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Implementation Of New System For Oxygen Generation And Carbon Dioxide Removal

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IMPLEMENTATION OF NEW SYSTEM FOR OXYGEN GENERATION AND CARBON DIOXIDE REMOVAL

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2017

Dedication

To my wife and all of those whose efforts made this product possible, especially the committee members and those in the space industry.

IMPLEMENTATION OF NEW SYSTEM FOR OXYGEN GENERATION AND
CARBON DIOXIDE REMOVAL

by

ANGELO PETER KARAVOLOS, B.S., M.S.

DISSERTATION

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Abstract

This research effort develops an integrated system for CO₂ removal and O₂ production. A unique material, dodeca-tungsto-phosphoric acid (H₃PO₄W₁₂O₃; henceforth referred to as DTPA) is mixed with tetra-ethyl-ortho-silicate Si(OC₂H₅)₄ or TEOS. This mixture exhibits unique properties of heat absorption and high electrical conductivity. In the system described herein, the DTPA resides within a cross linked arrangement of TEOS. The DTPA furnishes a source of O₂, while the TEOS furnishes structural support for the large DTPA crystals. In addition, the large amount of H₂O within the crystal also adsorbs CO₂. It can also be cross-linked with other polymers such as polycarbonate, for different applications and properties such as flexible textiles. A set of isolated bench experiments were designed to test CO₂ adsorption, O₂ production, heat production, and voltage production were conducted to test the hypothesis that DTPA can provide CO₂ adsorption, O₂ generation, heat generation and electrical generation. Five experiments with this apparatus were conducted: (1) a mass balance experiment; (2) an X-ray diffraction experiment; (3) a photo spectroscopic experiment; (4) a calorimetric experiment; and (5) a dielectric experiment. Results illustrate that approximately 2880 grams of this material produces 576 grams of O₂, and removes 1760 grams of CO₂. The reaction also produces approximately 844 kJ/mole heat, and can supply 12.2 V potential over a period of 4.5 hours. The amount of unused material and the recycling ability suggests the usefulness of the technique to achieve between a 50-75% closed system. In addition, an experiment using ¹⁸O tracer demonstrated that approximately 20% of the O₂ produced comes from processed CO₂ adsorbed by the crystal, while the remaining 80% of the O₂ produced comes from replaced O₂ within the crystal itself. The device has multiple applications including environmental control and life support for

aircraft cabins, space vehicle interiors, submarine pressure vessels, sealed armored vehicles, and personal protective equipment for individuals working in confined spaces such as mines.

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1. INTRODUCTION

1.1 Summary

This effort addresses the task of designing an integrated system for CO₂ removal and O₂ production, using a super oxide material within a capacitor chamber. The general chemical process involved in this approach can be summarized as:

1. Remove H₃PO₄ from H₃PO₄W₁₂O₃₆,
2. Introduce NaOH into a reaction chamber to form Na₂CO₃ and Na₃PO₄,
3. Use heat to release O₂ from WO and WO₂,
4. Regenerate H₃PO₄W₁₂O₃₆ from WO and WO₂ by using Na₂WO₄, H₃PO₄, HCl, and NaCl,
5. Remove waste C and Na₂CO₃ from the system.

This process can be used for enriching air with O₂, providing electrical current and heat, and removing CO₂. Using this process, a pressurized capacitor compartment could be constructed which can perform many functions needed for crew life support.

Several issues must be addressed in order to successfully meet the selected Lockheed Martin Environmental Control Life Support System validation process (Lockheed Martin Telecommunication, 2016). One system requirement shall be the need for a unit to produce at least 640 grams of O₂ per person per day (Lockheed Martin Telecommunication, 2016). A second systems requirement is that the unit removes 1760 grams of CO₂ per person per day. Thirdly, materials needed to accomplish the mission should be available as by-products of other sub systems. The amount of O₂ production and CO₂ adsorption must meet the needs of a person to perform respiration.

After a literature review of candidate oxide materials, several oxygen rich metal oxides were considered such as dodeca-tungsto-phosphoric-acid ($\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$). The material was chosen because it contains 560 grams of O_2 per mole for one person at rest, per day. Dodeca-tungsto-phosphoric-acid ($\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$) also contains one of the components needed to recharge the material, H_3PO_4 .

1.2 Material Selection Process Summary

Figure 1 below illustrates a summary of the process used for dielectric material selection. The selection process for the material $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ consisted of a survey of chemicals, both organic and inorganic that contains a high ratio of oxygen compared to the entire molecule. Such molecules include super oxides such as K_2O , Na_2O , and $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$. The molecule $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ was chosen because it contains 22 % by weight oxygen, and was not chemically unstable, as both K_2O and Na_2O are flammable.

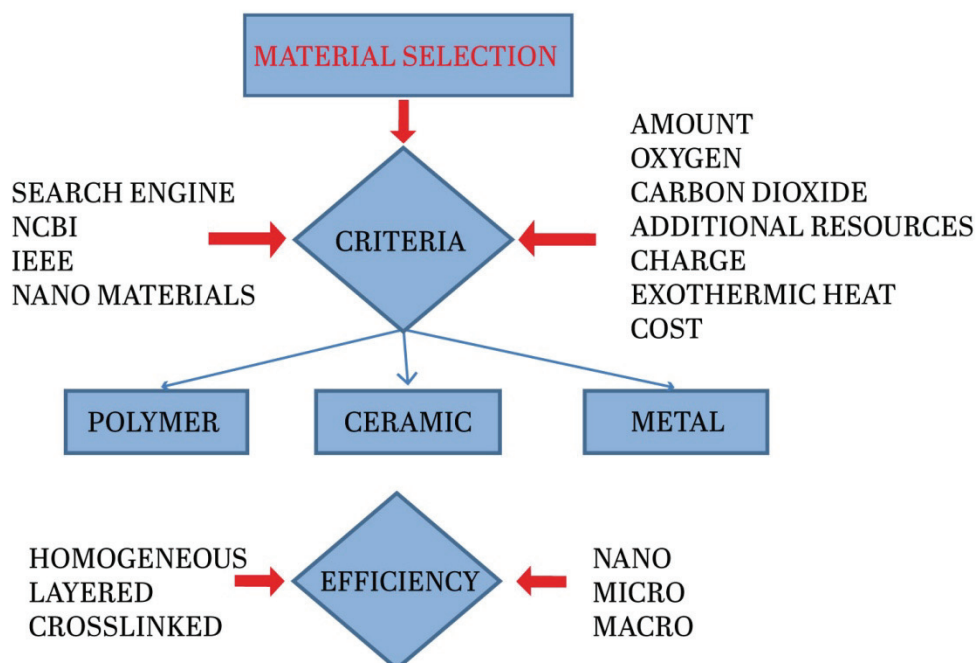


Figure 1: Decision process for material selection of dielectric, and matrix material.

