Final Technical Report

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Fundamental Studies of Plasma Air Separation

Investigators

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Abstract

This report describes our efforts of a one-year, exploratory study on the physics necessary to advance the development of a low power, small scale, air separation unit (ASU) based on non-equilibrium plasma discharges (PD-ASU). Our research focus is aimed at i) preliminarily design and selection of the test geometry of the air passage, plasma electrodes and discharge type, ii) constructing a prototype of the PD-ASU unit, and iii) simulating the unit using commercial software (COMSOL) to improve the separation performance. As for the design, a concentric electrode configuration, equipped with a copper/glass fiber-electrode dielectric barrier discharge (DBD) was selected and the corresponding prototype was constructed. Subsequent gas chromatographic analysis shows that the oxygen contents can be varied by approximately 1 % with this PD-ASU prototype. The simulation results show that the concentric PD-ASU design is effective in attracting negative ions (oxygen ions) toward a suction hole by concentrating the electric field while it is evenly distributed along linear electrodes with conventional DBD actuators. As an on-going project and future plans, a multistage PD-ASU (serial stacked version of our prototype) is being fabricated for improving the overall separation performance.

Introduction

Plasma discharge air separation is believed to have two potentially significant advantages over large scale cryogenic based ASUs, the state-of-the art process for separating air into oxygen and nitrogen. First, it is likely that the production of an enriched air stream will be more efficient than its cryogenic process counterpart, largely because the later requires significant heat removal to a thermal (warmer) reservoir thereby generating considerable entropy. Conversely, the process proposed here involves isothermal, but highly nonequilibrium kinetics, which can achieve the final state without thermodynamics limitations. The second potential advantage is one of practical significance – the likely portability of the PD-ASU can dramatically expand the use of pure oxygen combustion (to facilitate carbon dioxide sequestration) in vehicle transportation and in residential heating (where there are no practical separators), which is responsible for approximately 21 % of greenhouse gas emission [1]. We believe, however, that the PD-ASU can also replace large cryogenic based ASUs in some larger-scale operations.

The development of a compact, and/or efficient PD-ASU using this selective plasma transport process can lead to a significant decrease, if not elimination, of greenhouse gas emission generated by automobiles and in residential and industrial furnaces. We envision a scenario where a compact air separator is installed upstream of the air intake in an automobile engine, natural gas boiler, or natural gas furnace (amongst other devices). Such a modified unit will also include a device that may make feasible, the capturing and storage of the CO_2 emission, perhaps as a solid phase. The captured solid phase CO_2 can be harvested from these energy conversion systems periodically and appropriately sequestrated. Such an energy conversion system can, in principle, be a zero-emissions energy conversion process. The ability to provide the technology to allow compact, portable, and efficient air separation can result in a new way to think about zero-emission vehicles and other processes that continue to burn hydrocarbon-based fossil fuels.

Background

Pure Oxygen Combustion

At the center of increased greenhouse gas (particularly CO_2) emissions is the extensive, if not exclusive, use of carbon-based fuels in contemporary energy systems. Three basic solutions to reducing CO_2 emissions associated with energy conversion processes are a) increased efficiency in the utilization of carbon-based fuels, b) carbon-free resources, and c) nitrogen-free hydrocarbon combustion for facilitating CO_2 sequestration in combustion product gases. This later process also reduces the production of nitrogen-related pollutants resulting from hydrocarbon combustion. One way to achieve nitrogen-free combustion is through so-called “oxy-combustion” [2], which uses an oxygen purified air stream (typically 95% O_2). The products of pure oxygen combustion include CO_2 and H_2O, which are more readily sequestered. However, as mentioned above, state-of-the art pure oxygen combustion requires the energy intensive cryogenic process (the most widely used process) of air separation before combustion. The cost of this cryogenic separation technology is very high (some 0.24 eV per molecular oxygen), consuming approximately 28% of the entire power generated in a typical power plant operating at 40% efficiency [3]. Improvements in cryogenic air separation performance are likely to be incremental, in that the various thermo-mechanical processes associated with cryogenic air separation includes non-isentropic compression and expansion, evaporation, and heat transfer under large temperature gradients, leads to irreversible constraints and entropy generation not likely to be present in the near-isothermal process proposed below.

