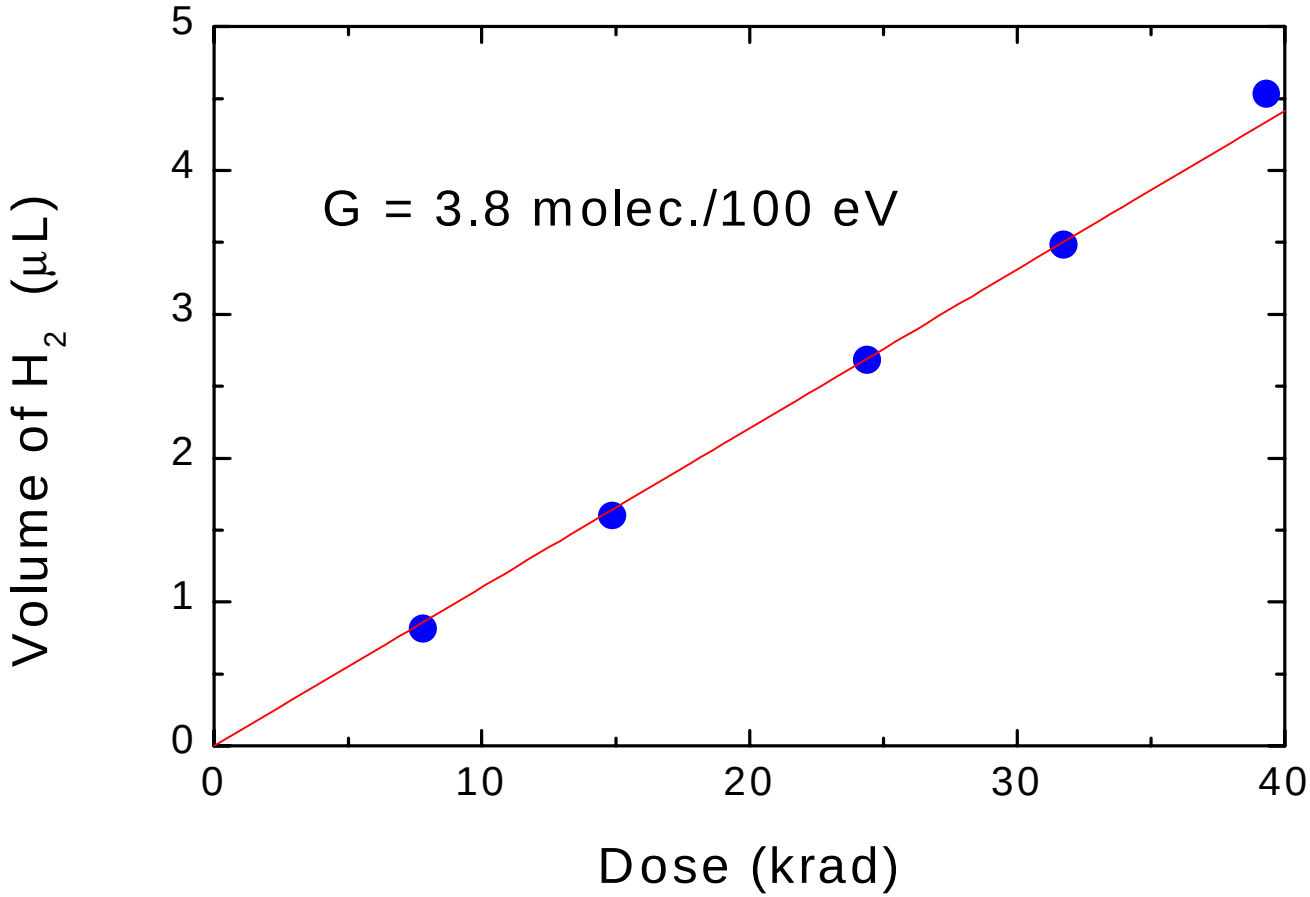
Hydrogen was collected by flowing a stream of N_2 across the face of the target and analyzing the effluent with a quadrupole mass spectrometer.

Gamma radiolysis was performed using a ^{60}Co source (~ 30 krad / min) with the same H_2 detection technique.

