

Oxygen Generation from Carbon Dioxide for Advanced Life Support

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The partial electrochemical reduction of carbon dioxide (CO₂) using ceramic oxygen generators (COGs) is well known and widely studied. However, complete reduction of metabolically produced CO₂ (into carbon and oxygen) has the potential of reducing oxygen storage weight for life support if the oxygen can be recovered. Recently, the University of Florida developed novel ceramic oxygen generators employing a bilayer electrolyte of gadolinia-doped ceria and erbia-stabilized bismuth oxide (ESB) for NASA's future exploration of Mars. The results showed that oxygen could be reliably produced from CO₂ at temperatures as low as 400 °C. The strategy discussed here for advanced life support systems employs a catalytic layer combined with a COG cell so that CO₂ is reduced all the way to solid carbon and oxygen without carbon buildup on the COG cell and subsequent deactivation.

Introduction

Though much of the technology needed for long-term manned space travel already exists, there are two critical unresolved issues: weight and metabolic carbon dioxide (CO₂) removal in inhospitable atmospheres. Specifically, current CO₂ removal technologies are not suitable for use on a Mars mission because of their weight and/or interaction with the Martian environment. For example, current CO₂ removal systems employing lithium hydroxide canisters, would require approximately sixty pounds of consumable lithium hydroxide (LiOH) for a five day Mars surface mission. Conversely, cycling bed and permeable membranes systems are unsuitable because the high CO₂ concentration in the Martian atmosphere precludes simply venting the CO₂ after its removal from a spacesuit. In addition, none of these technologies capitalizes on the presence of vital O₂ bound up in the CO₂ molecule. In this work, we address these two issues of weight and CO₂ removal, by revisiting the well-known technology of ceramic oxygen generators (COGs), but with new strategies and advanced materials.

In the past we investigated COGs for NASA's future manned exploration of Mars (1, 2). To reduce landed mass, in-situ resource utilization (ISRU) was proposed for obtaining both life-supporting oxygen and oxidant/propellant fuel, by converting CO₂ from the Mars atmosphere. To this end, we developed a COG cell employing a novel bilayer electrolyte of gadolinia-doped ceria and erbia-stabilized bismuth oxide for ISRU. Our results showed that oxygen could be reliably produced from CO₂ at temperatures as low as 400 °C without degradation in efficiency. More recently, the previous work has been furthered by adopting a tubular designed COG cell in

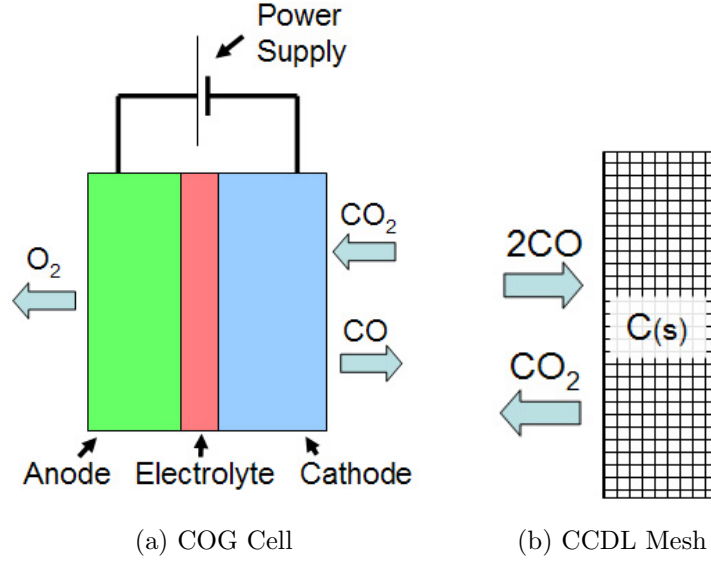


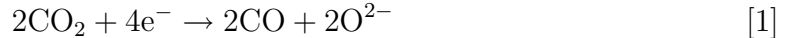
Figure 1: COG cell and CCDL mesh

concert with a catalytic carbon deposition layer (CCDL) (3, 4), which is the focus of this article.

The objective here is to fully convert available CO_2 from exhaled air to oxygen and solid carbon. To achieve this end a combination of a COG cell and a CCDL were used. The COG cell must not promote carbon formation, otherwise deactivation of the cell can occur. However, for full reduction of CO_2 , carbon will be formed and therefore the CCDL is employed. The carbon deposits on the CCDL and once saturated, it can be replaced without damage to the COG cell.