An added benefit to using DTPA chemistry for O₂ production can be seen by the production of heat and electrical charge within the container system.

1.3 Description of Device

The device itself consists of an internal container with several slots intended for individual filters. These filters are actually specialized capacitors containing a dielectric that changes as a function of CO₂ content.

The device could be described as a rectangular box. Other designs include a cylindrical shape. The total volume of the device was chosen such that a suitable amount of DTPA could adsorb approximately 1760 grams of CO₂ per day per person, and produce approximately 640 grams of O₂ per day per person. (Figure 2).



Figure 2: Illustration of CoorRS device.

The rectangular box contains a series of sandwiched dielectric material (DTPA and TEOS) that serves as a CO_2 adsorbent and O_2 , heat and voltage producer. The material, which lay between two conductive aluminum wafers, interacts with CO_2 , H_2O , and NaOH to produce carbonates (Na_2CO_3 , Na_3PO_4 , and WO) and O_2 . Figure 2 below illustrates some geometric configurations of the device.

TOP AND SIDE SCHEMATIC VIEW OF FILTER CHAMBER

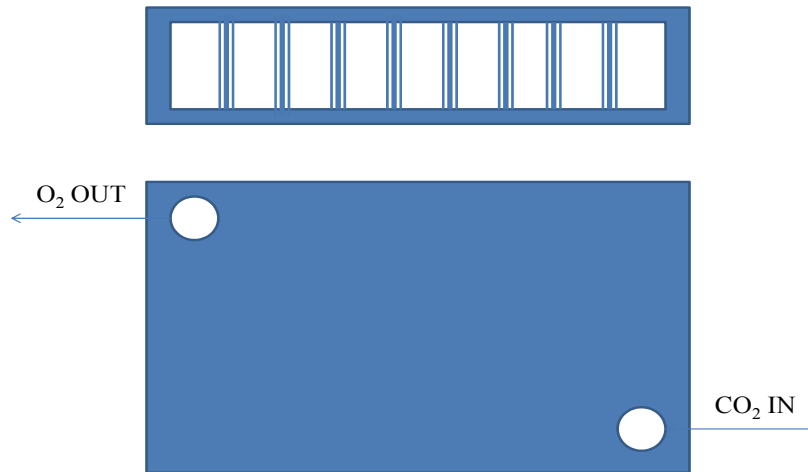


Figure 3: Schematic diagram of CO₂ Removal – O₂ Regeneration System (CooRS). The system consists of an outside shell housing the CO₂ or air pumped through the filters, and the filter itself, which could be described as a dielectric material sandwiched between two conductive materials. This dielectric material contains CO₂ adsorbing material, which generates sufficient heat in order to release O₂ from O₂-rich super oxides, such as H₃PO₄W₁₂O₃₆.

There are five components within the chamber of the CO₂ removal- O₂ production system, two material components within the filter system, and two chemicals within the dielectric system.

The chamber itself (Figure 2) houses the filters that adsorb the CO₂ and release the O₂. Attached to this chamber are the O₂ collection tank and the CO₂ feed tank. These are seen in Figure 6a.

The filters themselves (Figure 6b) contain the dielectric material itself. It could be applied to one side of the plastic grid, seen in Figure 6b. If the electrical current generated during the gas exchange process was desired, two polyaniline or aluminum wafers can be placed on both sides of the dielectric material. Two alligator leads could be connected to the grids, so that charge generated by the break- up of DTPA could collect on the surface of the wafers.

The dielectric material itself could be seen in Figures 7, 8 and 9. There are two chemical components of this system- the dodeca tungsto phosphoric acid (DTPA) and the tetra ethyl ortho

silicate (TEOS) gelatin. The arrangements of these two molecules were predicted using Ceres II and Spartan Chemical Modeling Software. The configuration represents the lowest energy state that the molecules can exist while 10-100 nm away from each other, at standard temperature (25 C) and pressure (1 atm) conditions. The material exhibits useful properties such as hydrophilicity, and stability at higher temperatures (25-80 C) as well.

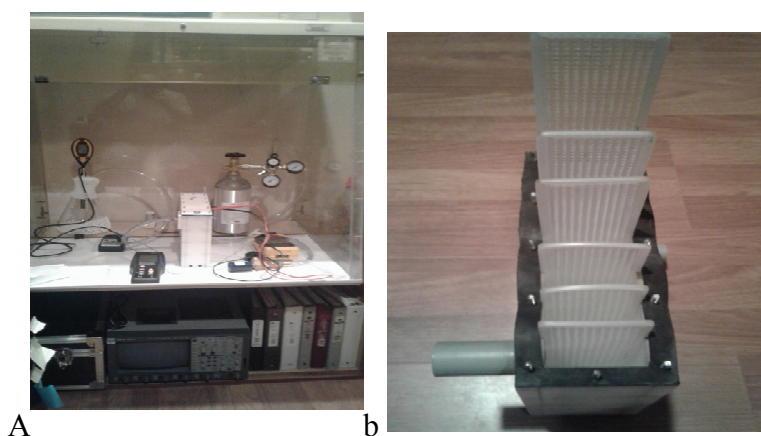


Figure 4: The device developed in this investigation, in which CO₂ was removed and O₂ regenerated in the system (Coors). The grids at the center were coated with H₃PO₄W₁₂O₃₆-Si(OC₂H₅)₄ mixtures. Grid spacing could be varied for larger or smaller throughput of gas. Carbon dioxide enters the port at the bottom left, and O₂ and N₂ gas were allowed to escape at the opposite end of the unit.

