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Hydrogen generation in a microhollow cathode discharge in high-pressure ammonia–argon gas mixtures

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Abstract

We explored the feasibility of using a single flow-through microhollow cathode discharge (MHCD) as a non-thermal plasma source for hydrogen (H_2) production for portable fuel cell applications. The MHCD device consisted of two thin metal electrodes separated by a mica spacer with a single-hole, roughly 100 μm in diameter, through all three layers. The efficiency of the MHCD reactor for H_2 generation from NH_3 was analyzed by monitoring the products formed in the discharge in a mass spectrometer. Using a gas mixture of up to 10% NH_3 in Ar at pressures up to one atmosphere, the MHCD reactor achieved a maximum ammonia conversion of slightly more than 20%. The overall power efficiency of the MHCD reactor reached a peak value of about 11%. The dependence of NH_3 conversion and power efficiency on the residence time of the gas in the MHCD plasma was studied. Experiments using pulsed excitation of the MHCD plasma indicated that pulsing can increase the power efficiency. Design and operating criteria are proposed for a microplasma-based H_2 generator that can achieve a power efficiency above the break-even point, i.e., a microplasma reactor that requires less electrical power to generate and maintain the plasma than the power that can be obtained from the conversion of the H_2 generated in the microplasma reactor.

Keywords: Hydrogen; Plasma chemistry; Fuel reforming; Hollow cathode discharge; Mass spectrometry

1. Introduction

Despite the remarkable development and rapid marketplace entry of handheld devices such as mobile phones, laptop computers, PDAs, and digital cameras, small batteries remain the only suitable choice to supply power to these devices to date [1]. However, there are many apparent shortcomings of conventional batteries such as their weight, their cost, the need for frequent recharging, and serious environmental problems associated with their final disposal. At the same time, the ever increasing capability of these devices results in an increased demand for power. Conventional power sources like lithium-ion batteries are becoming insufficient in terms of meeting the specific energy density required for future applications. In contrast, small fuel cell systems that operate on hydrogen-containing fuels such as methanol and NH_3 could decrease the weight of the power source. The need to recharge the device could be reduced to the comparatively trivial task of replenishing the fuel. Therefore, small fuel cell systems may be an attractive alternative power sources for portable applications [1,2]. One major hurdle to the use of fuel cells to power portable devices is the issue of providing a safe and easy way to supply the hydrogen, H_2. The disadvantages associated with the safe storage of H_2, even in small quantities, renders on-demand, in situ generation of H_2 the only feasible approach.

Current technologies for fuel processing include steam reforming, partial oxidation, auto thermal reformation, and thermal decomposition [3–5]. All these technologies rely on thermodynamic equilibrium reactions. Thus, in order to get a high conversion the reactor has to operate at high temperatures, e.g., higher than 500 °C for NH_3 [6] and 250–300 °C for methanol [7]. These temperature requirements cause serious thermal management problems [8]. Another issue is

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the comparatively slow start-up time. Since the key reactions occur at high temperatures, it takes usually several minutes before the generation of H_2 reaches a steady state. An attractive alternative to the current technology is the use of non-thermal plasmas [9], which have been shown to be suitable volumetric catalytic media. In a non-thermal plasma, the energy required to sustain the discharge is imparted to the electron component in the discharge, while the positive ions and plasma neutrals are at temperatures at or only slightly above room temperature (non-thermal plasmas are thus also referred to as non-equilibrium plasmas). Thus, a non-thermal plasma can drive "high-temperature chemistry" at low ambient temperatures using input energy levels that are much lower than the energy required to drive an equilibrium reaction. Radicals, ions and other active species are efficiently produced via electron impact dissociation, excitation and ionization of the feed gas.

