A MEMS Singlet Oxygen Generator for a MEMS Chemical Oxygen Iodine Laser

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Abstract
This paper elaborates on the MIT-led effort to develop a singlet oxygen generator (SOG) that operates on the microscale as part of a microfabricated chemical oxygen iodine laser (COIL) system. The micro singlet oxygen generator (µSOG) chip is implemented in a three–wafer stack. The device creates singlet delta oxygen (O₂(1∆)) in an array of packed bed reaction channels; the chip also has an integrated, microfabricated separator for the liquid and gas products and an integrated heat exchanger. The design, fabrication, and package of the device are briefly documented, as well as the testing apparatus. Experimental evidence to demonstrate steady-state generation of O₂(1∆) is provided. Optical measurements of the power in the O₂(1∆) flow are provided, as well as estimates of the lasing power that a full COIL system could produce by using this type of O₂(1∆) source.

Keywords: Singlet Oxygen, Chemical Lasers, multi-stack reactor.

1. INTRODUCTION
Singlet delta oxygen (O₂(1∆) or spin-excited molecular oxygen) is a useful reactant for organic synthesis and an energy carrier for the Chemical Oxygen-Iodine Laser (COIL). COIL systems are chemical lasers in which iodine acts as the lasing species [1]. Population inversion of the gain medium is sustained by collisions between ground state iodine atoms (I(2P3/2)) and O₂(1∆), i.e., COIL is a two-species, two-level laser. COIL is attractive for applications requiring very high average powers, portability, and overall system compactness. COIL has a lower emission wavelength than CO₂ lasers (1.315 micrometers vs. 10.6 micrometers), resulting in more efficient coupling to metals, thus reducing the power needed for welding and cutting. The lower wavelength also allows higher machining resolution because it can produce a smaller spot size and enables fiber-optic beam delivery for greater flexibility. In a flowing gas laser such as COIL, the waste heat in the gain medium flows out with the reactant exhaust gas stream; therefore, the laser average power is not limited by cooling, as are most high-energy solid-state lasers. The COIL system is scalable to average power output in excess of 1 MW.

SOGs typically generate O₂(1∆) by reacting gaseous Cl₂ with an aqueous mixture of concentrated H₂O₂ and KOH called basic hydrogen peroxide (BHP). Several successful macroscale SOG architectures have been implemented and reported in the literature, in particular using a bubbler [1], jets of liquid droplets [2], or a rotating wheel [3] to promote the multiphase reaction. However, these configurations have limitations: a small gas–liquid contact area for rotary SOGs, a large volume for the jet configuration, and significant deactivation of O₂(1∆) before separation from the liquid phase because of their macro dimensions. Modeling suggests that a COIL utilizing microfabricated components has key advantages compared to the fully macroscale systems. These include smaller hardware size for the same power level, reduced reactant consumption, gravity independence and batch manufacturing feasibility [4].

The present MEMS-based SOG (µSOG) has several advantages over macroscale SOGs. First, the µSOG has a large surface-to-volume ratio, which enhances reactant mixing and facilitates excess heat removal. Second, the device has no moving parts, which increases the robustness and reliability of the system. Third, the singlet-oxygen travels a shorter distance from the point of formation to the point of utilization in a microdevice, thus reducing O₂(1∆) losses. Finally, the integration of a microfabricated heat exchanger in the µSOG chip simplifies the overall COIL system.

2. SOG CONCEPT AND DESIGN
O₂(1∆) is a metastable molecule that may be synthesized through the highly exothermic multiphase chemical reaction of gaseous Cl₂ with an aqueous mixture of concentrated H₂O₂ and KOH:

$$\text{H}_2\text{O}_2 + 2\text{KOH} + \text{Cl}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{KCl} + \text{O}_2(1\Delta) \quad (1)$$