Dielectric Barrier Discharge and Oxygen Forcing

The typical dielectric barrier discharge (DBD) actuator that we have studied in our laboratory is a relatively novel, small scale plasma device, a schematic of which is shown in Fig. 1. Layered on top of a surface adjacent to a flow, it consists of an exposed thin conducting electrode and a second electrode that is buried below a dielectric material. The voltage (typically ~ 5 – 10 kV) between these two electrodes is driven at moderate frequencies (Hz to 100 kHz). Electrons released from the exposed electrode on the so-called "forward stroke" (that is, when it is negatively biased) migrate towards and can accumulate on the dielectric layer which covers the positively biased (at that time) buried electrode. The rise in surface charge will produce a countering field that will quickly lead to a condition of current self-termination. This self-termination usually occurs within a few tens of nanoseconds, resulting in nanosecond current bursts and a highly non-equilibrium discharge state. During the following "reverse stroke" (when the buried electrode reverts to be negative relative to the exposed electrode) the negative charge accumulated on the dielectric streams off of the surface and migrates towards to favored positive pole along the electric field.

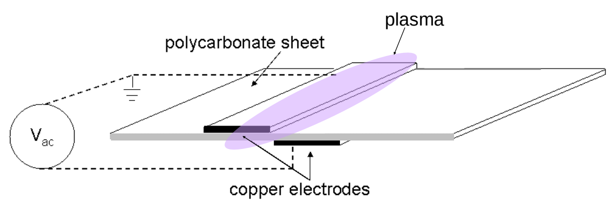

Figure 1. Schematic of a typical dielectric barrier discharge

Research in our laboratory has discovered that during the DBD process in atmospheric pressure air flows, the dominant ionic charge carriers are negative ion of molecular oxygen (O_2^-). During the early stages of the forward stroke, low energy electron attachment (releasing 0 – 0.2 eV/molecule) favorably forms O_2^-, over the more endothermic electron impact ionization process (~15 eV/molecule) to form N_2^+ (note that O_2^+ and N_2^- are highly unstable). As a result, there is a strong ion drift towards the surface due to O_2^- migration, and hence an accumulation of O_2^- ions in the vicinity of the surface. These ions will displace both neutral O_2 and N_2, but since N_2 is much more abundant in ambient air, the near surface region should be slightly enriched in oxygen. In essence, the plasma selectively transports oxygen across a diffusion layer. We describe in the next major section below, our experimental results that lead us to this discovery (until recently, no mention of negative oxygen ions was made in the air DBD literature). We also describe our plan to incorporate these findings into a discharge configuration that can effectively enrich air flows for air separation applications.

Results

Work during the year has focused on experimental and numerical investigations of the physics necessary to advance the development of a low power, small scale, air separation unit (ASU) based on non-equilibrium plasma discharges. During the first half, we have tested a few prototypes of the preliminary PD-ASU design and conducted numerical simulations suggesting an optimized ASU design concept. The optimization methodology was supported by an experimental result depicting that the plasma can selectively apply a body force on oxygen in air, and a simulation result providing a novel electrode design concentrating the electric field on a point. In the latter part of this study, various ASU cells were manufactured based on the optimized design concept and tested experimentally. Gas chromatography (GC) is used to estimate the performance of the unit by measuring the gas composition of the outlet gas. Also, a multi-stage ASU built in a pressure variable chamber is ready to operate for future research.

