

Quantification of Methane Generation using a Solid Oxide Electrolyzer with an Electrode-based Sabatier Reactor for Oxygen Regeneration

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ABSTRACT

Solid Oxide Electrolysis with an embedded Sabatier reactor is being developed for regenerative air revitalization. In a previous effort, an embedded Sabatier reactor was demonstrated using a nickel-based electrode in a SOE cell. To explore the performance potential, new experiments were performed at various operating temperatures and inlet gas compositions. Successful methane and oxygen regeneration was achieved. The gas compositions fed to the cell were a mixture of carbon dioxide, water, carbon monoxide, and hydrogen in ratios indicative of a previously electrolyzed stream of metabolically produced by-products (carbon dioxide and water vapor) of nominal crew activity. The composition was varied by simulating various degrees of oxygen regeneration by upstream electrolysis cells. All results are presented and compared to previous testing where applicable. Carbon deposition was observed in the inlet tube to the cell. Theory is presented that confirm carbon deposition did not occur inside the test cell.

INTRODUCTION

MOTIVATION – Current oxygen (O_2) regeneration processes used in space rely on electrolyzing liquid water (H_2O), where the resulting hydrogen (H_2) is vented to space since it is dangerous to store. Available resources of liquid H_2O within a habitat or spacecraft include metabolically produced H_2O by the crew (via condensation from the cabin atmosphere or post-processed waste) as well as that obtained as a fuel cell by-product (if fuel cells are present). These sources do not provide enough H_2O to regenerate all the necessary O_2 .

To increase the amounts of regenerated O_2 , O_2 must also be obtained from carbon dioxide (CO_2) produced by the crew. Current plans are to react H_2 left over from the electrolysis process with some of the CO_2 via a Sabatier reaction to produce methane (CH_4) and more H_2O in the form of a vapor. The H_2O vapor can be condensed and

then electrolyzed. The CH_4 would be vented (or possibly stored as fuel).

Mass balance calculations [1] have shown that, given a crew's diet, there is not sufficient H_2 available to convert enough CO_2 to completely regenerate all the O_2 required. The only way to provide enough H_2 is to supply the system with additional resources outside of those used for crew consumption. This is usually in the form of liquid H_2O .

To completely close the loop, the remaining CO_2 will have to be utilized. Solid oxide electrolysis (SOE) is a technology that can do this – it can generate O_2 from CO_2 . Further, it can also electrolyze H_2O . Thus, SOE with a Sabatier reactor can provide 100% O_2 regeneration. No consumables beyond those already required by the crew would be necessary.

SOE is an advantageous technology for space applications. As SOE is a high temperature process, all reactants and products are in the gas phase, mitigating two-phase flow challenges in low gravity inherent in other H_2O electrolyzer technologies. It also mitigates the need to condense the H_2O resource. Though it is a high temperature process, it has been shown that the total energy (power and heat) is the same as that required by any electrolyzer technology since a fixed finite amount of energy is required to breakdown a CO_2 or H_2O molecule [2]. As SOE produces pure O_2 , the need for O_2 purifiers and/or dryers is eliminated. Finally, as the SOE and Sabatier processes are both gas phase and high temperature, the two technologies can be merged into a single unit, simplifying system design and eliminating handling of H_2 .

BACKGROUND

Solid Oxide Electrolysis - SOE is an electrochemical process that can generate pure O_2 from CO_2 and/or H_2O vapor as well as pump O_2 . SOE uses an electrolyte made of a nonporous ceramic oxide, such as yttria-stabilized zirconia (YSZ) in this work, which conducts oxygen ions at or above 750°C. An electrically

conducting porous cathode and anode placed on opposite sides of the electrolyte facilitate gas/electron transport and act as a catalyst (Figure 1). At the cathode, an oxygen atom and carbon monoxide (CO) or H₂ molecule are liberated from the CO₂ or H₂O molecule, respectively. The oxygen atom picks up two electrons (that were transported through the cathode) to become a doubly-charged oxygen ion, O²⁻. This ion is then conducted through the nonporous electrolyte, driven by the applied voltage across the cell. When the ion reaches the other side of the cell, the ion transfers its charge (electrons) to the anode to become an oxygen atom and combines with another oxygen atom to form an oxygen molecule. This flow of electrons produces a current which is a direct correlation to O₂ production. Several SOE cells can be stacked to increase O₂ production.