Heavy Ion Radiolysis Assembly



Dose Dependence in Gamma Radiolysis

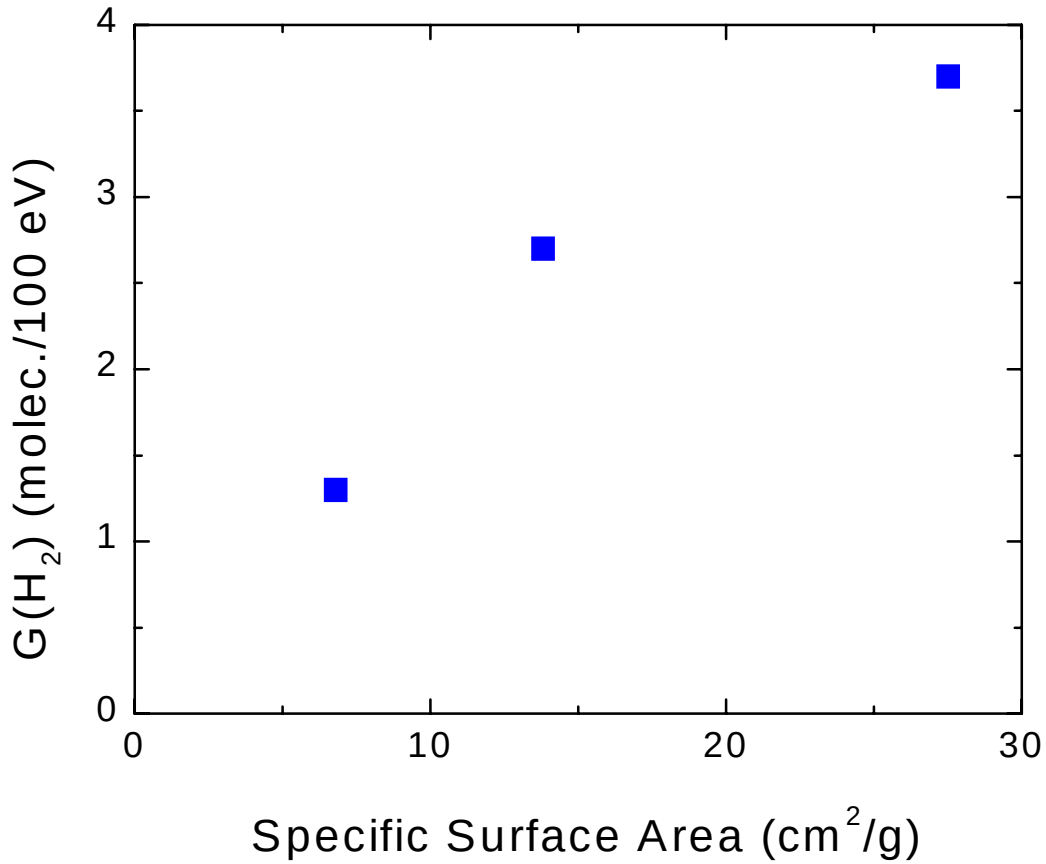


Gamma Radiolysis

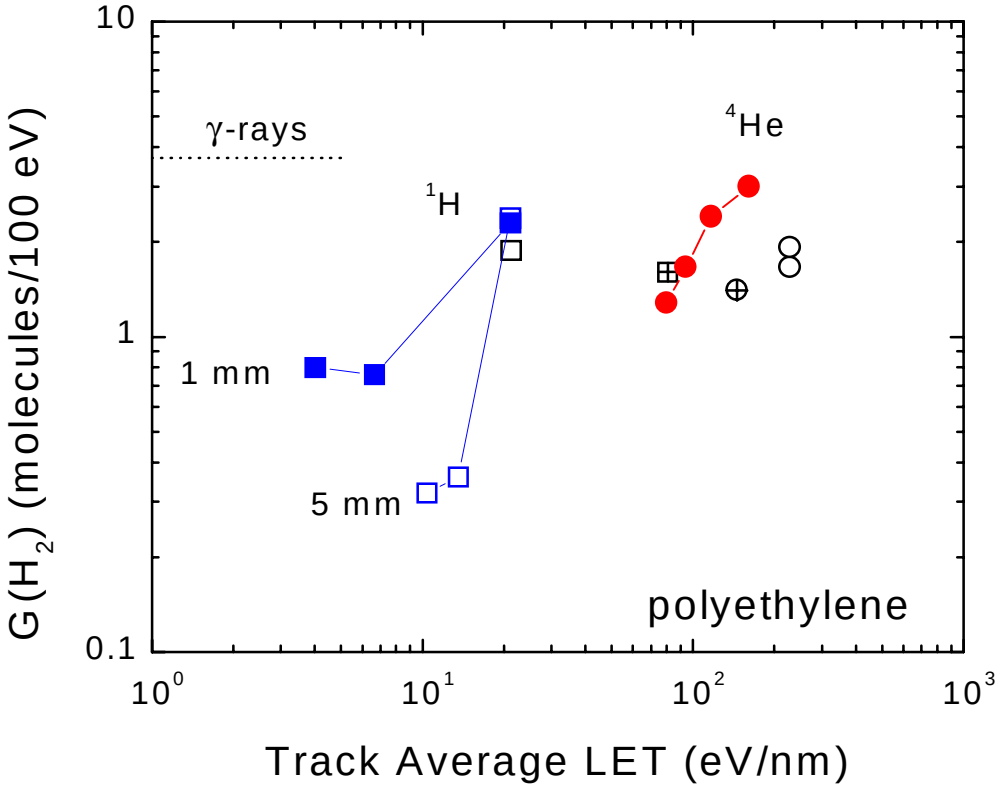
The gamma radiolysis of small pellets of high-density polyethylene leads to the production of 3.8 molecules of H_2 per 100 eV of total energy absorption. H_2 production is found to be linear with dose and the yield agrees well with other studies using gamma radiolysis.