COG Cell Function

In a COG utilizing CO_2 as the oxygen source, an electric potential is applied across a dense oxide ion-conducting electrolyte, as shown in Figure 1a. Under the influence of this potential, CO_2 is electro-catalytically reduced at the cathode to carbon monoxide and oxygen ions as follows



The oxygen ions are then incorporated into the lattice of the electrolyte and transported to the anode where they recombine to form O_2 molecules as follows



Hence, the overall reaction is given by



The oxygen flux through the COG is given by Faraday's Law:

$$J_{\text{O}_2} = \frac{i_{app}}{nF} = \frac{P_{app}}{V_{app}nF} \quad [4]$$

where J_{O_2} is the molar flux of oxygen (mol/s), i_{app} is the applied current (A), P_{app} is the applied power, V_{app} is the applied voltage, F is Faraday's constant, and n is the number of electrons transferred in the ionization of an oxygen molecule.

Conventional COGs use yttria-stabilized zirconia electrolytes that operate at temperatures greater than 700 °C (5). Consequently, electrolytes that perform well at lower temperatures exist and the potential weight of the proposed COG-based life support system can be reduced. Two such materials are gadolinium doped ceria (GDC) and erbia stabilized bismuth oxide (ESB) (1). GDC is known to be prone to electronic conductivity at low partial pressures of oxygen, but is stable. Whereas, ESB decomposes in low partial pressures of oxygen but exhibits no electronic conductivity. Therefore, in this work a bilayer electrolyte concept was employed in which ESB blocks the electronic current and GDC protects ESB from low partial pressures of oxygen (i.e. CO).

CCDL function

Complete reduction of CO₂ is perhaps the most crucial feature of our approach because it eliminates the need to vent exhaled CO₂ to a potentially inhospitable environment and, because of the oxygen recovery, it offers the possibility for reduced oxygen storage weight. Nevertheless, complete reduction of CO₂ is not without some difficulty because it typically results in "coking" of the cathode (i.e., carbon deposition), which can severely attenuate COG efficiency. Hence, control of "coking" is crucial for the viability of the COG cell. Therefore, the CCDL is employed. The CCDL operates by the common Boudard reaction shown below.



The CCDL converts carbon monoxide produced by the COG cell (equation [3]) to CO₂ and solid carbon. The CO₂ is then used again by the COG cell. The concept is displayed in figure 1b.

Experimental

COG Cell Processing

Commercially available 10 mol% gadolinium doped ceria (GDC, Nex Tech Materials) with carbon and cellulose pore former was tape cast and subsequently rolled into a tubular shape. The tubes were capped at one end using laminates of the same tape as the tube by application of organic solvent. The cathode tubes were then slowly pre-sintered, after which a low solids, organic slurry of 10GDC (Anan Kasei) with 1 mol% Fe as a sintering aid was coated on the inside of the tube as the electrolyte (6). The electrolyte and cathode support were co-sintered at 1400 °C for 10 hours. Next, the bilayer electrolyte, a low solids, organic slurry of 20 mol% erbia stabilized bismuth oxide (20ESB), was coated on the inside of the tube several times and subsequently sintered at 900 °C for four hours. Then the anode, consisting of a 50 vol% mixture of bismuth ruthenate (BRO) and 20ESB in a low solids, organic slurry, was coated on the inside of the tube and sintered at 800 °C for two hours. The 20ESB and BRO powders were manufactured following (7, 8). Finally, an aqueous copper