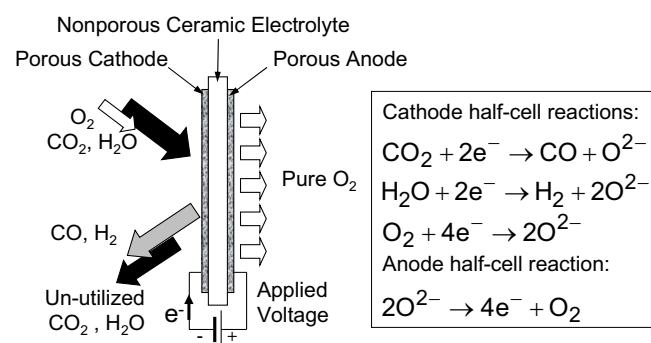
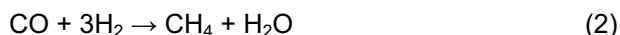
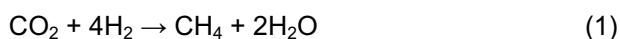


Figure 1: SOE Illustration (cell cross section)

To safely handle the CO and H₂ by-products of electrolysis, as well as to further regenerate O₂ from the CO, a reactor can be employed down stream of the SOE unit to catalyze Sabatier reactions, creating CH₄ and H₂O. The reactions are:



Embedded Sabatier Reactor - Nickel (Ni) is a catalyst for the Sabatier reaction. Thus, the Sabatier reactor can be “embedded” simply using a Ni cathode in the SOE cell. This allows for the embedded reactor to not only support Sabatier reactions but also perform electrolysis in the presence of an applied potential.

An example of Sabatier reactors embedded into a SOE unit is illustrated in Figure 2. The first cell uses platinum (Pt) cathodes to remove any trace O₂ that may have been separated from the cabin or habitat atmosphere with the CO₂ and H₂O. The output of the first cell will be CO, H₂, and unutilized CO₂ and H₂O. This output could be sent to an embedded Sabatier reactor to consume CO and H₂ and produce more H₂O. The process stream can be then sent to another embedded Sabatier cell that is operated under an applied voltage to increase the utilization of remaining CO₂ and newly-produced H₂O. Each cell in the SOE stack can be optimized as a

function of cathode material and applied voltage to control the final output from the stack.

