

Methane Production from Carbon under Combined Electron and Atomic Hydrogen Bombardment: Evidence for a Synergistic Effect?

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Carbon is in widespread use as a first wall material for fusion experiments. Recent reports on the existence of a strong synergistic effect, when carbon is bombarded simultaneously by atomic hydrogen and electrons, create concern over this use of carbon. Such an effect could result in an unacceptably high chemical erosion of the walls and detrimental release of impurities into the plasma and fuel recycling system. Contrary to these reports, the authors have observed only a weak synergistic effect when carbon samples were strongly baked and the experiments performed in a specially cleaned UHV system.

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Carbon or carbides are often employed as first wall materials in fusion devices because of carbon's low Z number and its refractory nature. Unfortunately, carbon is susceptible to the production of volatile species—particularly methane—under hydrogen plasma impact. Carbon mobilized in this way results in degradation of wall integrity and plasma contamination. In deuterium-tritium devices these gaseous compounds pose serious complications in the fuel recycle loop.

It is well documented that methane is released by chemical sputtering under energetic hydrogen ion and ~ 1 -eV neutral atomic-hydrogen bombardment.¹ It has been suggested² that a significant synergistic effect occurs for actual plasma impact where the total methane production from combined ion, atom, electron, photon, etc., impact is greater than the sum effect of these processes separately. For the case of combined 5-keV argon ion and < 1 -eV atomic-hydrogen impact on pyrolytic graphite, a strong synergistic effect has recently been reported.^{3,4}

The existence of a synergistic effect in the production of methane due to combined electron and ~ 1 -eV atomic-hydrogen bombardment, on the other hand, is a matter of some controversy. The purpose of the present communication is to clarify controversial results on the magnitude of electron-induced synergistic effects. Since these effects could influence the design of the next generation of fusion devices, clarification of the matter appears to be timely. One set of studies⁵⁻⁷ has shown a strong enhancement of CH_4 yield (over the yield from H^0 alone) as a result of electron impact on carbon of various types. Yields as high as $(0.1 \text{ CH}_4)/e$ have been reported. The possibility of such extremely high chemical erosion rates has generated concern over the use of

carbon in first wall locations.^{8,9}

We have also reported^{10,11} results from experiments involving simultaneous bombardment of carbon (Papyex) by H^0 and electrons and have arrived at different conclusions. We describe our findings here in a more extended form than previously published and report new results.

Carbon and carbide materials are generally made by processes involving hydrocarbons. In addition, many types of graphite are manufactured by prolonged high-temperature heating of carbon in air resulting in substantial uptake of H_2O , etc. It is thus likely that any given carbon sample will contain significant amounts of hydrogen from the time of its manufacture. In order to test for yields of CH_4 under electron and/or H^0 impact it is essential to reduce the influence of such H-C species, or other forms of hydrogen, preexisting in the sample. Otherwise, very high CH_4 signals can be observed even under pure electron bombardment alone (no H^0 impact)—thus obscuring the effect of bombarding species. For example, using Papyex carbon under electron bombardment alone, we measured very high methane signals, $\sim (0.01 \text{ CH}_4)/e$, when neither sample nor system was baked. The system used was an all-metal UHV device pumped by a turbomolecular pump to a base pressure of $\sim 5 \times 10^{-7}$ Torr at the time when the high methane signals were observed. By baking the system for 48 h at 500 K (reducing the base pressure to $\sim 10^{-10}$ Torr) and the sample at 850 K, the measured signal for electron impact alone was drastically reduced to $(10^{-4} - 10^{-5} \text{ CH}_4)/e$, dependent on sample temperature during H^0 exposure.

Our first conclusion, therefore, is that unless a carbon sample has been strongly baked (i.e., in vacuum, at $T \approx 850$ K for several days, or at

> 1200 K for 1–24 h), it is likely to contain large quantities of hydrocarbons or other forms of hydrogen from its time of fabrication which can yield copious amounts of CH_4 under only electron impact. This CH_4 production can easily be confused with CH_4 production arising from combined H^0 and e impact unless this preexisting hydrogen is substantially eliminated by baking.