Usually the reactant Cl₂ is buffered with a non-reacting gas such as helium. High conversion of Cl₂ to O₂(1∆) is achieved by effective mixing of the gas and liquid reactants. The laser application of O₂(1∆) generation requires a high yield to sustain laser emission, where yield is defined as the fraction of product oxygen in the
O_2(1^\Delta) state. Once produced, O_2(1^\Delta) may deactivate into ground-state oxygen by gas-phase collisions with water vapor, other oxygen or helium molecules, and by heterogeneous collisions with either solid or fluid surfaces:

\[ O_2(1^\Delta) + O_3(1^\Delta) \rightarrow O_2(1^\Sigma) + O_3(1^\Sigma) \]

\[ O_2(1^\Delta) + O_3(1^\Delta) \rightarrow O_2(1^\Sigma) + O_3(1^\Sigma) \]

\[ O_2(1^\Delta) + \text{wall} \rightarrow O_2(1^\Sigma) \]

Thus, the reactor design must provide large surface areas for initial O_2(1^\Delta) generation, balanced by subsequent rapid separation of gas and liquid phases, while maintaining low pressures (~50-250 torr) to minimize homogeneous deactivation and low temperatures (< 0°C) to minimize water vaporization and subsequent deactivation. Previous studies have shown that microreactors offer advantages with respect to mass and thermal transfer characteristics [5].

Figure 1 shows a schematic of the µSOG developed by our research team. The system is composed of 32 reactor packed beds that are fed in parallel with the gas and liquid reactants using suitable manifolds. The reactants are mixed inside the reactor beds, thus producing O_2(1^\Delta). The packed beds have a staggered configuration that increases mixing of the reactants. Pressure-drop channels located upstream of each packed bed aid in equalizing gas and liquid flow throughout the microdevice, thus acting as hydraulic impedances that ballast the reactor array. The µSOG has a separator downstream from the reactor beds, composed of an array of capillaries. The separator removes the liquid by-products from the gas-phase products. The O_2(1^\Delta) then flows to the exterior of the chip. In the previous analytical study [4], standard MATLAB numerical simulation techniques and estimates of physical parameters were used to optimize key SOG dimensions and operating points. The dimensions employed in the present µSOG mask design were based on the results and conclusions of this study.

3. FABRICATION CHARACTERIZATION AND PACKAGING

Figure 2 shows a picture of a completed µSOG chip made in a three-wafer stack. The dimensions of the chip are 36 × 27 × 3.3 mm, where the active region is 1.3 mm thick. The top wafer is Pyrex® and is intended to seal the flow channels of the chip while providing optical access to the reactor beds and separator. The middle wafer is silicon and contains the liquid reactants manifold, the pressure drop channels, the capillary separator, and the reactor packed beds.

Each reactor packed bed implements a hexagonal array of columns. This post-bed configuration is a two-dimensional approximation of a conventional packed-bed, providing reduced pressure drops while alleviating the need for subsequent packing of reaction channels. The separator is composed of a hexagonal array of capillary holes that relies on surface tension effects to separate the two-phase exit stream [6]. The bottom wafer is made of silicon and contains the heat exchanger and the flow channels that allow the external flow connections to be made from the bottom. The heat exchanger is made of 19 cooling channels.

Figure 3 shows a cross section of a µSOG, indicating key parts of the device. The process flow of the µSOG is documented elsewhere [7], as well as a detailed description of the key dimensions of each subsystem.

The µSOG package meets stringent requirements regarding chemical resistance (in particular to chlorine in presence of humidity and to KOH) and minimization of O_2(1^\Delta) losses [8] in order to maximize yield. The current µSOG package is made of Tefzel®, a high performance polymer that is as chemically resistant as...
Teflon®, but is far more machinable and stiffer. The package is composed of two parts: a chuck that has o-ring ports to interface with the ports of the chip, and a clamping plate. The clamping plate has an opening for optical access to the reactor beds and the separator. A set of Tefzel® screws clamp the chip to the package chuck. The package uses Simriz® and Kalrez® o-rings for chemical compatibility and robustness, and a Kalrez® gasket to seal the reactant inlet ports. Finger-tight Tefzel® fittings from Bio-Chem Valve Inc. (Boonton, NJ) allow easy package reassembly. The reactants, coolant and liquid by-products are carried to and from the package by Teflon® tubing. The O2(1Δ) molecules exit into a quartz optical cell to provide access for optical diagnostics.