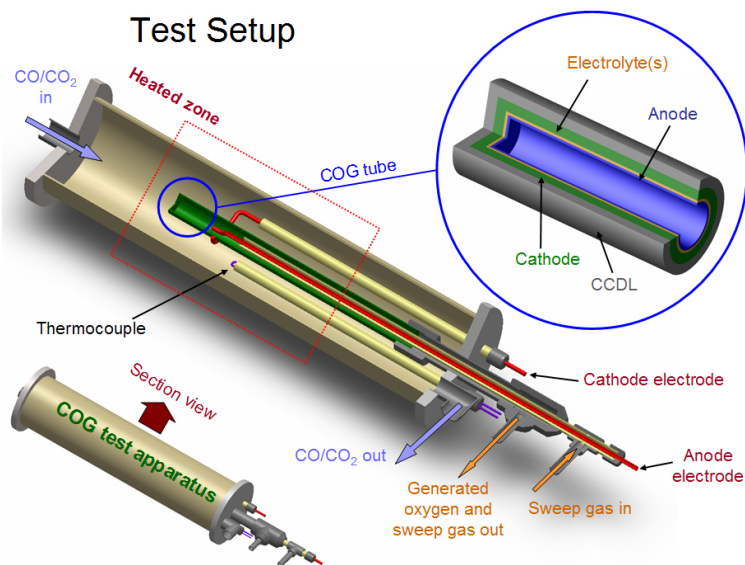


Figure 2: COG test apparatus

nitrate/ urea solution was vacuum infiltrated into the cathode support and heated to 450 °C several times following the work of Jung et al. (9). This process resulted in tubular COG cells approximately 18 cm long and 0.64 cm in diameter.

CCDL Processing

To fabricate the CCDL, Ni- or Fe-based catalysts were deposited on a ceramic tape that was first heat-cleaned to remove a protective coating and thus facilitate the adsorption of active metals on its surface. Three different catalysts were manufactured and tested: Ni, Fe, and Ni on alumina nano-particles. Nano-particles of NiO and FeO were dispersed in de-ionized water using ultra-sonication and then dripped onto the heat-cleaned ceramic tape. In the case of NiO on alumina nano-particles, nickel nitrate was precipitated on alumina nano-particles by evaporating water from an aqueous nickel nitrate solution containing the alumina. The resulting paste was applied to the heat-cleaned ceramic tape. Finally, the catalysts were dried and calcined at 450 °C. During testing, the Ni and Fe oxides are reduced to metal by carbon monoxide.

COG Setup and Testing

The cathode at the open end of the COG cell was infiltrated with epoxy to fill in porosity and inserted into a gas fitting. Next, the COG cell was electroded with gold paint and silver mesh on both the cathode and anode. Only 4 cm of the closed end of the tube were electroded (as well as infiltrated with copper), so that oxygen pumping only occurred within a constant temperature region in the test furnace. Finally, the CCDL tape was wrapped around the outside of the COG cell and secured with silver wire.

Figure 2 shows a schematic of the COG test setup. Argon sweep gas is flowed through the inside of the COG cell to collect pumped oxygen. On the outside of

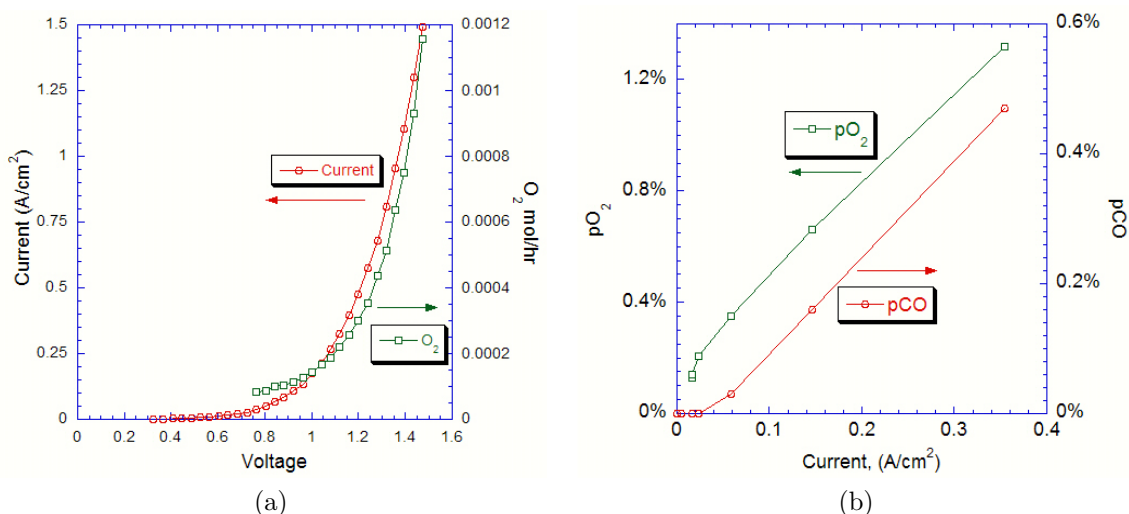


Figure 3: COG test without CCDL at 600 °C showing (a) current-voltage-flux characteristics and (b) relationship between O₂ and CO flux

the tube, CO, CO₂, and mixtures thereof are flowed. The effluent Ar was measured using an oxygen sensor and/or gas chromatograph. Also, the CO/CO₂ exhaust was measured using a gas chromatograph to determine the CO concentration.