This paper reports the results of experiments aimed at using a single microhollow cathode discharge (MHCD) as a non-thermal plasma source for hydrogen production. The fuel used in this study was NH_3 which was diluted in Ar as the carrier gas. The dependence of NH_3 conversion and the power efficiency on the gas residence time in the MHCD plasma was studied in detail. Experiments using pulsed excitation of the MHCD plasma indicated that pulsing increases the power efficiency. Based on these experimental results, a design and operating criteria for a MHCD-based microplasma H_2 generator was developed that potentially can achieve a power efficiency above the break-even point, i.e., a microplasma reactor that can generate and maintain the plasma with less electrical power than the power that can be obtained from the conversion of the H_2 generated in the microplasma reactor.

2. Experimental details

2.1. The microhollow cathode discharge

The MHCD reactor used in this study is identical to the device described in earlier publications [10,11]. In this study, the gas discharge is formed between two electrodes made from 0.1 mm thick molybdenum foils (the cathode and anode) that are separated by a dielectric (mica) spacer of 0.25–0.40 mm thickness with a hole through the cathode, the dielectric, and the anode. Fig. 1 is a schematic diagram of a MHCD device. Traditionally, hollow cathode discharges are operated at reduced pressures in the range from hundreds of mTorr to a few Torr. A scaling law [12] involving the operating pressure, p, and the hole size, D, stipulates that atmospheric-pressure operation of a hollow cathode discharge is possible provided the hole size is in the range of a 100–250 μm (hence the nomenclature microhollow cathode discharge, MHCD). The MHCD can be powered either by dc voltage or it can be operated in a pulsed mode with unipolar pulses. Typical breakdown voltages of MHCDs are

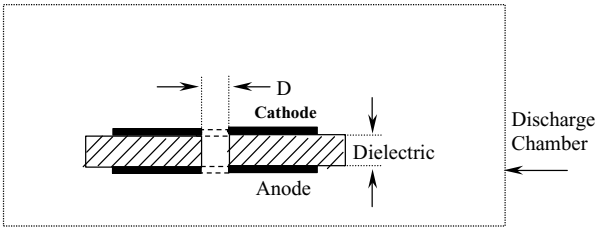

Fig. 1. Schematic diagram of a MHCD. The hole diameter, D, is of the order of 100 μm and the dielectric spacer has a thickness of about 250 μm.

500–700 V and discharge sustaining voltages are in the range of 200–300 V [10,11]. The electron density in a MHCD in a rare gas can be of the order of 10^{13} cm^{-3} for dc operation and up to 10^{15} cm^{-3} for pulsed operation [13]. Moreover, the electron distribution is highly non-Maxwellian with a significant fraction of electrons with energies above 20 eV and some electrons with energies corresponding to voltages close to the discharge sustaining voltage. Thus, there is a sufficient fraction of electrons in a MHCD that have enough energy to break chemical bonds such as the N–H bond in ammonia (bond dissociation energy 4.75 eV [14]).

2.2. The plasma reactor

Fig. 2 shows the schematic set-up of the MHCD plasma reactor and the data analysis system. The MHCD was mounted inside a sealed chamber and gas could only flow through the hole in the MHCD device. The external power supply was connected to the MHCD via a 100 kΩ ballast resistor (R_1). The constant dc power supply could alternatively be pulsed using a function generator, which controlled the duty cycle and the frequency of the unipolar pulses delivered to the plasma device. The discharge current, I, was derived from the voltage drop across the resistor R_2. The discharge sustaining voltage, V_S, is given by $V_S = V - I \times R_1$ where V is the applied voltage. The gas flow rates of Ar and NH_3 were controlled by mass flow controllers and the mixing ratio of the two gases is determined by the ratio of the respective flow rates. Typical NH_3 concentrations ranged from 2 to 7%. Higher NH_3 concentrations led to plasma instabilities, which may be overcome by using a different dielectric material, e.g., alumina instead of mica [13] or by pulsing the plasma (see below). A vacuum pump was connected to the system to evacuate the MHCD chamber before backfilling it with the gas mixture under study. The gas composition at the exit of the MHCD reactor was monitored by a mass spectrometer (MS).