Examination of the effects of surface area on the production of H_2 found a large variation in observed yields. Polyethylene in the shape of rods of 6.4 and 3.2 mm diameter, 50 mm long, with specific surface areas of 6.8 and 13.8 cm^2/g, respectively, gave relatively low yields of H_2 production due to trapping in the bulk. The apparent effective diffusion distance of H_2 at room temperature and over the time scales of these experiments is about 1 mm.

Surface Area Effects in Gamma Radiolysis



LET Dependence of H_2 Formation



colored symbols: this work
open symbols: L. Calcagno and G. Foti, Appl. Phys. Lett, 1985, 47, 363.
cross in open symbol: M. B. Lewis and E. H. Lee, Nucl. Instr. Meth. 1992, B69, 341.

Heavy Ion radiolysis of Polyethylene

High LET is expected to enhance radical-radical combination processes because of the increase in radical density. These reactions can lead to a significant increase in the production of H_2 and cross-linked polymer formation. An increase in H_2 formation is found with increasing particle LET.

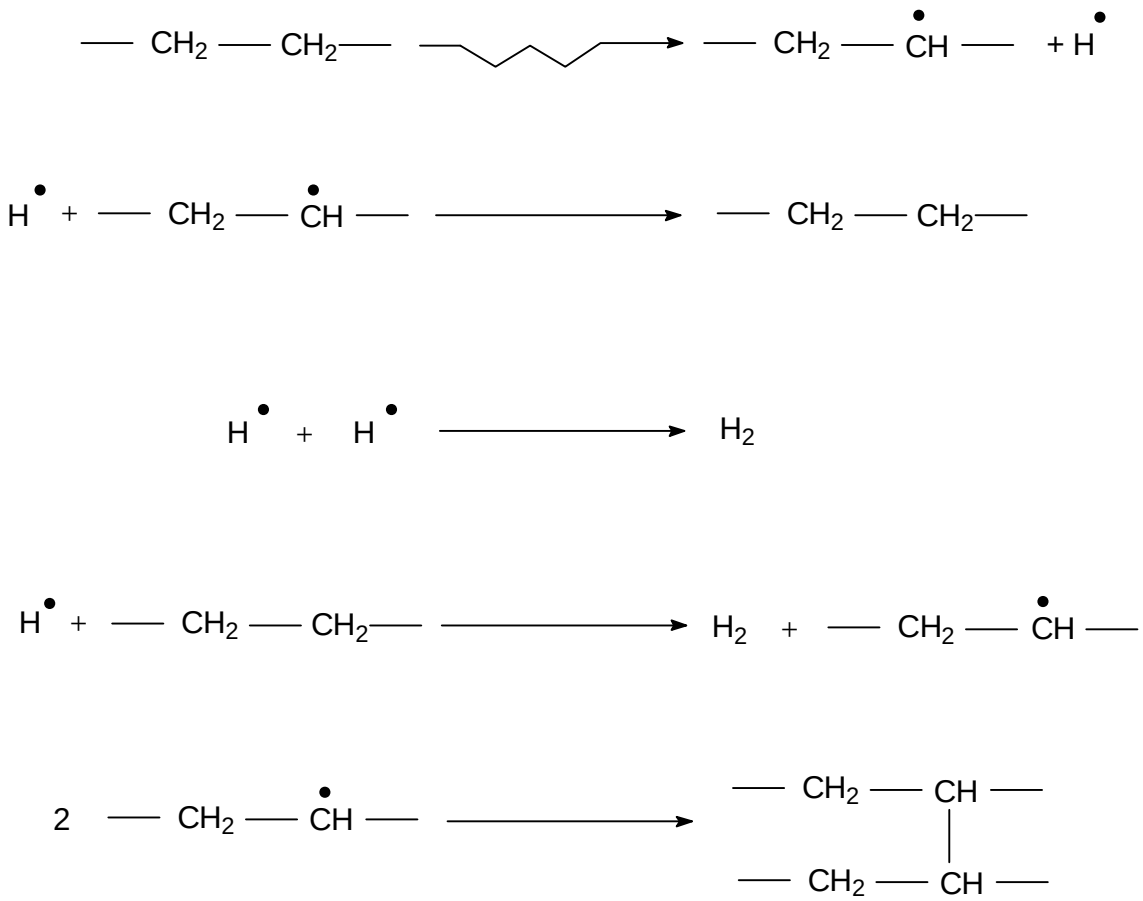
Although the H_2 yield increases with increasing LET its magnitude with low LET heavy ions is less than that for gamma rays. Low LET, high energy, particles have relatively long ranges in the polymer. It is possible that H_2 is being formed with higher yields, but it is not diffusing out on the time scales of the experiment. Irradiation of thin samples seems to confirm these observations.

Things to Do

1. Carbon ions will be used to extend these studies to higher LET and shorter range.

2. Other polymers such as polystyrene will be examined because of the fundamental information they offer. Resins and other plastics will be examined because of their practical importance.

3. Different atmospheres, such as O_2 and water vapor, will be examined for their effects on the polymer surface.

4. Diffusion of hydrogen for the bulk will be examined theoretically and experimentally by variation of sample thickness.

Reaction Scheme