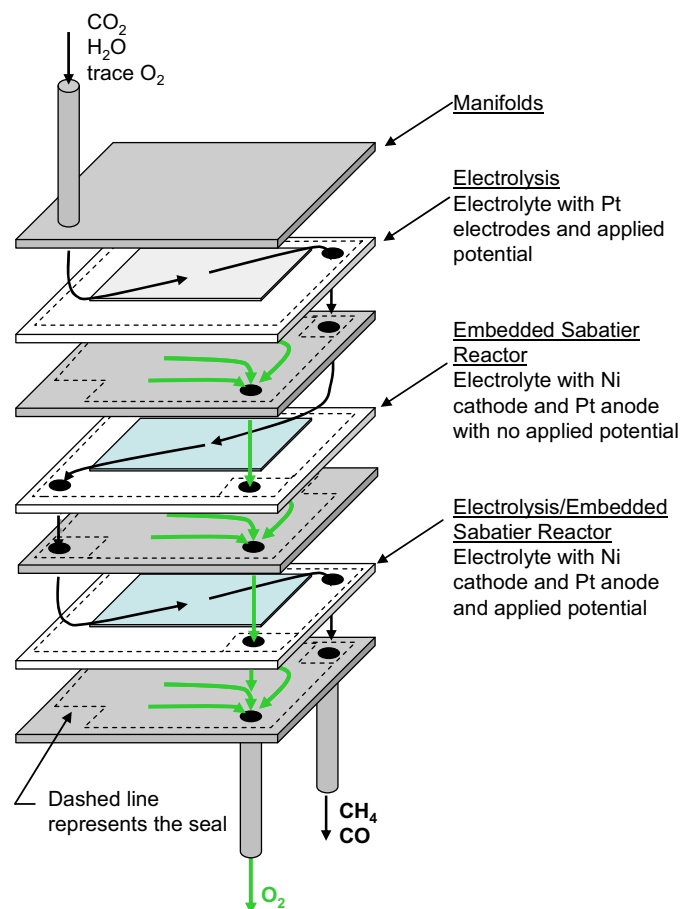


Figure 2: Example SOE Stack in Series with Embedded Sabatier Reactors

OBJECTIVES – In a previous effort [1], successful operation of an embedded Sabatier reactor was demonstrated using a nickel-based electrode in an SOE cell. To explore the performance potential, new experiments were performed at various operating temperatures and inlet gas compositions. Results and analyses are presented here. First, the test article and test process are described. Then, embedded Sabatier reactor electrolysis and CH₄ generation performance are presented and analyzed.

TEST SET UP

TEST ARTICLE CONSTRUCTION – An embedded Sabatier reactor (labeled PSDC cell 05) was manufactured and assembled similar to that described in pervious work [1]. The major difference was the manifolds. The previous manifolds were manufactured from CRF, an electrically conducting oxide dispersion-strengthened alloy Cr-5 Fe-1 Y₂O₃ by Plansee, Ltd. As CRF is no longer available, SOE testing was performed using different manifold materials to ascertain their performance. New manifolds were made specifically for this work using the material that exhibited stable performance and resisted corrosion in high temperature O₂ environments.

A Positive electrode/Electrolyte/Negative electrode (PEN) assembly was used from the same batch manufactured for the previous work. The cathode is a NiO-based electrode that requires reduction to Ni using a H₂/He flush at 800°C. The anode is Pt-based.

TEST BED – A SOE/embedded Sabatier reactor test bed was constructed in Paragon's Research & Development Laboratory. The test bed is similar to that used in previous work [1]. Figure 3 is the schematic of the test bed.

In general, MKS type 1179A Mass-Flo Controllers meter the flow of gases to achieve proper mixing of the required cell input. Valves direct the flow to the cell either directly (for cathode reduction or dry input) or through a humidifier (to simulate metabolically-produced H₂O). Lines containing humidity are heated to prevent condensation. Two Vaisala HMP330 sensors measure relative humidity and temperature of the inlet gas and

cathode exhaust. H₂O is removed from the cathode's exhaust via a Nafion dryer.

The cell is heated in a Paragon model Q-11A (max temperature 1260°C) furnace controlled by a Sentry 2.0 controller. An Agilent E3633A (0-8V, 20A/0-20V, 10A) DC power supply applies voltage across the cell. Current is independently measured using a shunt resistor.

O₂ production is measured with a rota-meter (Omega Engineering, FL-3861G) and MKS type 1179A Mass-Flo Controller set to full open. The cathode flow rate is monitored with a rota-meter (Omega Engineering, FL-2010). Either cathode or anode exhaust can be sent to a Hewlett Packard Series II 5890 gas chromatograph (GC) for analysis. All exhaust (cathode, anode, and GC) is vented through a fume hood. The cathode inlet pressure (Gems Sensors & Controls, 2200 series) and anode outlet pressure (Setra, model 205-2) are monitored and recorded.