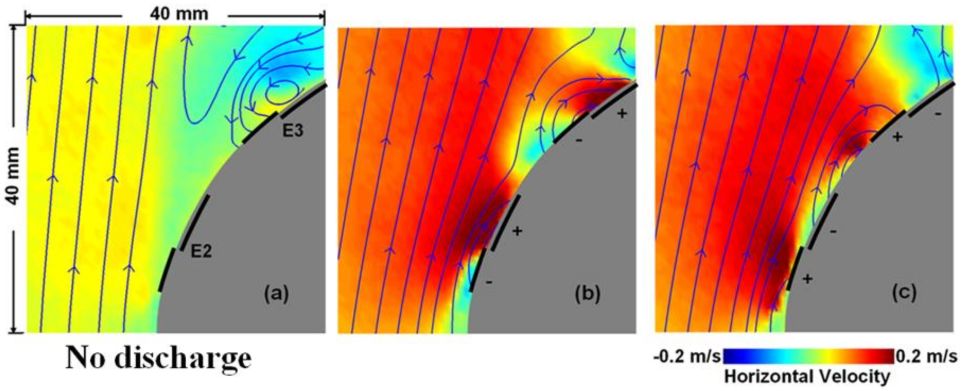

Figure 2. Phase Locked PIV images depicting negative ion (O_2^-) attraction toward anode.

Preliminary Design of PD-ASU and Design Optimization

Phase locked PIV images presented in Fig. 2 demonstrate the selective oxygen transport phenomenon observed in a plasma flow actuation process. It was found that negative ions (O_2^-) produced by the plasma are attracted toward positively biased electrodes along the electric field, which would induce oxygen enriched air flows. Accordingly, the first preliminary ASU design employs this conventional DBD actuator configuration of a pair of parallel linear electrodes separated by a dielectric barrier (glass fiber in this study), as shown in Fig. 3. An electric field simulation in quiescent air was conducted using Multi Physics (COMSOL). The exposed electrode is driven by a RF power supply of 20 kHz frequency and 10 kV peak voltage, and the other electrode beneath the dielectric barrier is grounded (0 V). Figure 3 shows the direction of electric field in the vicinity of the DBD actuator during a forward stroke (exposed electrode is negatively biased), presumably, parallel to the path of negative ions. The result predicts that the DBD would produce oxygen (negative ion) enriched directional flow; nevertheless, entrainment of ambient air immediately dilutes the flow preventing oxygen separation.

In parallel and guided by these simulations of field configuration, a PD-ASU design optimization scheme has been developed to find suitable DBD configurations to collect

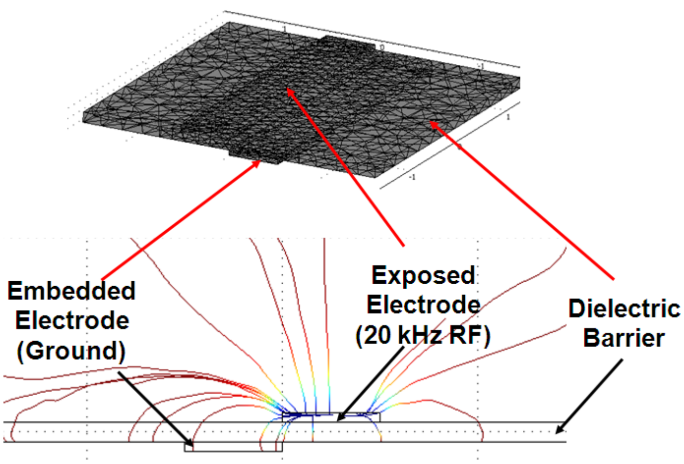

Figure 3. An electric field simulation conducted with a conventional DBD actuator.