2.3. Data analysis

Two quantities are important to evaluate the utility of the MHCD reactor, the conversion of NH_3 into H_2 and the power consumption. The conversion efficiency, κ, for producing H_2 (and N_2) from the conversion of NH_3 via plasma-induced dissociation was derived from the change of the partial

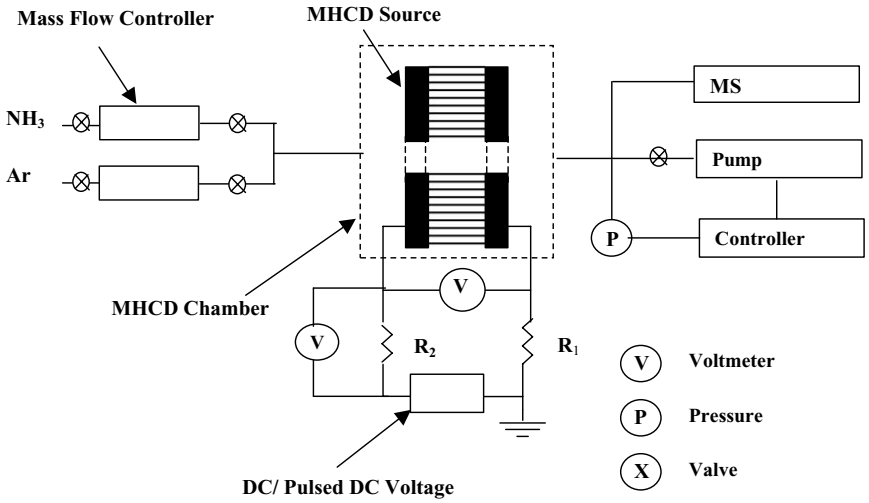

Fig. 2. Schematic diagram of the MHCD reactor set-up.

pressure of NH_3 due to the MHCD, $\kappa = (P_{in} - P_{out})/P_{in}$, where P_{in} and P_{out} are, respectively, the partial pressure of NH_3 at the MHCD inlet and exit with the plasma on. The conversion efficiency may be given as a number between 0 and 1 or, alternatively, as a percentage. We estimated the overall power efficiency ε of the microplasma reactor as the ratio of the electrical power which can be generated by the H_2 production rate of the microplasma reactor to the electrical power consumed by the microplasma reactor to sustain the plasma. From the experiments, we measured the current I and the voltage V to calculate the electrical power consumption, $P_{el} = I \times V$. For the electrical power generation, we assumed a 100% efficiency of the fuel cell for converting the chemical energy of H_2 and O_2 into the electrical energy, although most fuel cells operate around 60–80% in practice [1,2]. Thus, an efficiency $\varepsilon = 1$ denotes the break-even point, i.e., the fuel cell generates exactly the same amount of power that is required to sustain the MHCD. Obviously, economical and commercially feasible systems must achieve power efficiencies much larger than unity, which means that only a small fraction of the power generated by fuel cell is being be used to power the plasma reactor.

3. Results and discussion

The mass spectrometric analysis of the NH_3/Ar gas mixture (with a 6.25% NH_3 concentration at 760 Torr) at the exit of the MHCD plasma reactor using a dc plasma showed an immediate reduction of the concentration of NH_3 and increased the concentrations of both H_2 and N_2 in the gas flow when the plasma was ignited. The partial pressure of Ar decreased very slightly, which coincided with the appearance of a mass peak corresponding to the formation of ArH. Fig. 3 shows in detail the temporal behavior of the concentrations of NH_3, H_2, and N_2 recorded over an extended period of time. From the change of the partial pressure of NH_3, we estimate that the about 20% of the NH_3 is dissociated in the plasma. We note that the time delay between the ignition of the plasma and the resulting change in the gas concentrations displayed in Fig. 3 is the result of the fact that the gas was sampled a considerable distance downstream from the plasma volume because of the geometrical constraints of the MHCD reactor. The dead time was estimated to be about 10 min based on the gas flow conditions and the volume of the chamber surrounding the actual plasma between the MHCD and the mass spectrometer. Bench-scale experiments exposing hydrocarbons to a non-thermal plasma demonstrated that the effect of the plasma on the gas decomposition is essentially instantaneous [15].