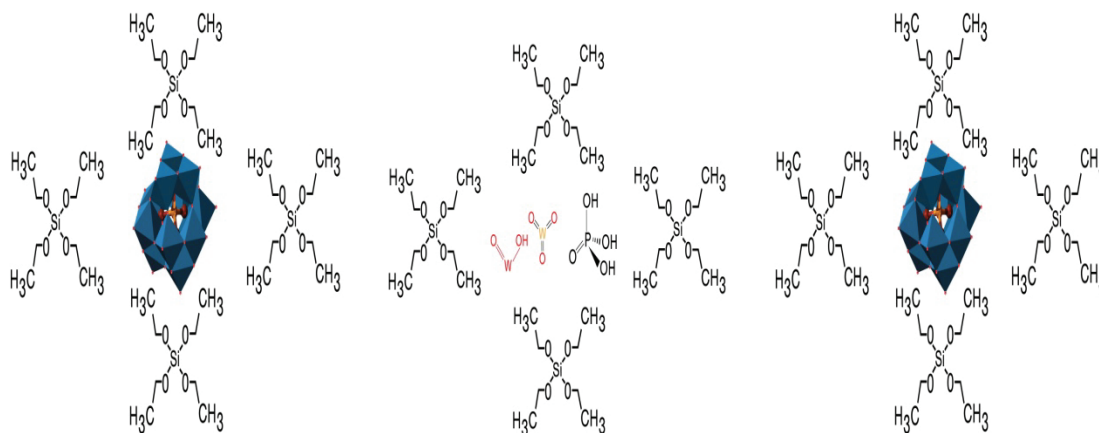


Figure 5: The structural arrangement of Si(OC₂H₅)₄ and H₃PO₄W₁₂O₃₆. The H₃PO₄W₁₂O₃₆ lies in the center while four Si(OC₂H₅)₄ molecules, surrounding the center molecule. The configuration returns to H₃PO₄W₁₂O₃₆ upon addition of Na₂WO₄, NaOH, PO₄, and HCl.

The center molecule consists of a central H_3PO_4 molecule (phosphoric acid) surrounded by twelve W atoms, which are in turn surrounded by thirty-six oxygen atoms. This molecule is a crystalline that has a dodecahedron shape (Figure 5). The entire complex contains multiple H_2O molecules.

The configuration of the dielectric once CO_2 begins to percolate through the TEOS and reacts with $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, according to reaction probabilities calculated by chemical modeling (Series II).

1.4 Device Function

The device functions as a receptacle container for gas that has been exhaled from human occupants, and transferred to the container using a positive pressure, with a regulator device for adjusting gas flow rate. In addition, the device contains ports for electrical leads connecting each of the conductive layers of the filter to a voltmeter. The voltmeter device collects information on the electrical activity of the conductive surfaces, such as contact with ions within the dielectric. Once the CO_2 was adsorbed within the dielectric, heat was released and O_2 begins to move from the solid phase to the dissolved gas phase within the dielectric. In order to harvest the O_2 dissolved in the dielectric, the pressure in the system is lowered below the partial pressure of O_2 , and O_2 is released.

1.5 Methods of Measurement

There were seven methods of characterizing the chemical process involving the release of O_2 from $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ (DTPA) during NaOH and CO_2 adsorption. These were mass balance, X Ray

Diffraction, Raman Spectroscopy, Mass Spectroscopy, Photo Spectroscopy, measurement of dielectric constant, and calorimetry. The first method used was mass balance experimentation. This process involved measurement of the incoming CO₂ from a container of known volume and weight. The tank was connected to a pressure gage and regulator so that the flow rate, pressure, and flux could be calculated. This experiment was completed during real-time release of CO₂.

Two other sets of experiments were completed to identify quantities dielectric constant and heat output. The dielectric was separately encased between two conductive polymer materials (polyaniline or thin aluminum wafer), so that a voltage potential could be generated during the ionization of H₃PO₄W₁₂O₃₆, NaOH and CO₂.

Several experiments were completed in order to characterize the quantity of heat released. A sample of the dielectric material was placed in a double glass tube calorimeter fitted with a port for CO₂ gas insertion. About 200 grams of NaOH were added through a top port, and then CO₂ gas fed into the inner glass tube. Water was placed in the outer tube, and a thermometer was placed in the tube to measure the temperature increase. This heat value was compared to the heat generated within the chamber containing initial reactants.

The fourth experimental method involved measuring samples of initial reactants, and products during CO₂ introduction. These methods were X Ray Diffraction, Raman Spectroscopy, Mass Spectroscopy, and Photo Spectrophotometry. Samples were prepared for each method using the respective spectrometer sample preparation protocols. In addition, a smaller experiment to determine the source of O₂ (H₂O, H₃PO₄W₁₂O₃₆ or CO₂), were completed using doped H₂O, and CO₂ doped with ¹⁸O before reaction with H₃PO₄W₁₂O₃₆.

This experiment was repeated for both H₃PO₄W₁₂O₃₆ degeneration and WO regeneration. Thus, a capacitor containing H₃PO₄W₁₂O₃₆ and NaOH, and one containing tungsten residue were

used as the dielectric. The capacitor containing $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and NaOH were introduced to CO_2 . The final products were compared to the initial reactants using X Ray Diffraction, Raman Spectroscopy, and Photo Spectroscopy. Another experiment whose dielectric material was WO_3 , NaOH, H_3PO_4 , and HCl mixed prior to application were also evaluated using these spectroscopic techniques.

