The generation of ammonia from atomic hydrogen and nitrogen has been demonstrated by means of cavity enhanced absorption spectroscopy. The atomic species are produced in a thermal plasma source in which plasma is created from mixtures of hydrogen and nitrogen. It is shown that for large atomic flux conditions, 2% of the hydrogen and nitrogen can be converted to ammonia. The process in which the ammonia molecules are formed from atomic radicals at the fully covered surface is called plasma-activated catalysis. © 2002 American Institute of Physics.

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and partially ionized (5\%–10\%) nitrogen flow. The hydrogen molecules were injected into the vessel at a flow rate, $f_{H_2}$, between 0 and 1.45 slm. The background pressure is kept constant by controlling the pump speed. The absolute density of ammonia as a function of the relative flow rate of hydrogen with respect to the total flow rate is shown in Fig. 2 for a background pressure of 100 Pa. The ammonia density in the background gas reaches a maximum of $2.5 \times 10^{19} \text{ m}^{-3}$ at a $H_2$ flow rate of 0.25 times the total flow rate. The increase and saturation can be understood by noting that the hydrogen molecules can only be dissociated by the $N^+$ ions from the arc delivering two $H$ atoms via the reactions $N^+ + H_2 \rightarrow NH^+ + H$, followed by dissociative recombination of $NH^+$, forming $N$ and $H$. Then the $H$ production will increase with $H_2$ flow until all $N^+$ ions are consumed. This explains the saturation behavior of the ammonia density as can be seen in Fig. 2. Under the condition of maximum $NH_3$ production, 0.2\% of the background gas is $NH_3$, independent of the background pressure over the measured range, i.e., from 10 to 200 Pa. Starting from atomic radicals, volume production of $NH_3$ would require more reactions and/or three particle association reactions. However, these reactions are slow for the present pressure range. Also the production would show a stronger than linear dependence on pressure, which is not observed.

In the second situation, the same experimental settings were used as in the first situation, except that the hydrogen flows through the arc while nitrogen molecules are injected into the vessel. In this case no $NH_3$ was detected. Note that with $H_2$ in the arc the ionization degree is substantially less, and thus less $N$ radicals are produced. This shows the importance of the need for atomic radicals in the production of $NH_3$.

In the third situation, the highest efficiency of ammonia production is reached, i.e., when plasma is produced in the cascaded arc with both nitrogen and hydrogen flowing through the arc. In Fig. 3, the results are shown of the ammonia density as function of the relative $H_2$ flow rate to the total flow rate, which was 2.0 slm. The maximum ammonia density under these plasma conditions is achieved at $\phi_{H_2} = 1.44 \text{ slm}$ and $\phi_{N_2} = 0.56 \text{ slm}$, which is close to the stoichiometric ratio of hydrogen and nitrogen in $NH_3$. This indicates that for both nitrogen and hydrogen the dissociation degree of the thermal plasma source does not depend strongly on the $N_2/H_2$ flow ratio. The maximum density of $NH_3$ at 20 Pa background pressure is about $4 \times 10^{19} \text{ m}^{-3}$, which is 2\% of the background gas at a temperature of 600 K. This temperature is determined from the width of the measured $NH_3$ transitions. For these experiments the density of ammonia shows a slightly less than linear dependence on background pressure.

We conclude that under our experimental conditions $NH_3$ is mainly produced at the vessel wall. This has also been concluded from a self-consistent kinetic model,\textsuperscript{9} which predicted fairly well the measured relative $NH_3$ density as a function of the $H_2$ percentage in a low-pressure $N_2$–$H_2$ flowing discharge.\textsuperscript{10}

For the efficient production of ammonia the hydrogen and nitrogen atoms have to arrive at the same area on the vessel wall.\textsuperscript{11} However, due to the large difference in mass, the light hydrogen atoms diffuse out of the jet, while the
nitrogen atoms tend to stay closer to the axis. This so-called mass-defocusing effect has been reported in Ar–H\textsubscript{2} and pure H\textsubscript{2} plasma expansion.\textsuperscript{12,13} In view of this effect the production efficiency of 2\% is remarkably high.

We have shown that by using high fluxes of atomic nitrogen and atomic hydrogen radicals, produced from N\textsubscript{2}–H\textsubscript{2} plasma, ammonia is produced at the vessel wall. Since the plasma is used to produce the radicals, and the wall acts as catalyst, the process is called plasma-activated catalysis. By tuning the plasma parameters and choosing the right wall material, the process could be a promising new way for small scale selective production of molecules, starting from their atomic constituents. It could be extended to hydrazine (N\textsubscript{2}H\textsubscript{4})\textsuperscript{1} or even organic molecules like methanol. In the latter example one could start from natural gas and oxygen.\textsuperscript{14}

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\textsuperscript{8}HITRAN (high resolution transmission molecular absorption) database (http://www.hitran.com).