Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Failure analysis of novel microhollow cathode discharge microplasma reactors

Peter J. Lindner [a,b,*], Eugene Bender [a], R.S. Besser [b]

[a] Department of Chemical Engineering, Manhattan College, 4513 Manhattan College Parkway, Riverdale, NY 10471, USA

[b] Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, One Castle Point on Hudson, Hoboken, NJ 07030, USA

ARTICLE INFO

Article history:
Available online 16 July 2014

Keywords:
Microplasma
Microhollow cathode discharge
Reforming
Scanning electron microscope
Lifetime reliability

ABSTRACT

Compact fuel cells are one logical progression for portable power in comparison to batteries since fuel cells have much higher energy densities. However, fuel cells have not fully entered the portable power market as they require a readily available hydrogen feed. Microplasmas offer a way to produce hydrogen portably. Microplasma reactors developed from standard semiconductor fabrication techniques, specifically microhollow cathode discharge (MHCD) devices, have been tested by our group in reforming various hydrocarbons.

Experiments with these reactors were successful in showing the feasibility of a portable microplasma fuel reformer, but they regularly had short lifetimes (<10sec to 2–3 h). In this work the electrical and physical properties of failed microplasma reactors have been investigated with the goal of determining what caused their malfunction. These devices have been tested by recording their electrical characteristics under low loads (<20 V) under a non-current limited power supply and they were imaged using a scanning electron microscope (SEM) to determine the point of failure. Energy-dispersive X-ray spectroscopy (EDX) was used to identify the distribution of elements in the channel, anode surface, and cross-section of the microreactor.

SEM imaging has shown the formation and re-deposition of silicon and silicon dioxide on the inner walls of the microchannel. The thickness of this layer has been found to be directly linked to device lifetime. Input electrical power as well as flowrate has also shown to be related to this deposition and overall device lifetime. This failure analysis study enables us to improve the design of the microplasma reactor and further advance the development of a portable fuel reformer-fuel cell system.

* *Corresponding author*. Department of Chemical Engineering, Manhattan College, 4513 Manhattan College Parkway, Riverdale, NY 10471, USA. Tel.: +1 (718) 862 7296 (voice); fax: +1 (718) 862 7819.
E-mail address: Peter.Lindner@manhattan.edu (P.J. Lindner).

http://dx.doi.org/10.1016/j.ijhydene.2014.06.137

Introduction

Plasma fuel reforming has many advantages when compared to conventional catalyst technology [1]. Sulfur components commonly found in hydrocarbon fuels poison catalyst sites. Catalysts sites are also blocked by solid carbon deposits, known as coking, a common byproduct of hydrocarbon reforming. Processing with these catalysts also requires a high temperature (>500 °C) regeneration step [2].

Plasma technology offers a means of reforming free of these issues since catalysts are avoided. Plasmas in fuel streams have been known to convert sulfur components into hydrogen sulfide which can then be removed with a hydrogen desulphurization step (HDS) [3]. Since carbon is electrically conducive, carbon deposits on the electrodes should not cause processing issues. Plasmas also perform chemistry at higher efficiencies in a non-thermal (room temperature) mode than a thermal (high temperature) mode [4]. Despite all these operational advantages plasmas have not yet replaced catalysts as the principal means of activating hydrocarbon reforming.

Plasmas also exhibit a few disadvantages that must be overcome for fuel processing applications. First, to ignite a plasma, a large amount of electrical energy is needed at the outset. To reduce the input electrical power for conventional large scale plasma devices a low operating pressure is required. This requires additional vacuum equipment such as pumps, and high pressure seals, which can make the entire process more expensive, more cumbersome, and more complex. Microplasmas, a plasma apparatus with an electrode distance of less than 1 mm [5], can mitigate this problem, exploiting Paschen's Law. Paschen's law states that for each gas there exists an ideal pressure, p, and electrode distance, d, that in combination will require the lowest breakdown voltage to ignite a plasma [6]. Lower breakdown voltages relate to even lower sustaining voltages for the plasma and lower power requirements. The ideal pd product, depending on the gas, is roughly between 0.5 torr-cm and 2 torr-cm (0.7 Pa-m and 2.7 Pa-m) [6,7]. At atmospheric pressure this correlates to an electrode distance of 6–24 μm.