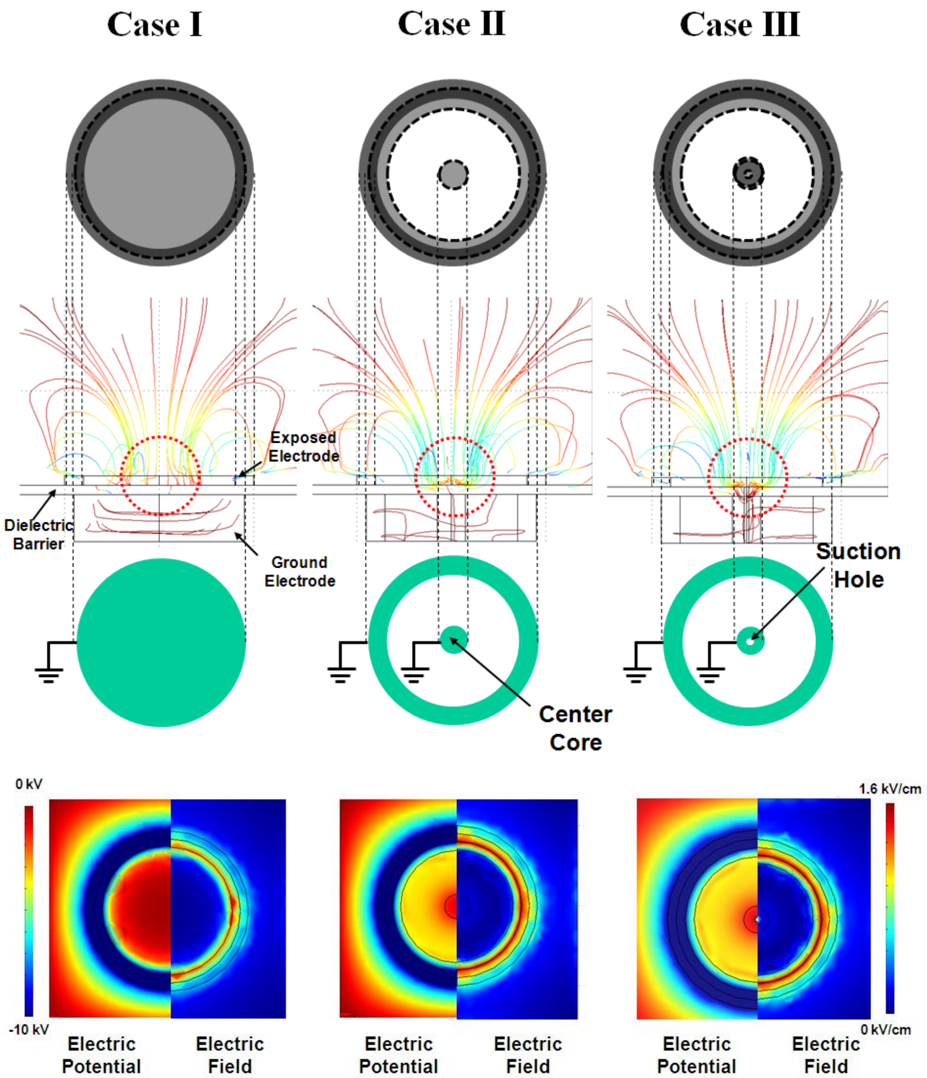

Figure 4. Electric field/potential simulated with various electrode designs.

oxygen negative ions produced in the discharge region. Figure 4 describes a simplified design optimization procedure aided by the electric field/potential simulation. The design of Case I employs a concentric electrode configuration which provides a stagnation point by inducing negative ion flow toward the center of the concentric electrode pair. This simple ASU design consists of a ring-shaped exposed electrode (copper) and a ground electrode of an aluminum cylinder. It is found that a modification of the ground electrode, as shown in Case II, is effective in further concentrating the electric field at the center of the unit. Here, the ground electrode is divided into a hollow cylinder and a core cylinder located at the center separated by dielectric material (glass fiber). The ratio of the core and the hollow radii was optimized at 1:6 providing maximal electric field strength at the center. Finally, a suction hole (gas outlet) for collecting negative oxygen ions is added at the center point (Case III). To maximize the ion attraction force, the suction hole is not covered by dielectric material. As presented in Fig. 5, the highly concentrated electric field at the center of the unit (Case III) is expected to induce the strongest oxygen ion wind toward the suction hole. In addition, we carried out preliminary measurements of cell separation performance (Case III electrode configuration) taken using a gas chromatograph. Photographs of a PD-ASU and the discharge plasma are presented in Fig. 6. The result shows that the air chemistry is easily changed by as much as 1 %. Oxygen concentration measured at the suction hole was approximately 1% higher than that of the gas in the vicinity of the discharge just above the hole.