1.6 Experimental Methods

Mass Spectroscopy

Mass Spectroscopy could be described as an analytical technique where molecules could be separated according to their ratio of charge to mass by the interaction with an energy source and a magnet. The energy source splits the large molecules into desired species and the magnet separates the different molecules according to mass and charge. The chemicals must be isolated within a special compartment in order to apply the energy for ionization.

The samples in this investigation were Na_2WO_4 , with and without $^{18}\text{O}_2$, $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, with and without $^{18}\text{O}_2$, and WO_3 , with and without $^{18}\text{O}_2$. These were diluted to a concentration that would not contaminate the column of the instrument while measuring the concentration of ^{18}O above background in each sample. Samples were mixed thoroughly for 2 hours in order to ensure uniform exchange between $^{18}\text{O}_2$ in H_2O and in each species.

Raman Spectroscopy

Raman spectroscopy could be used in chemistry to identify molecules and study chemical bonding. Because energy frequencies are specific to a type of bond, the structure and species of a chemical could be characterized.

The Raman effect could be explained as an interaction between the electrons in the orbital shells and the external electrical field produced by incident energy. This change in energy changes the chemical dipole moment during the excitation, and then relaxes when the excitation discontinues. Scans of Na_2WO_4 , with and without $^{18}\text{O}_2$, $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ were taken by sampling the dielectric material before and after the flow of CO_2 was initiated. Samples were taken using a small syringe (1 mm diameter) and inserting it into the dielectric material.

Photo Spectroscopy

Photo- Spectroscopy could be described as the measurement of the amount of reflection or transmission of energy as it passes through a material. For example, reactions can occur in the forward and reverse direction have various species in various concentrations can be shown through a clear glass container that houses the sample. Certain wavelengths of light could be adsorbed and others transmitted, based on Beer's Law. The amount of light that was transmitted indicates the concentration of a particular chemical species. Samples of material for analysis were taken using a 1 mm syringe and scraping the dielectric before and after CO_2 was allowed to flow into the chamber.

X Ray Diffraction Spectroscopy

X-ray diffractometers operate by heating a wire filament, producing electrons, which could be then directed using electromagnets toward a target sample. Electrons that have sufficient energy to dislodge an electron of the target material. A target material such as Copper, that produces x rays of a specific energy when they are exposed to high energy electrons are used in this technique. Once these x rays interrogate the sample and create a pattern of exposure, they were

collected using an X ray detector. The intensity and energy of these X-rays are analyzed and displayed as spectral lines.

Samples of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and Na_2WO_4 were dried in an oven to 100 C and placed in desiccators for future analysis. The samples were in a dried powder form and were placed on the instrument sample containers with no special preparation.

Heat Capacity

To find the heat energy change (enthalpy per mole) of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and Na_2WO_4 in a reaction between two substances A and B, the substances are added to a calorimeter and temperature before, during and after the reaction were recorded using a thermometer.

In this particular experiment, the temperature of the container was taken with a Soil Survey Instruments Thermometer, before, during, and after the CO_2 was fed into the container. The temperature data was compared to other data such as concentration of O_2 , and dielectric constant of the material as a function of experiment time.

Dielectric Constant

During this experiment, two 14 gage wire leads were connected to a Texas Instrument Voltmeter, and one to each end of the aluminum wafers confining the dielectric. This dielectric was the CO_2 adsorbing- O_2 releasing material. The dielectric constant was calculated by measuring the voltage at subsequent times (one hour) during the introduction of CO_2 into the system. These data were compared to temperature data, and O_2 concentration data, so that thermodynamic data can be correlated with electrical property data.

1.7 Modeling Experiments

For this approach, several thermodynamic parameters are needed in order to predict or quantify the types of reactants, products and their rates of formation/decomposition. This particular approach is a mathematical model or approximation, and should be used when no experimental data can be obtained.

In this particular exercise, various reactants were selected and products predicted as candidate dielectric materials. Thermodynamic data for each scenario were recorded for comparison. In particular, parameters of interest were the temperature during the experiment, the Gibbs Free Energy, and Enthalpy of the system. These pieces of information provide clues for predicting the likelihood of the reaction, or whether the reaction could be possible at all.

1.8 Comparison with Existing Data

It is also useful to compare the modeled predictions and experimentally measured parameters to data that has been previously obtained by other researchers. Again, these parameters include the temperature, entropy, enthalpy and free energy of the system. In addition, other values such as reaction rates, pH, solubility, and activation energy (the energy needed to overcome electrostatic forces between two species) could be used to identify possible reactions between reactants, and probable reaction products.

2. OBJECTIVES

2.1 Summary

The primary objective of this investigation is to investigate and implement a chemical process that adsorbs CO₂ and releases O₂. Several experimental and modeling efforts were undertaken in order to test and validate the hypothesized system. One test, a mass balance test, describes the release of concentrated CO₂ from a known volumetric source and its adsorption on a dielectric material placed between two conductive plates. The second mass balance test describes the release of O₂ from H₃PO₄W₁₂O₃₆ within dielectric. This dielectric consists of a Si(OC₂H₅)₄ and H₃PO₄W₁₂O₃₆ powder homogeneously dispersed throughout the mixture. A third test describes the regeneration of the decomposed dielectric H₃PO₄W₁₂O₃₆ material through a sequence of chemical reactions. A fourth test outlines the procedure for computing the dielectric constant of the dielectric, and a fifth experiment outlines a method to calculate the temperature change of the dielectric during the decomposition of the dielectric material.

Other experimental procedures described in this investigation pertain to characterization of the species produced by the decomposition and recombination reactions within the dielectric. These instrumental techniques include Mass Balance Testing, X Ray Diffraction Spectroscopy, Mass Spectroscopy, Raman Spectroscopy, and Photo Spectroscopy. In addition, experiments were completed which outline the chemical pathway for dielectric regeneration to H₃PO₄W₁₂O₃₆ from WO₃, and a special experiment demonstrating how to use ¹⁸O₂ to determine the origin of outgassed O₂. Specifically, the experiment design illustrated whether O₂ within the DTPA (H₃PO₄W₁₂O₃₆) came from H₂O within the crystal, or from CO₂.