Microplasma reactors are often produced using semiconductor materials and photolithography processes to develop a microelectromechanical systems (MEMS) reactor. Microplasmas not only offer the advantage of significantly lower power requirements at atmospheric operation, but they also share the advantages of microreactors. Microreactors allow for portability, they have high surface to volume ratios allowing for more homogenous products, and they reduce wastes and minimize unwanted byproducts. Microreactors also avoid scale-up issues. To increase the amount of desired product for microreactor systems the process of numbering up is used, where a larger quantity of reactors are used in parallel [8].

Generally two major types of microplasma reactors have been studied. The more commonly used plasma reactor is the dielectric barrier discharge (DBD) [9]. DBDs provide the first example of plasmas being used for chemical reaction. DBDs consist of two electrodes separated by a dielectric material (e.g. glass). These devices are useful and robust but issues with efficiencies for reactions in these devices persist. Scaling these devices down to the millimeter range results in a pattern of point plasmas that limit the reaction volume space causing the reduced efficiencies [10].

The other major device type is a micro hollow cathode discharge (MHCD) device. The MHCD was coined by Schoenbach [11]. The idea is that it is similar to a hollow cathode discharge but has two electrodes again separated by a dielectric, but one of the electrodes (the cathode) has a hollowed out region where the plasma is contained. The MHCD has a higher electron density than conventional plasma devices due to the Pendel (electrons) effect [11]. Plasmas are produced in an MHCD by applying either direct current or an oscillating/pulsing direct current. MHCD devices have recently been fabricated using common semiconductor techniques and then tested for property characterization for various applications.

MHCD devices have successfully shown the feasibility of a portable microplasma fuel reformer [12–18]. These chemical reactors have shown relatively high conversions despite system constraints. However they have suffered from low energy efficiencies and low device lifetimes. This study aims to determine why the MEMS reactors fail by inspecting a series of tested reactors.

Materials and methods

The MHCD reactors used in this study were fabricated by the authors at the Cornell Nanoscale Facility (CNF). They are manufactured by starting with 400 mm n-doped silicon wafers. An oxide layer is then thermally grown in an oven at 1100 °C. Photoresist is deposited on the top of the wafer and developed for the entire layer to protect the silicon oxide on the top of the wafer. The silicon oxide is then removed from the bottom of the wafer using wet chemistry. A metalized layer is added to the backside to allow for good electrical contact to the cathode. The layers for the backside contact are 125 Å (12.5 nm) of titanium, for adhesion, and 875 (87.5 nm) Angstroms of gold, for high electrical conductivity. This backside contact is added using e-beam evaporation. The resist is then removed and a new layer of resist is added for the lift off process. Using photolithography the resist is patterned and developed to allow for the metallic anode to be added. The anode is also deposited using e-beam evaporation. First 250 Å (25 nm) of titanium is deposited to the top of the device, and then 1750 Å (175 nm) of nickel are deposited. The wafer is then placed into developer to remove the photoresist and lift-off the excess metal. Photoresist is then applied and developed first to pattern the silicon oxide layer. The resist is then left on and the silicon cathode is etched. To get a very clean rectangular channel, deep reactive ion etching (DRIE) is used to remove the silicon. Afterwards the devices are then cut into individual reactors. Fig. 1 shows a depiction of the process used to make the MHCD reactors.

Thirty-six variations of the reactor were produced. The variations were produced with two oxide thicknesses, three widths, three depths, and with or without an enhanced perimeter (E.P.). The enhanced perimeter is the anode patterned at the edge near the channel, this was done to increase the area for electrical conductivity. Two oxide thicknesses were formed by changing the time for the thermally grown oxide in step 2.