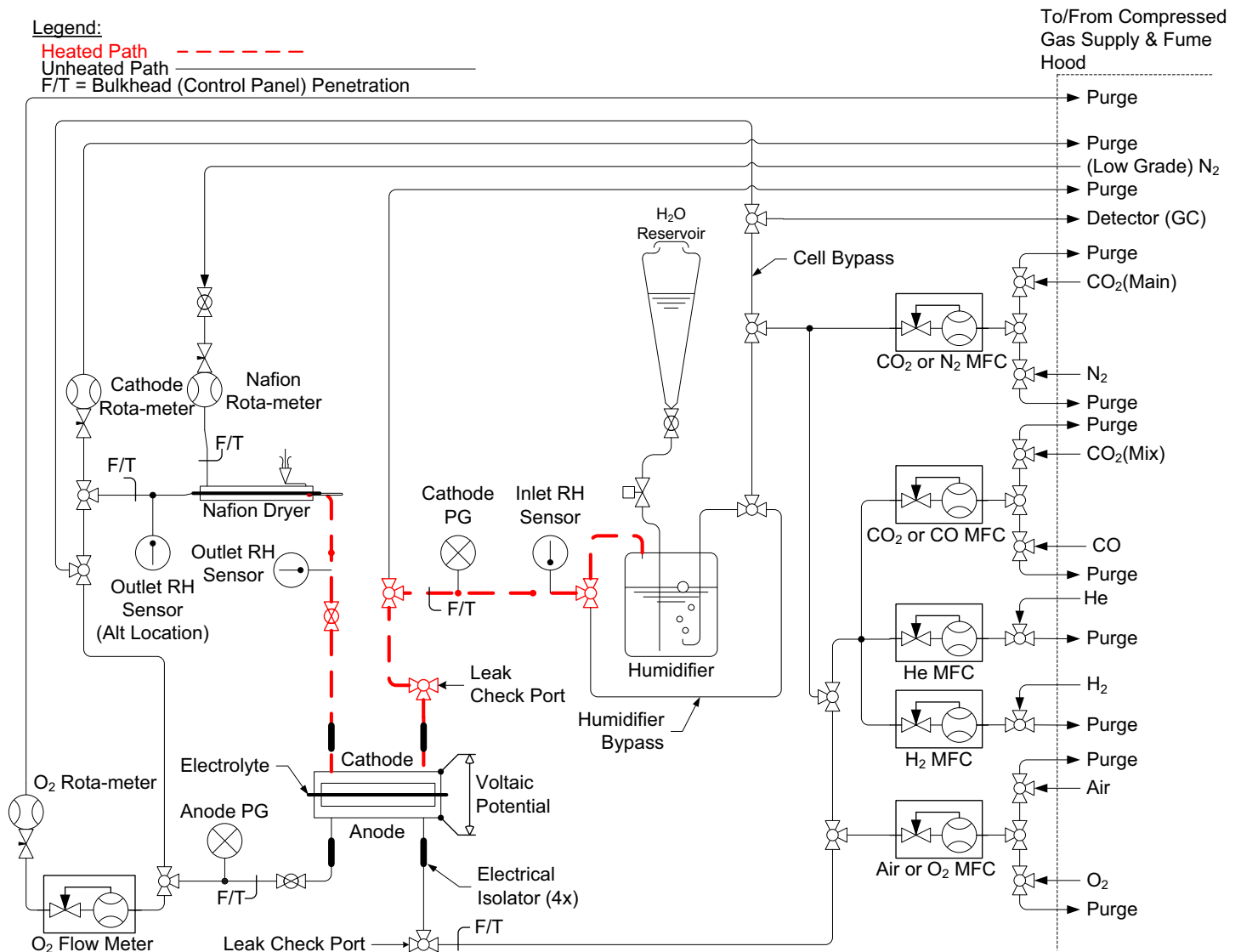


Figure 3: Schematic of Test Bed

Temperature data were acquired using an MMC USB-TC thermocouple input DAQ (data acquisition) device

while all other electronic data were acquired using NI USB-6008 Multifunction DAQ devices. Data acquisition