The NH_3 conversion and the power efficiency were examined as a function of the residence time of the NH_3/Ar gas mixture in the MHCD plasma. The residence time is

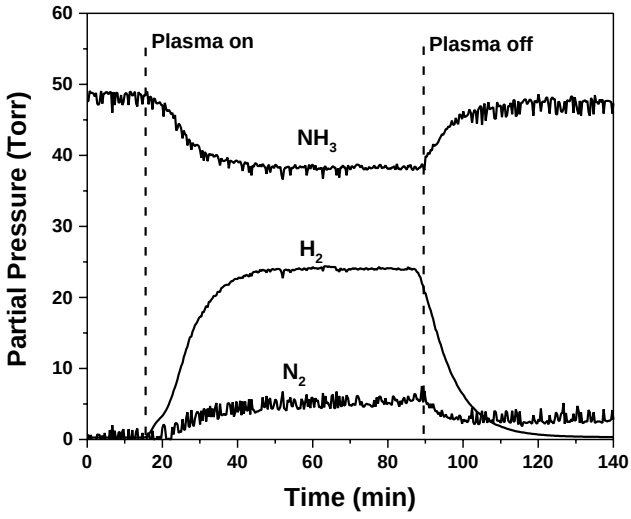

Fig. 3. Temporal behavior of the NH_3, H_2, and N_2 concentrations of a one atmosphere gas mixture of 6.25% NH_3 in Ar exposed to the plasma generated in a MHCD.

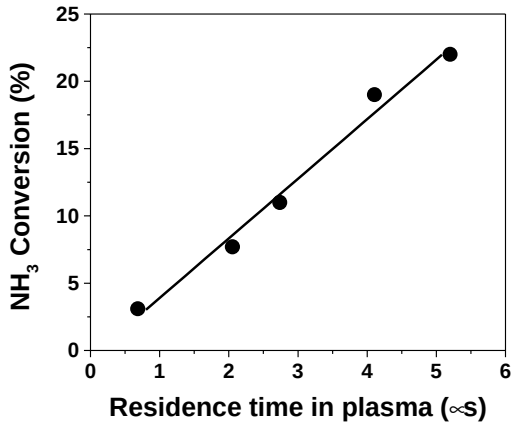

Fig. 4. NH_3 conversion (in percent) as a function of residence time of the gas mixture in the MHCD plasma.

determined by the gas flow rate, the pressure, and the MHCD dimensions. Fig. 4 shows the effect of the residence time on the NH_3 conversion. The relationship is essentially linear in the regime of residence times studied, which were in the range of a few microseconds. Similarly, Fig. 5 shows an essentially linear increase in the power efficiency as the residence time increases and reaches a value of about 10% at a residence time of 5 μs. Extrapolation of the results depicted in Figs. 4 and 5 suggest that—under the same operating conditions—a residence time of about 25 μs in the plasma would result in a complete conversion of all NH_3, which, in turn, would lead to a power efficiency of about 0.5. This would still be less than the desired break-even point of $\varepsilon = 1$.

Preliminary experiments were conducted using the MHCD reactor excited by unipolar dc pulses. These experiments were motivated by the earlier observation that the efficiency of light sources based on MHCDs increases appreciably when the discharge is operated by pulsed dc as opposed to dc [13,16]. In our case, the pulse length was varied from 40 ms to 100 μs and the duty cycle from 0.83 to 0.11. Even though the NH_3 conversion rate decreased from 17 to 7% as the pulse length and duty cycle were decreased, the power efficiency increased by a factor of 2.5. This result indicates that a combination of short pulse excitation and suitable duty cycle may lead to a minimization of the power input into the discharge thus improving the power efficiency, while maintaining a sufficiently high NH_3 conversion.