2.2 Technical Objectives

The primary objective of this investigation was to validate the proposed CO₂ adsorption – O₂ generation design satisfies the requirements for a self-enclosed life support system. These requirements were specified by sources from NASA and Lockheed Martin Space Systems Inc (NASA, LMCO Telecommunication, 2016). Carbon dioxide gas was allowed to pass through the dielectric of the filter material to determine CO₂ absorptivity. Guidelines were established outlining how to measure the CO₂ adsorbed by the system. Another mass balance experiment was conducted which outlines how to measure the amount of O₂ produced from dielectric decomposition (H₃PO₄W₁₂O₃₆ break up). The amount of gas in each container, as well as the dielectric constant was measured before and after the experiment. The difference between the amount of CO₂ gas released and the amount of O₂ collected in a collection bottle should be approximately equal to the amount of carbon accumulated in the dielectric material. The amount of CO₂ adsorbed and O₂ produced shall be comparable to the requirements outlined for space missions. (Lockheed Marin Telecommunication, 2016).

A third objective shall outline procedures to measure the temperature change by the decomposition reaction of H₃PO₄W₁₂O₃₆. The filter chamber was placed within another Styrofoam container filled with water, and lined with polyethylene to prevent seepage. A thermometer was placed into the water periodically (1 hour) during the decomposition process.

A fourth objective shall outline procedures for measuring the dielectric constant of the dielectric. During periodic releases of CO₂ into the filter container, the voltage would also be measured hourly.

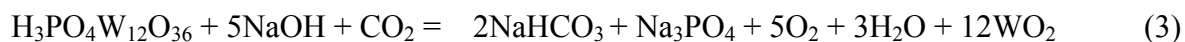
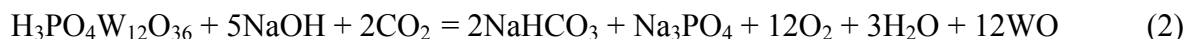
2.3 Degeneration and Regeneration Chemistry

The reactions involved in this system are pH reactions. Initially, reactions involving a change in pH occur where CO₂ interacts with a large molecule, DTPA, which breaks down to WO, WO₂, WO₃ and H₃PO₄. Once these species migrate within the dielectric, they begin to move toward a specific pole. At this point, REDOX reactions begin to occur where the tungsten (W) reduces from WO, WO₂ and WO₃. The charge released by these ions collects on the charged capacitor plates.

Initially, HCl and NaOH were introduced into the system as products from other processes in other systems. For example, NaOH could be produced from electrolysis of NaCl and H₂O. Hydrochloric acid could be produced from the chlorination of water. Once these reactants were produced, the reactions described in the following sections could be completed in order to remove CO₂, produce O₂, and regenerate H₃PO₄W₁₂O₃₆.

2.3.1 OXYGEN PRODUCTION

There are many reactions that produce O₂. The most well known of these reaction are those of potassium or sodium permanganate and heated H₂O. These reactions were well documented in reports by (Yu et. al., 2012, Wachsman, 2003, 2007, Chang et. al., 2010 and Lide, 1995). The reaction proposed in this investigation could be illustrated below:



2.3.2 REGENERATION PROCESS

The regeneration of $\text{H}_3\text{PO}_4\text{WO}_{36}$ can be expressed as



This research develops an integrated CO_2 removal and O_2 production system using dodeca-tungsto-phosphoric acid ($\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$; DTPA) and tetra-ethyl-ortho silicate-polycarbonate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS) filler material. Mixing these two compounds provides packed oxygen atoms in a dodecahedral arrangement and functions as a dielectric.

3. LITERATURE REVIEW

3.1 Summary

The relevant literature describes methods of CO₂ removal and O₂ generation. The super oxide DTPA, or its hydrate, H₃PO₄W₁₂O₃₆*59H₂O presents a better material for O₂ production and CO₂ removal than current CO₂ removal techniques such as LiOH.

Historically, LiOH was the material of choice for CO₂ removal in space vehicles and submarine (NRL, 1993). This material, though very effective, has toxic effects when becoming airborne by surface particle convection (NRL, 1993). In addition, in order to produce O₂, another system was needed, involving the breakdown of another valuable resource: water (Breaux et. al., 1978). In an attempt to replace LiOH a substitute material was developed: amines (Breaux et. al., 1978). In addition a CO₂ removal system and an O₂ production system were needed in current space applications (NRL, 1993).

A particularly promising material is H₃PO₄W₁₂O₃₆ (DTPA). The unique chemistry of this material discovered in the literature (Keggan, 1937), Nakamura et.al., (1979), Akimoto et. al., (1985), Subramanian et.al., (2007), characterizes the nature of the conductive properties of H₃PO₄W₁₂O₃₆. Other characterizations of the material demonstrate a high O₂ content and mechanisms for oxygen release within the crystal (Lee and Chen, 2005). The high conductivity and oxygen content of this material make it ideal for an oxygen supply. Added benefits of material are its exothermic release of heat upon introduction to water, or NaOH. A very important property of the H₃PO₄W₁₂O₃₆ crystal resides in its ability to retain water (Estrada et al. (2003). In addition, the crystal has the ability to transfer O₂ from the interior to the exterior of the crystal in the form of hydroxyl ions (Lee and Chen, 2005). Oxygen can be harvested from

$\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ using electrostatic separation (Lee and Chen, 2005) followed by a depressurization of the dielectric.

Two innovative functions discovered in this investigation were that O_2 could be harvested from CO_2 through the following steps. First, add it to water to form H_2CO_3 . The bicarbonate (H_2CO_3) then becomes trapped within the $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ - $\text{Si}(\text{OC}_2\text{H}_5)_4$ complex, and the O_2 can be liberated from the crystal using a small amount of heat, followed by a decompression of the material within a chamber. The carbon from CO_2 incorporates within a carbonate ion.