Results and Discussion

COG Cell Performance

Figure 3a shows the performance of a COG cell tested in CO₂ at 600 °C without a CCDL. As displayed in the figure, current through the cell increases as the applied voltage is increased. As the current increases the concentration or flux of oxygen measured in the inside of the tube increases. In figure 3b, the partial pressure of oxygen in the Ar sweep gas is plotted along with the partial pressure of CO in the CO₂ exhaust. This shows that as oxygen is being produced inside the COG cell, CO is being produced on the outside of the cell, following equation [3]. After removal of the COG cell from the test, there is no evidence of carbon deposits on the surface of the tube indicating that only partial reduction of the CO₂ occurred. This leads to the conclusion that the copper based cathode does not promote carbon deposition and subsequent deactivation of the cathode.

In figure 4a, the cell performance versus temperature is shown. Also plotted is the theoretical oxygen flux based on Faraday's Law, equation [4]. As expected and seen in the figure, oxygen flux increases with increasing temperature due to the lower ionic resistance of the cell at higher temperatures. However, unexpectedly, the oxygen flux deviates from the ideal case at all temperatures. Further investigation of this behavior indicated that infiltrated copper metal was penetrating cracks in the electrolyte thereby creating an electronic conducting pathway between the cathode and anode discussed below.

Figure 4b shows the electrochemical reduction of infiltrated copper oxide in the cathode support. Initially, as voltage or current is applied to the cell, oxygen is pumped from CuO thereby forming Cu. In the figure, Faraday's Law is followed until

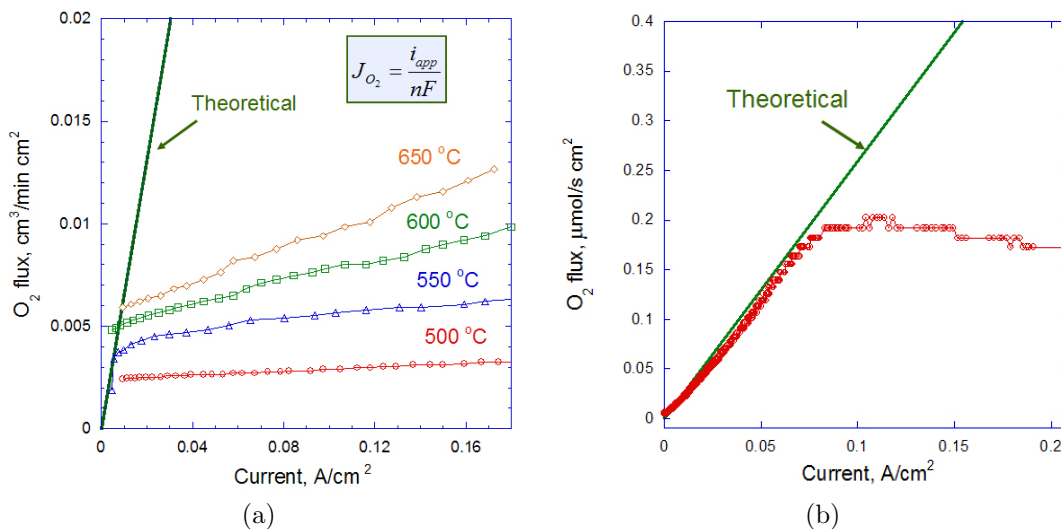


Figure 4: COG test showing (a) current-flux characteristics at multiple temperatures and (b) electrochemical reduction of CuO in cathode support

a certain time (current increasing with time) at which point enough CuO has been reduced to form a continuous Cu network. It is at this time that electrical shorting across the Cu infiltrated cracks in the electrolyte occurs, causing a deviation from the theoretical flux of oxygen.

Evidence of cracking in the GDC electrolyte is shown in figure 5. Shown in the inset are two metals located at the crack that both can potentially lead to electrical shorting between the cathode and anode. The copper comes from the infiltration step and the bismuth most likely existed as ESB deposited in the crack that was reduced by CO from the cathode.

The electrolyte cracks do not occur during testing. The most likely cause of the cracking is differential shrinkage between the cathode support and electrolyte during sintering. Upon sintering the electrolyte densifies much more than the cathode support and therefore a strain mismatch develops between the two bodies resulting in tensile fracture of the electrolyte. To alleviate this cracking, the green or pre-sinter density of the electrolyte should be increased.