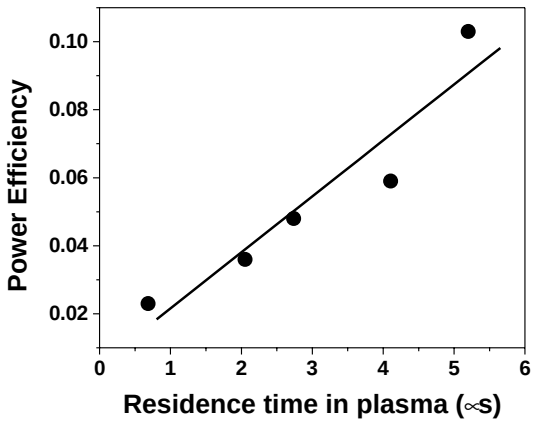

Fig. 5. Power efficiency as a function of the residence time of the gas mixture in the MHCD plasma.

Lastly, preliminary experiments using a two-dimensional array of 16 MHCDs operated in parallel were carried out [17]. In this arrangement, the MHCDs were separated from each other by a center-to-center distance of three to four times the size of the hole in each MHCD. The experiments demonstrated that such an arrangement allows the processing of a larger gas flow and also showed an increase in the power efficiency by about a factor of 2. The power saving is the result of the fact that the MHCDs in such an arrangement are electrically not entirely separated. The plasmas generated by two MHCDs in close proximity overlap and the current required to operated the two MHCDs is less than twice the current required to operate a single MHCD.

4. Summary and conclusions

A series of experiments, in which we explored the use of a flow-through single-hole MHCD plasma reactor for the generation of H_2 from the conversion of NH_3 in a diluted NH_3/Ar gas mixture at pressures of up to one atmosphere, led to the following results:

1. NH_3 conversion rates of up to 20% could be realized for residence times of the gas mixture in the dc plasma of up to 5 μs.
2. Bench-scale experiments demonstrated that the effect of the plasma on the gas decomposition is essentially instantaneous.
3. Power efficiencies of up to 0.11 (11%) could be achieved under these conditions, which are well below the break-even point of $\varepsilon = 1$.
4. The NH_3 conversion and the power efficiency are proportional to the residence time of the gas mixture in the plasma; under the present conditions, a residence time of 25 μs would yield a 100% NH_3 conversion and lead to a power efficiency of 0.5.
5. As the power efficiency is directly proportional to the amount of H_2 generated from the conversion of NH_3, the use of gas mixtures of high NH_3 concentrations (up to pure NH_3 with no feed gas) are desirable.
6. The overall power efficiency can also be increased significantly by pulsing the plasma.

Based on these findings, we conclude that the plasma-induced generation of H_2 from H-containing molecules such as NH_3 or CH_4 for portable fuel cells is possible in principle using microplasma reactors such as a MHCD device. However, it is also apparent from our results that an economical MHCD plasma reactor for H_2 generation has to involve

more than a single flow-through MHCD and gas mixtures with much higher concentrations of the gaseous hydro-fuel. Some design and operating considerations for practical realizations of more efficient microplasma reactors are discussed in Appendix A.