3.2 Previous Studies

Previous patent work developed by Karavolos et al. (1999, 2000, 2000) discussed the mathematical basis for characterizing gas dissolved in aqueous gelatin media. This work serves as the framework with which to start a model for a new material that adsorbs CO_2 and produces O_2 . Other investigators made similar contributions such as Quin et al. (2000), Qui and Hu (2013), Sakar (1979, 1995), Estrada et al. (2003), Pourjavadi et al. (2006), Karewicz et al. (2010), Qi, et. al., (1985), Malek et. al., (1997), Kondo and Gray, (1991), Kruielen et al. (1993), Khan et al. (2010), and Shariff et al. (2007). These investigators developed protocols and hardware that remove CO_2 from media, or produce O_2 from various oxide species.

Investigators such as Li and Chen (2005), Yang and Cussler (1986), Malek et al. (1997), and Kruielen et al. (1993) have provided particularly useful information concerning the fluid dynamics describing the O_2 and H_2O within the crystal. These papers provided valuable insight for deciding what experimental parameters such as equilibrium constants of species such as WO , WO_2 , $\text{PO}_4\text{W}_{12}\text{O}_{36}$. Based upon these papers, the important parameters are the

system temperature, system pH, and the heat required to release CO₂ gas dissolved in solution. Several research efforts have addressed this question (Weiss, 1974, Bando et.al., 2003).

Quinn et al. (2000), Qui and Hu (2013), Khan et al. (2010), and Kondo and Gray (1991) outlined experimental techniques that identify cellulose compounds that have suitable properties for use as gelatins. These gelatins could be used to emulsify CO₂ capturing agents such as amines. Shariff et al. (2007), Karewicz et al. (2010), and Pourjavadi et al. (2006) developed novel concepts for encapsulating material in polymeric substrates. These efforts support the supposition made in this investigation that gelatins could be used to emulsify CO₂ capturing agents such as O₂ rich super oxides. Kruehlen et al. (1993) and Malek et al. (1997) developed useful models for describing gas transfer within materials. The work is similar to models developed to describe how N₂ moves from the dissolved phase to the gas phase in various media. This work supports the supposition made in this investigation that dissolved gases could be removed from media using a drop in external pressure.

3.3 Current Commercial Techniques for Oxygen Production

There are three basic methods used for producing O₂. One method involves the use of energy from a laser or electrical current (energy ablation) to split a singlet oxygen or O₂ from carbon. This requires a considerable amount of energy, over 1000 kJ/mole. Oxygen could be harvested by separating oxides from oxide minerals such as Na₂O₂, K₂O and others. Electrical current can remove O₂ from these minerals and they could be dissolved in an aqueous solution. This process requires less energy than energy ablation, but requires voltages between 3-12 volts. Other methods utilize catalyst molecules that lower the activation energy of a chemical complex, and it is this approach that was used in this investigation.

Investigators such as Perry et al. (2006), Ward et al. (1993), and Ryder et al. (1998) have
desi air.

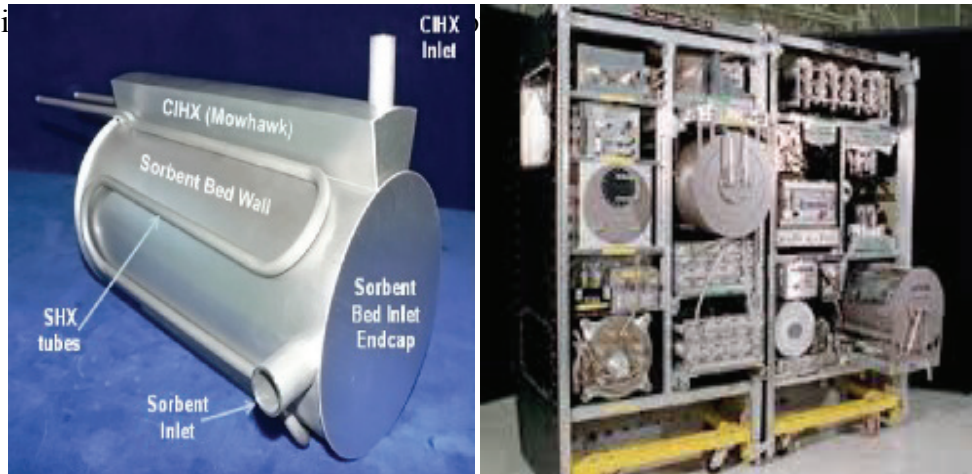


Figure 6: (Right) The ECLSS CO₂ removal system, used by NASA on the space station (Perry et al., 2004). (Left) The CO₂ removal system developed by Paragon Space Corporation (Paragon Space Systems, 2010).

The ECLSS life support system on the right, developed by Perry et. al., (2004), was demonstrated within the decade. In this system, CO₂ was recovered on the left and O₂ was produced on the right side of the system.

Paragon Space Corporation, Inc. has proposed using an approach where one surface was heated to drive off CO₂ while another captures CO₂ (Paragon Space Corporation Report, 2016). Their unit draws the air from one bed to another. The process repeats itself with alternating collection surfaces (one collects while one heats) so that total removal time is increased.

The systems developed by Paragon Space Corporation describe methods for CO₂ removal. The methods are not able to be regenerate O₂. They also require separate systems for O₂ production (Paragon Space Corporation Report, 2016).

In the case of the amine materials, some amine byproducts such as $\text{RNH}_3^+\text{RNHCO}_2$ are produced which require detoxification treatments (DaSilva and Svendsen, 2010). Mechanical approaches consume about 1-2 W/hr to operate (DaSilva and Svendsen, 2010).



Both of the products, R-NH_3^+ (aliphatic ammonium) and CNH-R-CO_2^- (ammonium carbamate) are toxic according to their respective material data safety sheets. Qi and Cussler, 1985). Figure 2 below illustrates the effectiveness of amines in CO_2 removal. These compounds are ammonia and nitrogen amine groups that have a high affinity towards CO_2 . The symbol R represents a cyclic benzene molecule. However, these compounds are toxic to human health, and thus a disadvantage in using this approach to removing CO_2 from an air supply. The use of this approach shall require safety systems to ensure that these toxic groups would not be introduced into the air supply.