These two sets of studies^{5–7, 10, 11} on combined H^0 and e bombardment of carbon have involved the use of the H_2 back-fill method¹² to produce H^0 , i.e., the vacuum vessel is filled to a relatively high pressure of H_2 , 10^{-6} – 10^{-4} Torr, and H^0 is produced by surface dissociation on a hot tungsten filament. This technique, however, entails a serious experimental problem—as was also observed by Gould¹² in his (nonsynergistic) studies. Unless the vacuum system is very thoroughly cleaned, spurious effects of two basic types are encountered. First, H^0 striking the walls of the chamber produces CH_4 from carbon impurities there. Thus the quadrupole signal being used to monitor CH_4 from the sample can be confused by CH_4 from the walls—particularly since the signal correlates with H^0 production. A similar effect has been observed by Dietz, Waelbroeck, and Wienhold,¹³ and by Dylla and Blanchard¹⁴ in connection with H^0 produced by quadrupole filaments in stainless-steel systems. A comparable problem arises in glass systems¹⁵ interfering with studies of surface phenomena. We found that normal baking alone (500 K for a few days yielding a base pressure 10^{-10} Torr) was not sufficient to reduce this wall CH_4 production adequately: CH_4/H_2 levels were $\sim 5 \times 10^{-3}$ upon back-filling to $P_{\text{H}_2} = 10^{-4}$ Torr. It was also necessary to bombard the chamber walls with electrons and H^0 during the baking process. While this did not result in further decrease in base pressure (which was principally H_2), it did result in a reduced CH_4/H_2 level when the chamber was back-filled with H_2 (CH_4/H_2 was reduced from $\sim 5 \times 10^{-3}$ to $< 10^{-4}$). Consequently, this resulted in a reduced wall production of CH_4 when the tungsten filament was turned on to produce H^0 . The latter conclusion is based on an experiment in which the carbon sample was removed from the system and was replaced by a tungsten sample, thus permitting discrimination between wall and carbon-sample CH_4 production.

A second consequence of employing the UHV system in anything less than the “super-cleaned” mode of operation is that CH_4 molecules produced at the walls—from H_2 or H^0 bombardment there

—apparently adsorb on the surface of the test sample. When the sample is then bombarded with electrons this CH_4 is impact desorbed, giving a spurious CH_4 yield. This latter conclusion is also based on the experiments employing tungsten samples in place of carbon, as now described.

After operation of the system under super-clean conditions for two months without breaking vacuum the system was opened to air for a few hours while the carbon sample was replaced with a tungsten one. The system was then baked conventionally (500 K, 50 h) and a base pressure of $\sim 10^{-10}$ Torr was attained. Under these vacuum conditions (no H_2 back-fill) no detectable methane signal could be observed [$< (10^{-5} \text{ CH}_4)/e$] by electron bombardment of the tungsten sample. The chamber was then back-filled with H_2 to $P_{\text{H}_2} = 10^{-4}$ Torr. Presumably, because the system has only been open to air for a short time after two months of super-clean operation, the walls were still quite clean and the CH_4/H_2 level only came up to $\sim 3 \times 10^{-4}$ as a result of the H_2 back-filling. In this condition the tungsten sample was bombarded simultaneously with H^0 atoms [$\sim 10^{15} \text{ H}^0/\text{cm}^2 \text{ s}$] and electrons ($\sim 2 \times 10^{15} e/\text{cm}^2 \text{ s}$). An electron-enhanced CH_4 signal from the tungsten was observed in this situation at a level of $\sim (3 \times 10^{-4} \text{ CH}_4)/e$. The vacuum system was then “super-baked” (500 K, 12 h with H^0 wall bombardment). This evidently increased the cleanliness of the system since back-filling with H_2 now resulted in a CH_4/H_2 level of only $\sim 8 \times 10^{-5}$. In this situation the electron-enhanced CH_4 signal was also reduced by a factor of ~ 4 to $\sim (8 \times 10^{-5} \text{ CH}_4)/e$. These results using a tungsten sample imply that CH_4 released from the system walls by H_2 and H^0 impact adsorbs on the sample where it can be released by electron impact. While the absolute CH_4/e levels observed for this effect with the present vacuum system are quite low, this probably reflects the fact that even after short exposure to air the system is still quite clean. In a different vacuum system—such as a conventionally baked diffusion-pump/Pyrex system^{5–7}—the absolute CH_4/e levels resulting from CH_4 adsorbed on the sample may be significantly larger, leading (in the case of carbon samples) to a spurious $\text{H}^0 + e$ synergistic yield of CH_4 .

It is therefore our second general conclusion that $\text{H}^0 + e$ synergistic studies using the H_2 back-fill method must be carried out in extremely clean conditions if spurious effects are to be eliminated.

