HIGH-TEMPERATURE MICROCOMBUSTION-BASED AMMONIA MICROCHEMICAL HYDROGEN GENERATOR REACTORS FOR PEM FUEL CELLS

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ABSTRACT

A high-density source of hydrogen for proton exchange membrane (PEM) fuel cells is being actively pursued in order to create a MEMS-based micro-power-generator (MPG). The approach presented is to generate hydrogen and power by decomposing ammonia (NH₃) in a high-temperature microchemical system. Three critical components of this MPG have been fabricated and tested: (i) a high-temperature microcombustor and (ii) a decomposition microreactor, and (iii) a PEM fuel cell. The critical breakthroughs to achieve this MPG hydrogen generator are a *sub-millimeter* critical length scale microcombustor and a high surface area microchemical reactor.

INTRODUCTION

The development of MEMS-based micro-power-generators (MPG) can enable a new class of portable electronics. Micro-fabricated proton exchange membrane (PEM) fuel cells can supply electrical power with a power density that exceeds lithium ion batteries, provided a high-density source of hydrogen is supplied. There has been a great deal of work on creating high-density source of hydrogen, including metal hydrides, and reforming of liquid hydrocarbon fuels to hydrogen, such as methanol. However, only liquid H₂ (@ 20K) and CH₄ (@ 147K) have a higher hydrogen density than liquid ammonia (NH₃). Moreover, NH₃ remains liquid at ambient temperatures and pressure (9.6 atm @ 300K), which is also useful since the higher pressure eliminates the need for liquid pumping. A key issue, therefore, is how to convert NH₃ to H₂ efficiently and completely, so that NH₃ poisoning of the PEM anode catalyst is minimized.

One viable approach to convert NH₃ to H₂ is to thermally decompose ammonia, by

The hydrogen from the reactor is then fed into a PEM fuel cell to generate electricity. The minimum amount of heat to spontaneously thermally decompose NH₃ at the minimum temperature ($T_{\text{crit}} = 183.04^\circ\text{C}$) required is remarkably small (7.92 {kcal/(mol H₂ produced)}). However, the kinetics are extremely slow, making decomposition at that low a temperature impractical, particularly in a microscale reactor with small residency times. To increase the kinetics high enough that nearly 100% of NH₃ can be converted to N₂ and H₂, a high temperature, catalytic microreactor is needed. However, operating a microreactor at high temperatures present a new set of challenges: (i) producing a high-temperature source at the microscale, (ii) loss of efficiency due to heating losses, and (iii) catalyst degradation.

Figure 1. Concept of counterflow heat exchange 600°C microchemical ammonia (NH₃) decomposition reactor, sandwiched about a high-temperature ($>1000^\circ\text{C}$) microcombustor. Reactor area and size is far larger than the microcombustor, in order to maximize high-temperature efficiency of burner and match heat output of the burner to heat input to the reactor.

Presently, several reactors for ammonia decomposition have already been proposed. Many use electrical energy to heat the reactor to high temperatures, satisfying challenge (i), since resistive heaters can be relatively easily integrated into a micro-fabricated reactor. However, the use of electrical energy to generate heat lowers the overall efficiency of the system, making (ii) even more difficult to achieve. As heat losses tend to be significant for microscale systems, and must be supplied for steady-state operation, electrical power must also be supplied for the losses as well as any pump power needed, which non-linearly decreases the overall efficiency with increasing losses. Therefore, the conversion of NH₃ to H₂ in an electrically heated MPG system can consume more electrical energy to heat the reactor than is produced by the H₂ in the fuel cell.

To supply sufficient heat for both decomposition and heat losses, we utilize a high-temperature microcombustor that can burn hydrocarbon fuels, such as butane, methane, and acetylene. In addition to not using H₂ to supply the heat energy, the direct heating content of hydrocarbon fuels even exceeds that from H₂ due to 50% conversion efficiency in the PEM to electrical power. Therefore, the overall fuel load of both NH₃ and a fuel such as butane is smaller than with NH₃ alone. To realize a NH₃ to H₂ converter, a microcombustor is coupled to the ammonia decomposition reactor, as shown schematically in Figure 1. Fuel is consumed in a microcombustor to provide heat for the microreactor, which sandwiches the heater to reduce losses. The only electricity needed to run the device is the electricity to run an air pump. The critical breakthroughs to achieve this MPG hydrogen generator are a *sub-millimeter* critical length scale microcombustor and a high surface area microchemical reactor.