CCDL Performance

The Ni-based catalysts both performed well in COG tests, the catalyst with alumina nano-particles showing much more carbon deposition than without. The Fe-based catalyst, on the other hand, did not appear to be significantly catalytic toward carbon deposition. Figure 6 shows the results for two of the catalysts tested simultaneously on a COG cell at 650 °C. From the figure, there appears to be little or no carbon deposition on the Fe-based catalyst (the grey post-test color arising from iron metal). However, the Ni on alumina nano-particles has carbon soot on the outside, and after unraveling shows soot buildup between the COG cell and the CCDL. Finally, no soot buildup appears on the COG cell itself, reiterating the conclusion that the cathode does not promote carbon deposition.

The CCDL with the COG cell was therefore able to promote full reduction of CO₂

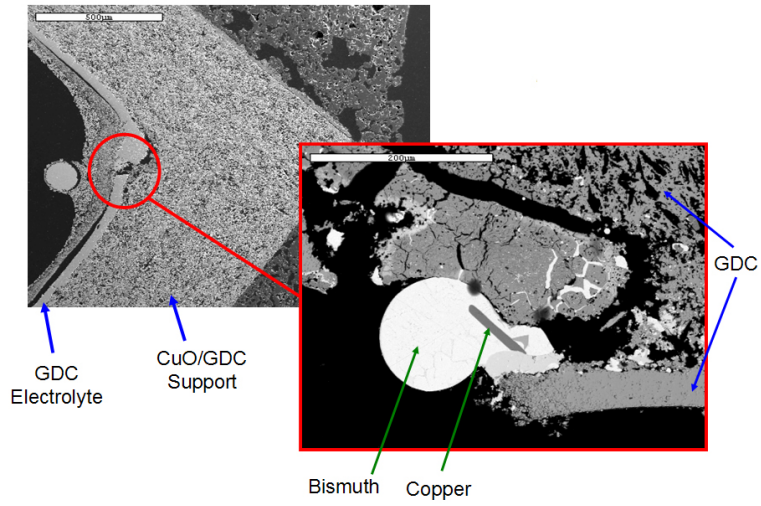


Figure 5: Crack in GDC electrolyte that results in an electronically conductive path of Cu

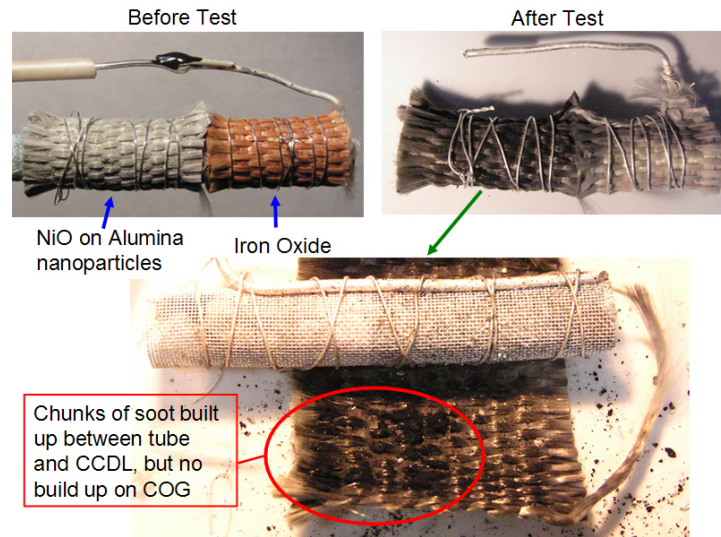


Figure 6: CCDL test at 650 °C in CO with Fe and Ni/alumina nano-particles showing carbon soot formation on Ni

to carbon and O₂. Since the flexible CCDL tape was wrapped around the COG, it was shown that the CCDL is removable and replaceable. The issue of full reduction of CO₂ without cathode deactivation has thus been approached and resolved.

Conclusion

It has been shown that a COG cell used in concert with a CCDL can be used for full conversion of CO₂ to O₂ and solid carbon. The COG cell was able to electrochemically pump oxygen from CO₂ gas. However, the cell did not obey Faraday's Law because of processing related cracks in the electrolyte. With improved processing methods, though, the cracking problem can be alleviated.

The CCDL was shown to be catalytic towards carbon deposition, the best results were found with Ni dispersed on alumina nanoparticles. When the CCDL was used in conjunction with the COG cell, carbon only deposited on the removable CCDL. Therefore, the problem of carbon deactivation of the cathode during full CO₂ reduction has been addressed.

Acknowledgements

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