After baking the Papyex sample at 1500 K for

several minutes under UHV conditions, and after baking the vacuum system for several days at 500 K while simultaneously bombarding the walls with H_2 and H^0 , an apparent low-level, electron-induced synergistic effect was still observed from the Papyex. For equal electron and atom total fluxes of $\sim 10^{16} \text{ s}^{-1}$ ($\sim 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$) the methane production was approximately doubled by simultaneous H^0 and electron bombardment over the case of H^0 flux alone. Signals varied in the range 10^{-4} – 10^{-3} CH_4 per electron or per H^0 depending on the exact sample temperature (between 500 and 1200 K), flux rates, electron voltages (300–100 V), and degree of graphite thermal reactivation.¹¹ In the absence of the H_2 back-fill and H^0 flux, CH_4/e signals were $< (10^{-5} \text{ CH}_4)/e$. It is possible that further baking of sample and system would reduce the observed apparent synergistic effect still further.

Using a quite different experimental technique, Vietzke, Flaskamp, and Philipps³ have also recently reported on electron- H^0 synergistic production of CH_4 from carbon. The main characteristics of their system are (a) the use of an H^0 beam source, and (b) the positioning of the beam source, target, and quadrupole mass analyzer in separate chambers in such a way that the last two components can be kept at very low pressures even during sample bombardment. The various problems associated with the H_2 back-fill method are thus largely avoided. Their pyrolytic graphite samples were baked for 1 h at 2200 K before use. Employing an H^0 flux of $1.5 \times 10^{16} \text{ H}^0/\text{cm}^2 \text{ s}$ and an electron flux of 6×10^{13} – $3 \times 10^{17} \text{ e}/\text{cm}^2 \text{ s}$ at voltages up to 500 V and sample temperatures of 300–800 K, Vietzke, Flaskamp, and Philipps observed signal enhancements due to electrons smaller than 50% of that observed for H^0 atoms alone at a sample temperature of 400 K [$\sim (10^{-4} \text{ CH}_4)/\text{H}^0$]. They concluded "that a significant synergistic effect on the reaction of atomic hydrogen with graphite is not observed by simultaneous electron irradiation."

With regard to *sequential* rather than *simultaneous* bombardment of the carbon to a given fluence of H^0 followed by electron bombardment, we have found insignificant CH_4 production arising from the electron bombardment. This experiment consisted of exposing the sample to an H^0 flux of $\sim 10^{15} \text{ H}^0/\text{cm}^2 \text{ s}$ up to a fluence of $\sim 10^{18} \text{ H}^0/\text{cm}^2$. The system was then evacuated to $\sim 10^{-9}$ Torr and an electron flux of $\sim 10^{15} \text{ e}/\text{cm}^2 \text{ s}$ (300–1000 eV) was directed onto the hydrogen-loaded sample. The CH_4/e signal was found to be almost

unmeasurable, about 1% of the CH_4/H^0 signal.

With regard to the latter experiment, however, it should be noted that a fluence of $\sim 10^{18} \text{ H}^0/\text{cm}^2$ may not result in significant loading of the sample with H^0 . While Hucks, Flaskamp, and Vietzke¹⁶ have reported fairly high levels of hydrogen retention for ≈ 1 -eV H^0 on carbon, $\sim 1\%$, our own preliminary studies have shown relatively low retention: $\sim 3 \times 10^{13} \text{ H}^0/\text{cm}^2$ retained for a fluence of $10^{18} \text{ H}^0/\text{cm}^2$. This latter matter is, however, the object of continuing investigation. It is well established, on the other hand, that the retention of 100–1000-eV H^+ ions in carbon is quite high, $\sim 50\%$ until saturation.¹⁷ Thus Cohen's conjecture⁴ that strong electron-induced CH_4 production may occur in actual tokamaks (associated presumably with the high levels of trapped hydrogen arising from energetic ion bombardment) remains to be tested. This latter matter is also an object of our current investigation.

In summary, our results indicate that in $H^0 + e$ synergistic studies of methane production from carbon using the H_2 back-fill method to produce H^0 , at least three spurious effects must be eliminated: (a) The hydrogen or hydrocarbons existing in the carbon from the time of its manufacture must be removed; otherwise electron impact (alone) can give large CH_4 signals from the sample. (b) The vacuum system walls must be extremely clean, or H^0 wall impact can cause large CH_4 signals which *directly* confuse the signal from the sample. (c) Such wall-produced CH_4 can adsorb on the carbon sample causing an *in-direct* confusing effect due to electron-impact desorption.

The implication of these findings is that the system and procedures employed in the work of Refs. 5–7 may be inadequate to avoid spurious effects in $H^0 + e$ synergistic studies using the back-fill method of H^0 production. With regard to ≈ 1 -eV H^0 bombardment, therefore, it is our conclusion that the present evidence points to the absence of any strong $H^0 + e$ synergistic effect.

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ERRATUM

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