Acknowledgements

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Appendix A. Design and operating considerations for a power-efficient microplasma H_2 reactor

Based on the experimental findings in this work, the following design and operating criteria are suggested for a MHCD-based microplasma reactor to generate H_2 from NH_3 (or from other H-containing gaseous hydro-fuels) that can achieve a power efficiency larger than the break-even point of $\varepsilon = 1$:

1. *Operation of the MHCD with a gas mixture that contains a large fraction, if not 100% NH_3 (or any other hydro-fuel), so that the amount of H_2 that can be produced is maximized.* The instabilities of the MHCD plasma excited by a dc voltage that was observed when the NH_3 concentration exceeded 10% in the present experiments can be overcome by pulsing the plasma (see below).
2. *Increase of the residence time of the gas mixture in the plasma region to ensure a complete conversion of the NH_3 even at high NH_3 concentrations, which may require residence times in the range of hundreds of microseconds*. The geometry constraints of the currently used single-hole MHCD limit the plasma volume that can be generated and thus the maximum residence time in the plasma. This limitation can be overcome by incorporating a third electrode that is spatially separated from the MHCD structure by a few milllimeters. A suitable bias voltage applied to this third electrode will "draw" the plasma out from the MHCD hole structure and create a larger plasma volume, which, in turn, facilitates longer exposure times of the gas mixture to the plasma (Fig. 6, top). It is noted, however, that the plasma density in the region between the pulsed electrode and the bias electrode (see Fig. 6, top) is lower than inside the MHCD. A way of generating a larger plasma volume of high plasma density involves the series operation of several MHCDs arranged in a sandwich structure. This can be achieved by alternating metal electrodes with dielectric spacers and connecting the electrodes to respectively high voltage and ground potential as shown in Fig. 6 (bottom). However, the practical realization of such a sandwich structure using conventional fabrication techniques and, in particular, the proper alignment of the multi-hole arrangement are non-trivial issues (K.H. Schoenbach, private communication, 2002).
3. *Pulsing the plasma using short pulses in the regime of microseconds (to minimize the electrical power input) in conjunction with an appropriately chosen duty cycle (to guarantee a high conversion of NH_3 to H_2)*. In addition to reducing the power required to maintain the MHCD plasma, pulsed MHCD plasmas are known to be much less susceptible to instabilities and have been operated successfully in gas mixtures containing complex polyatomic molecules and even electronegative (attaching) gases [13,16].
4. *Parallel- and/or series-operation of many MHCDs*. As it is apparent from our experimental results that an economical MHCD plasma reactor for H_2 generation has to involve more than a single flow-through MHCD, practical realizations may be based on the parallel operation of several single, flow-through MHCDs, the series operation of MHCDs in the stacked configuration shown in Fig. 6 (bottom), or on a combination of several stacked MHCDs operated in parallel.

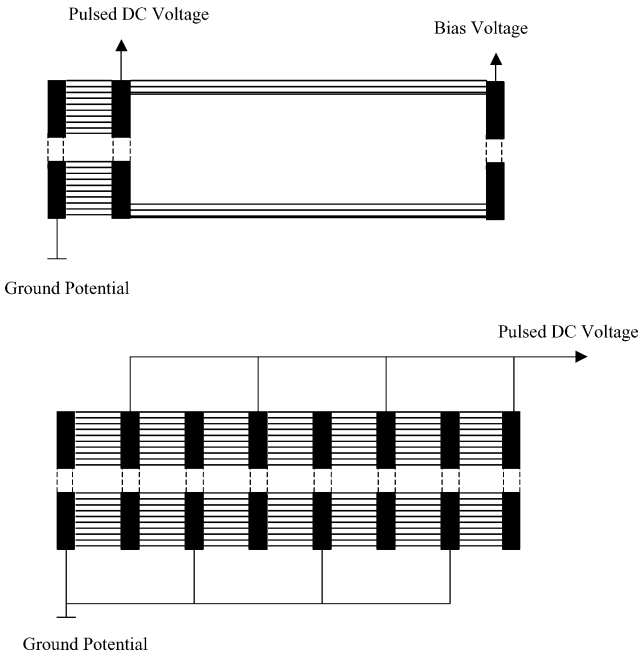

Fig. 6. Conceptual designs of (1) a single MHCD with bias electrode to create an extended plasma region (top), and (2) a "sandwich" of stacked MHCDs to create an enlarged volume of high-density plasma (bottom).

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