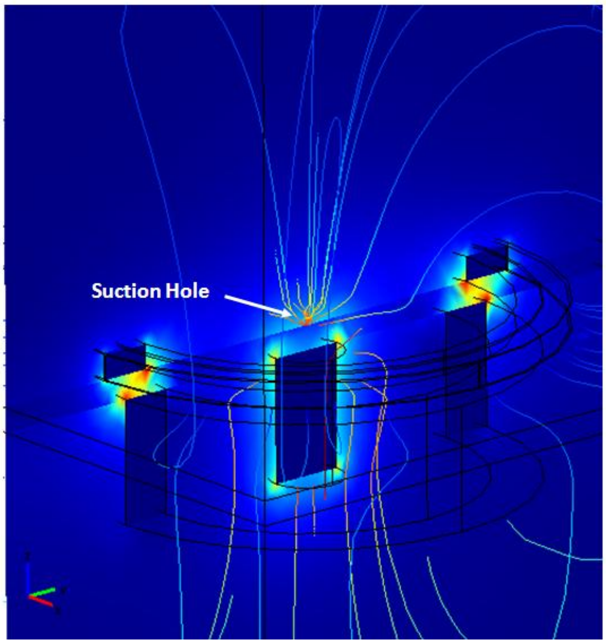

Figure 5. Electric field simulation in three dimensional view (Case III).

Multi-stage ASU Design

A multi-stage ASU is necessary for improving PD-ASU performance. Such a unit consists of serially connected PD-ASU modules as shown in the schematic of Fig. 7. A prototype of two-stage ASU was built in a pressure variable chamber (Fig. 8) for a parametric study varying ambient gas pressure. The ambient gas conditioning is one of the most crucial engineering problems because the gas condition alters plasma characteristics such as ion concentration and distribution of plasma density (e.g. thickness of sheath). Each stage has the concentric electrode configuration (Fig. 8 (b)) chosen by the design optimization scheme (Case III). The gas outlet (suction hole) of the first stage was directly connected to a transparent gas confinement accommodating second stage module (Fig. 8 (c)). Another engineering issue arising from the connection between stages is the nitrogen accumulation in the gas confinement. Ongoing work regarding this issue is the design of a bypass line extracting accumulated nitrogen.

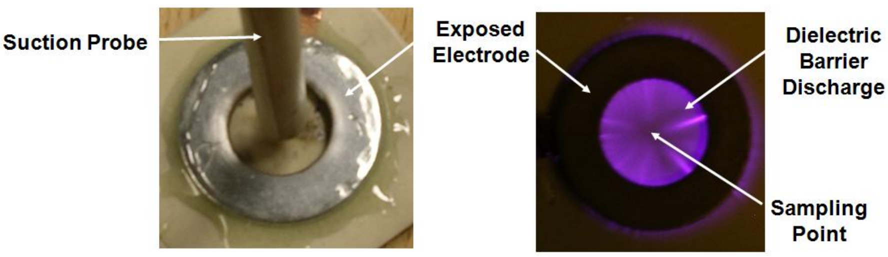

Figure 6. Photographs of a proposed ASU cell and the plasma discharge.