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Figure 2. Photograph of an anodized aluminum reactor bed with the upper right inset showing 300 by 300 μm square posts 3000 μm long forming the high surface area reactor. The surfaces of the posts shown in the lower right inset are anodized to a thickness $\sim 1/6^{\text{th}}$ of the post. The anodized surface, shown in the lower left inset, is impregnated with platinum, utilizing the monodisperse 30 to 60 nm diameter pores.

FABRICATION

The microreactors tested in this study were fabricated by electrical discharge machining (EDM) of 1100 aluminum alloy bar stock. Two different reactor bodies were fabricated. As shown in Fig. 2, one had an array of 3350 posts arranged in an area 25x50 mm. The second, as shown in Fig. 3 had an array of approximately 250 square posts 300 μm on a side, and 3 mm high. The posts were arranged over a square area 9.5 mm on a side. The posts (insets of Fig. 2) were then anodized to yield a high surface area alumina with an average pore size of 30-60 nm. To do so, the reactors were degreased in acetone and potentiostatically anodized in a 0.16 M solution of oxalic acid for a period of 24 hours. The anodization voltage was varied to test the effect on the anodic alumina. Finally, the microreactor was impregnated with catalyst via treatment with platinum hexafluoroacetylacetonate $[\text{Pt}(\text{hfac})_2]$ or Ruthenium hexafluoroacetylacetonate $[\text{Ru}(\text{hfac})_2]$ in 2-pentanedione.

The microcombustors were fabricated in two ways. The first combustor was fabricated from polished polycrystalline sintered silicon carbide (SiC) wafers that were diced to 2.5 by 5 cm rectangles. Longitudinal slots 1 cm wide were made various depths ranging from 300 to 800 μm deep in one wafer. The micro-

combustion chamber was formed by bonding a slotted and unslotted wafer together, as shown in Fig. 4(a). Before bonding, the surfaces were coated with multiple layers of silica and alumina, approximately $(140 \text{ \AA}/100 \text{ \AA})_n$ for each set, alternatively deposited by e-beam evaporation, until the total thickness of the coating was approximately 0.5 μm . The coated wafer was then annealed at 1550°C. The second burners were fabricated by molding green alumina sheets with a 300 μm deep slot by 5 mm wide, and then sintering together. Both burners were then surface treated to remove impurities. The completed combustors were placed in holders that delivered fuel and air to the slot, premixed in a small (O(1 mm)) chamber immediately before the slot.

Figure 3. A picture of the smaller microreactor. This reactor can produce 8 sccm (i.e. about 2 watts) of 99% pure hydrogen when run at 650°C.

Figure 4. Close-up in (a) of a 600 μm deep etched slot in aluminosilicate coated and bonded SiC burner shown in Fig. 7. A monolithic, treated alumina microcombustor is shown in (b) with slot depth of 300 μm , which also sustained gas-phase combustion.

RESULTS and DISCUSSION

The key goal for this NH_3 -based MPG is to extract more electrical energy than heat energy supplied, by utilizing the high chemical potential of the H_2 in the PEM vs. the relatively low dissociation energy of the NH_3 in the catalytic microreactor. For the microreactor, several issues were addressed, including heat transfer, pressure drops, and most importantly, stationary catalyst structures that are not subject to degradation at high temperatures.

The reactor structures shown in Figs. 2 and 3 allow easy flow of reactants and products due to the relatively large passageways, thus pressure drops were negligible. Since the reactor body was made from an aluminum alloy, and the core of the posts, as seen in the inset in Fig. 2 remained metallic with relatively large aspect ratio of about $1/10^{\text{th}}$ cross-sectional area to length, the reactor structures and posts were essentially isothermal. This would not necessarily be the case for smaller posts made entirely from anodized alumina. When anodized at the conditions described above, the size of the posts did not change upon anodization. However, the resultant structure is porous as shown in the lower left inset in Figure 2. The surface area for reaction greatly increases during the anodization process, thereby increasing the conversion rate within the reactors. For example, the penny sized microreactor shown in Figure 3 has an internal surface area of 0.82 m^2 , about 1000 times its physical surface area. In addition to high area, the anodized alumina structure with the platinum immobilized onto the posts by impregnation, calcination and reduction is stable at elevated temperatures and does not degrade.

The first ammonia reforming results are shown in Fig. 5. During this experiment 92 sccm of ammonia was fed into the reactor in Fig 2, and the conversion was measured as a function of temperature. The figure shows that 99% pure hydrogen is produced in the reactor at 650°C . A mass balance shows that $140 \text{ standard cm}^3$ of hydrogen gas/min is produced by the reactor under these conditions. This is enough hydrogen to produce 20 watts of electricity in a 50% efficient fuel cell. More importantly, the reformat stream does not contain CO to poison the hydrogen PEM fuel cell downstream. However, the remaining NH_3 can also poison the anode catalyst of the PEM. Therefore, further work is needed to reduce the NH_3 to negligible amounts by

increasing catalyst area and increasing the reactor temperature above 650°C , which requires a higher temperature substrate than the aluminum alloy used. In addition, an ammonia trap is needed to scavenge any trace amounts of NH_3 remaining.