4. TESTING RIG
The testing rig has mass flow controllers (MFCs) that control the flowrates of the Cl₂ and He. The BHP is pressure fed to the chip. The liquid by-products are collected in the BHP collector reservoir, which is connected to a liquid nitrogen trap and then to a pump. The gas by-products are first analyzed optically as shown in Figure 4 and then fed to a mass spectrometer (GC/MS) and eventually to the inlet of a pump.

5. EXPERIMENTAL DEMONSTRATION OF O2(1Δ) GENERATION
The µSOG has been successfully operated to produce O2(1Δ). The production of O2(1Δ) is supported by three types of experimental evidence. The first relies on the fact that two O2(1Δ) molecules can collide to form a dimol. When the dimol emits, it appears as a pink glow (Figure 5).

In the second approach, an optical system is used to monitor the spontaneous decay of the O2(1Δ) molecule to its ground state, O2(3Σ), in the quartz flow cell, and the resulting emission of a photon. Spontaneous emission was measured using both the apparatus shown in Figure 4 and an absolutely-calibrated spontaneous emission diagnostic created, provided and deployed by Physical Sciences Inc. [9]. Figure 6 shows that the emission of the µSOG is centered around the 1.268 micrometer wavelength of the O2(1Δ) - O2(3Σ) emission, and that the chip reaches steady state within seconds of activation.

Finally, the gas by-products were analyzed using a GC/MS. Figure 7 shows that the oxygen increases whenever a plug of chlorine is fed to the chip.

6. FLOW POWER MEASUREMENTS AND LASING ESTIMATES
Quantitative flow power measurements were obtained using the above-described optical measurements. Each photon detected at the appropriate frequency

Figure 6 – Spectral measurements from a µSOG. Each spectrum was obtained by integrating the emission from the quartz optical cell for 5 sec.

Figure 7 – MS signal of oxygen mole fraction as a function of time during two contiguous runs.
corresponds to emission by one singlet delta oxygen molecule; the measured emission peak combined with geometric factors yields the concentration of O$_2$(\(\Delta\)) in the test section. Multiplying the O$_2$(\(\Delta\)) concentration (scaled by the total concentration) by the total molar flow rate of the gas output stream yields the flow rate of O$_2$(\(\Delta\)). Finally, the power in the flow is determined by multiplying the flow rate of O$_2$(\(\Delta\)) by the energy of the O$_2$(\(\Delta\)) - O$_2$(\(\Sigma\)) transition. Figure 8 shows the experimental power flow data and the estimated power flow at the μSOG chip’s gas outlet as a function of the pressure at the SOG’s outlet, taking into account the singlet-oxygen deactivation between the chip outlet and the measurement point. Powers as high as 1.3 W are estimated at the chip’s gas outlet.

![Figure 8. O$_2$(\(\Delta\)) flow power vs. pressure at the outlet, both at the measuring point and at the chip outlet.](image)

Only part of the power in the O$_2$(\(\Delta\)) flow would be converted to laser output power if μSOG chips were used to drive a COIL system. The reported power corresponds to a yield of 70%; however, only that part of the yield that exceeds the threshold yield of about 7% is available to power the laser. In addition, the overall power extraction efficiency with which this available power is used by the laser is less than 100%. The previously-cited μCOIL modeling study [4] predicted a power extraction efficiency of approximately 90% for the μCOIL system; the extraction efficiency for conventional systems is more typically about 80% [10]. Taking into account the finite threshold yield and assuming a power extraction efficiency of 80%, the 1.3 W of power in the μSOG output flow is expected to source about 0.94 W of laser output power.

7. CONCLUSION

We have successfully designed, built and tested a microfabricated singlet oxygen generator for a chemical oxygen iodine laser. When employed as part of a chemical oxygen iodine laser, the μSOG chip is expected to source an estimated 0.94 W of power per chip. A laser powered by an array of μSOG chips would be useful for a variety of industrial applications.

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9. REFERENCES