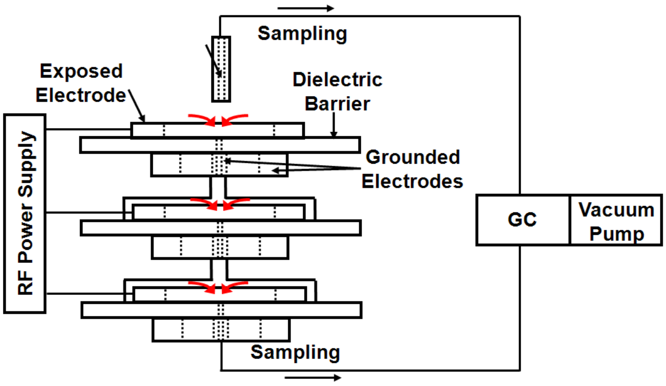

Figure 7. A typical schematic of a proposed multi-stage ASU.

Future plans and conclusions

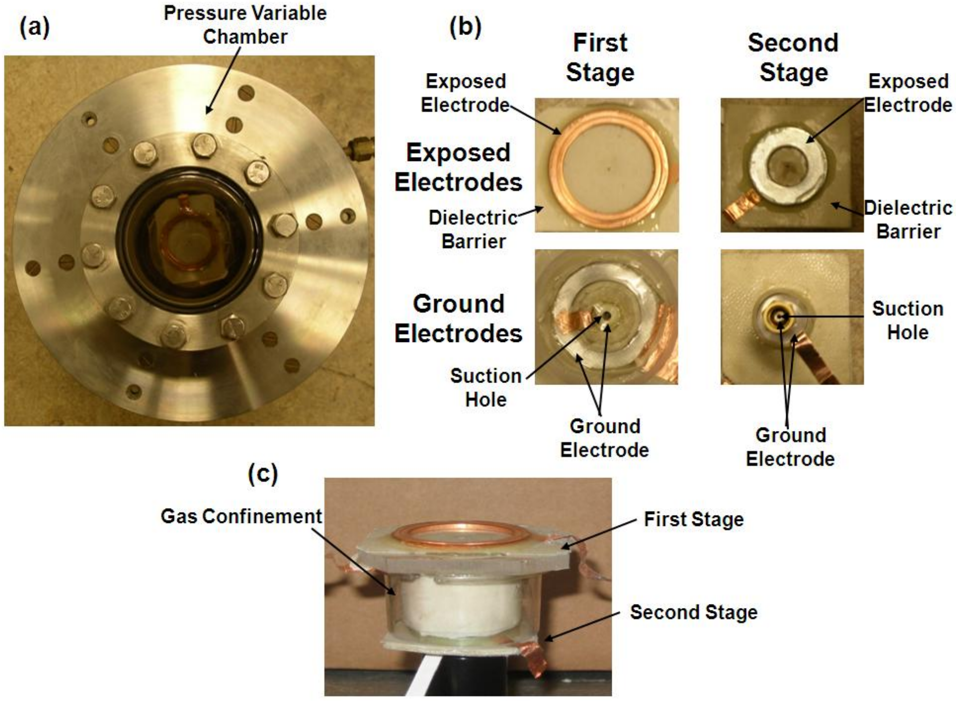

Figure 8. Two-stage PD-ASU built in a pressure variable chamber.

The investigation conducted during the year resulted in the need for designing a new multi-stage ASU. At the time of writing this report, we have assembled and are currently testing the two stage unit. In theory, each stage should boost the separation of oxygen from air linearly; however this experiment is yet to be conducted. Research on this problem continues outside of GCEP funding.

References

[1] World Energy Outlook, International Energy Agency, 2002.
[2] A.P. Simpson and A.J. Simon, Energy Conversion and Management 48, 3034, 2007.
[3] K. Thambimuthu, et al., IPCC Special Report on Carbon Diaoxide Capture and Storage, Cambridge University Press, Cambridge, 2005, pp. 105-178.
[4] W. Kim, H. Do, M. G. Mungal, and M. A. Cappelli, Appl. Phys. Lett. 91, 181501 (2007).
[5] B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin, P. H. Wallman, M. Neiger, O. Wolf, T. Hammer, and S. Broer, Appl. Phys. Lett. 68, 3719 (1996).