The thermal losses from the reactor to the surroundings, as well as the fluid flow design has a large impact on the amount of heating power that needs to be supplied to the microreactor. A poorly insulated device might consume 17 watts of fuel and only produce a net of 4 watts of electricity. However, due to supplying heat via combustion, there is still a net production of electricity by the MPG. But it is still important to design for optimum thermal management to reduce losses to a minimum. By employing counter flow heating fluids and reactor products, enthalpy losses can be minimized. By sandwiching the micro-combustor between reactors, heat losses from the burner to the surroundings are minimized. In addition, placing the lower temperature reactors on the outer surfaces, and separating the reactors from the surroundings using vacuum insulation and radiative shielding, combined with high quality aerogel insulation can reduce heat losses to less than 1 W for each 4 to 5 W of electricity produced.

To efficiently generate the high-temperature heat required, we utilize gas-phase combustion of hydrocarbon fuels, due to their very high energy density and operating temperatures. However, to supply the desired heating rate and $> 650^\circ\text{C}$ temperatures to the reactor, the microcombustor needs to be much smaller than the reactor: sub-millimeter in size for low power ($< 1 \text{ W}$) applications. MIT has developed high-temperature silicon-based combustors [1-2], but it is about 1 order of magnitude larger than we require for the MPG. Simply reducing its size, though, is a major issue, since steady-state homogeneous combustion flames thermally and chemically quench below a critical length scale. Figure 6 shows our measured quench lengths for various materials with hot and cold walls. When the walls are "cold" (below about 400°C), all materials quench around 2.5 mm. However, for hot walls, the surface material strongly matters, with quench lengths down to 100 microns possible. By using burner walls coated with alumina-magnesia-silicates, we have fabricated and tested SiC and alumina microcombustors (Fig. 4) with quench lengths far below 1 mm [3].

Figure 5. Results for the conversion of ammonium to hydrogen and nitrogen via decomposition in the anodized catalytic microreactor shown above as a function of temperature, with a NH_3 flow rate of 92 sccm.

Figure 6. Data for quench lengths for different wall materials for (a) cold walls at 300°C and (b) hot walls at 1000°C. Note that for cold walls, the quench lengths are approximately the same for all materials, in agreement with values reported in the literature, due to dominant thermal quenching of the flame. However, for hot walls, wall composition has a very strong effect, and treated compounds of alumina/silica/magnesia have quench lengths of $< 100 \mu\text{m}$, an order of magnitude below silica alone.

Figure 7 shows a SiC burner producing watts of steady-state heat energy at high temperatures ($>1000^\circ\text{C}$) without quenching. The ability to burn hydrocarbon fuels in air in a sub-millimeter critical quench length combustor allows very small, high-efficiency burners to directly deliver the high-quality heat needed to drive the NH_3 to H_2 conversion efficiency to near 100%. The high heating value of gas-phase combustion of hydrocarbon fuels, such as butane, also allows the overall size of the combustor to be much smaller than if lower energy fuels were used, or if lower temperature catalytic combustion was employed, although both these techniques are also possible. The key benefit to having the burner much smaller than the reactor is that the overall fuel use is lower. Thus, both the microcombustor and fuel supply are smaller, minimizing the overall system size.

Figure 7. Self-sustained gas-phase combustion of CH_4 and air in a coated SiC microcombustor with a slot depth of $600 \mu\text{m}$, with a critical quench length of $300 \mu\text{m}$. Flame ignited at around 550°C , and walls reached over 1000°C .

CONCLUSIONS

The goal for this work is to generate pure hydrogen gas from ammonia, a high-hydrogen density source, for PEM fuel cells for micro-power and larger, electrical generators. We have been able to thermally decompose 99% NH_3 feedstock at 650°C to H_2 in first generation aluminum micromachined reactors with anodized alumina supported catalysts. Further work is needed to increase the reactor temperature and effective catalyst area to approach 100% conversion efficiency. The reactor is directly heated via combustion of hydrocarbon fuels in air in a high-temperature microcombustor. Two types of microcombustors have been demonstrated that achieve greater than 1000°C temperatures with critical quench lengths well below 1 mm to provide the heat source for the next generation of ammonia microreactor.

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