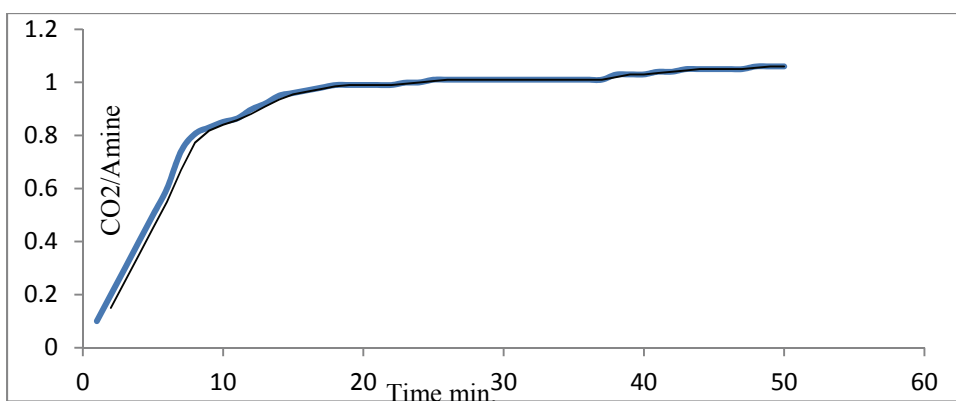


Figure 7: Illustration of the mole weight of CO_2 removed per mole weight of amine, as a function of time. Notice that the amount of CO_2 removed remains stable after a small amount of time. From Dibenedetto et al., 2002.

3.4 The Case for Use of WO_3 for O_2 Release

Tungsten crystals offer four distinct advantages over conventional LiOH , Amine, and K_2O techniques. First, the crystals have unique water adsorption properties. Secondly, they are effective in adsorbing water that has been saturated with CO_2 . In addition, the same H_2O absorbing mechanism can be modified to an HCO_3^- or H_2CO_3 mechanism. Thirdly, this same mechanism also initiates a process where O_2 can be expelled from the crystal, and the O_2 within the crystal and this O_2 can be regenerated using water. Finally, the tungsten crystal can generate both heat exothermically, and electrical charge.

Lithium hydroxide can only provide CO_2 adsorption, and because of its low valence cannot provide significant electrical charge. It can produce heat exothermically, but this heat output cannot be sustained, because the LiOH process for removal of CO_2 cannot be sustained.

Amines provide CO_2 adsorption and some residual heat output, but like LiOH , cannot generate O_2 within the same process, and the reaction does not proceed in a manner that can be sustainable.

Potassium super oxide (K_2O) holds more promise since it can adsorb CO_2 and produce O_2 , but due to its low valence cannot produce significant quantities of charge, and also does not output a significant amount of heat.

3.5 Example of an Integrated System Design

The lessons learned from previous investigations were applied to the research design of this investigation. First, the most efficient environmental habitats are those that are sustainable (Kibert, 2005). This means that the products produced by one system could be used as reactants in another system, ideally a closed system. Second, materials with high surface area are best suited for maximum adsorption of CO₂ (Bennett, 1989). Most importantly, materials such as zeolites and gels appear to be well suited for clatheritically trapping super oxide, water. Such a chemical environment would allow gases such as CO₂ and O₂ to move in and out of the substrate.

This investigation expands upon the concepts developed from a previous patent submission, (Karavolos, Patent Application US 5855570A, 2014, 2015) by integrating CO₂ adsorption mechanisms with O₂ releasing mechanisms. The selected metal oxide H₃PO₄W₁₂O₃₆ were integrated using first principles of capacitor physics Halliday and Resnik, (1978) and barrofluid mechanics (Halliday and Resnik, 1978). Such a device can provide CO₂ elimination, O₂ production, heat production, and voltage generation.

The relation describes the total flow between each chamber:

$$Q=VA, \tag{8}$$

Where Q represents the volume of gas moving per unit time, V is the velocity of the gas, and A is the cross sectional area of the chamber (Bennett, 1989).

Solid oxide electrolysis cell works on the principle that, using elevated temperatures, ceramic oxides, become O₂ conductors. A solid electrolyte cab be sandwiched between two porous electrodes. For oxygen generation from carbon dioxide, CO₂ diffuses through the porous electrode ([cathode](#)) and reaches the vicinity of the electrode-electrolyte boundary. Through a

combination of thermal dissociation and electro catalysis, oxygen atom can be liberated from the CO_2 molecule. The net reaction is shown below:

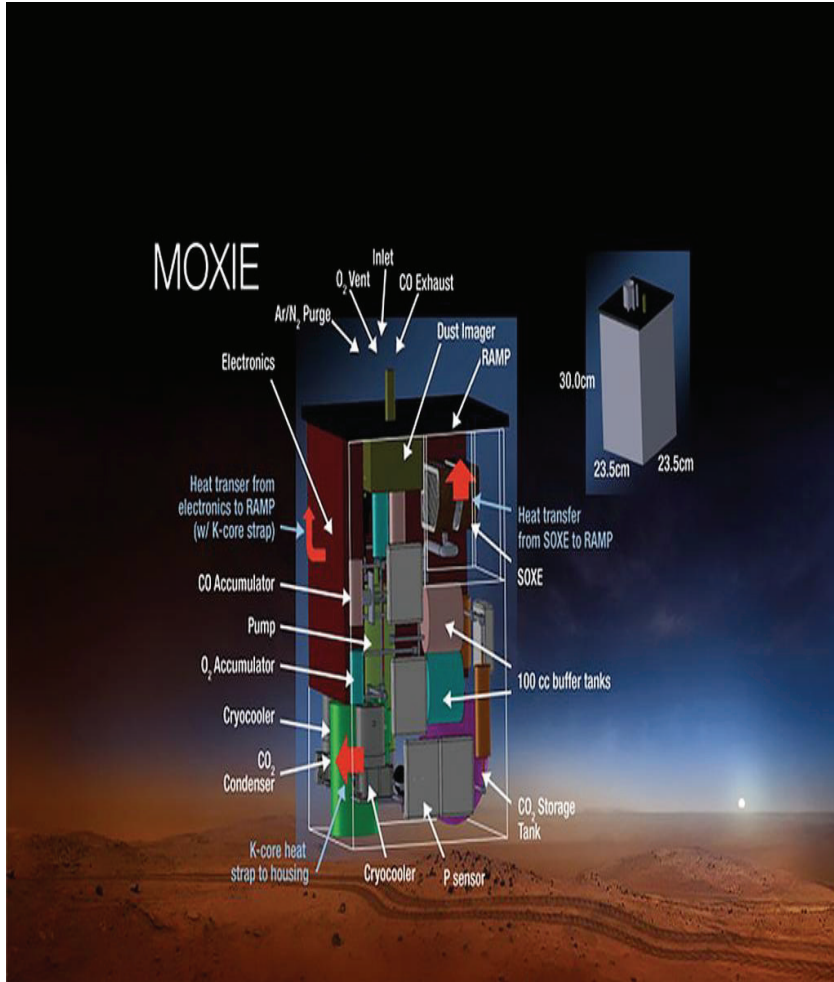


Figure 8: Illustration of MOXIE Carbon Dioxide- Oxygen Production system. (with permission from authors)

The present system has dimensions of approximately 22 cm. by 10 cm, by 3 cm. Three kg of material, and a 0.5 kg cartridge, can produce 560 grams of O_2 per day, and remove 1760 grams of CO_2 per day. It does not require an external power source because the driving energy was an

exothermic reaction. In fact, it can produce heat and electrical voltage- approximately 844 kJ/day, and about 6.2 volts for 2 hours.

The difference between the two technologies can be seen as that the current proposed system contains a silicon sol gel, which can produce H_2 during certain reaction conditions. Another advantage of using a sol gel, can be seen in that H_2O and other liquids can be introduced into the system for easier control of reaction parameters. In addition, the MOXIE system produces CO , which can be toxic for human physiology, and not a very suitable propellant, such as H_2 . Finally, the MOXIE system uses electrodes to drive the reaction, and in the present embodiment, charge (voltage) can be produced.

Using these ideas, a portable, self-contained device can be designed for CO_2 removal and O_2 production (US 5855570A). This work was completed as a design requirement of the current chamber design.

4. RESEARCH DESIGN

4.1 Summary

There are specific purposes for each experiment of the system. The container was constructed to be approximately 600 cubic cm, so that it could process 880 grams of CO₂, and produce 640 grams of O₂.per day per person. Secondly, the unit contains sufficient space for filters, which can absorb approximately at least 880 grams of CO₂. This is the amount of CO₂ exhaled by one person per day. (Mcardle et. al., 1991). Third, the unit contains ports for inserting electrical leads, so that the charge collected on the plates of the filter could be measured by a voltmeter. An optional component of the system entails a water-filled Styrofoam box so that heat produced by the exothermic reactions can be transferred to the water.

The filter itself consists of three components. The top and bottom layer consists of either a layer of conductive polyaniline or thin metal grid so that charge can collect on the top and bottom surface of the capacitor. The dielectric material itself was a H₃PO₄W₁₂O₃₆-Si₂H₁₂O₄ mixture. The H₃PO₄W₁₂O₃₆ within the dielectric can break down to WO, WO₂ and WO₃ upon introduction of CO₂ and NaOH.

In addition, the WO, WO₂ or WO₃ could be regenerated to H₃PO₄W₁₂O₃₆ by introduction of Na₂WO₄, H₃PO₄ and HCl using classic chemical techniques (Keggin,1937). This section discusses the reasoning and strategy behind the individual experimental procedures. The strategies were structured to accommodate the systems requirements of the customers who will eventually use this system for space exploration, navy operational vehicles, army operational vehicles, and the mining industry. These system requirements could be summarized as follows:

1. The material must be able to function within an ECLSS system (NASA Countermeasures Office, telecommunication, 2014).
2. The system must produce at least 640 grams of O₂ per day per person (NASA Countermeasures Office, telecommunication, 2014).
3. The system must remove approximately 1760 grams of CO₂ per day per person (NASA Countermeasures Office, telecommunication, 2014).
4. The system optionally can provide heat for other systems.
5. The system optionally can provide electrical current for other systems.

In order to validate the requirements of the system five experiments were implemented to show that:

1. Carbon dioxide (CO₂) could be removed from the air supply.
2. Oxygen (O₂) could be introduced into the air supply.

Another requirement shall be that the O₂ should be furnished from within H₃PO₄W₁₂O₃₆. A tracer gas containing (¹⁸O₂) could identify the origin of O₂ by using GC mass spectrometry and Raman spectroscopy. A final requirement shall be that the material should be capable of breaking down and release O₂ upon adsorption of CO₂. It should be able to regenerate itself using water and carbonates.

4.2 Theoretical Considerations

A desirable capability for CO₂ removing- O₂ producing material could be a high surface charge capacity. This would provide a large charge to the device.

In the arrangement of Figure 9, CO₂ interacts with H₃PO₄W₁₂O₃₆ -Si₂H₁₂O₄ dielectric sandwiched between two permeable, electrically charged surfaces (b). A reaction occurs within

the plates (b) that allows the O_2 in the dielectric to escape. In Figure 9, the reaction proceeds, and species such as PO_4 , and WO_3 begin to appear as the $H_3PO_4W_{12}O_{36}$ begins to break apart as the pH increases. The reverse process begins where the reaction proceeds from WO_3 to $H_3PO_4W_{12}O_{36}$ as it begins to react with $NaOH$, Na_2WO_4 , HCl and H_3PO_4 .

The molecule illustrated in Figure 5 was modeled using the Spartan and Ceres II molecular modeling software packages. Using the software, it was predicted that $Si_2H_{12}O_4$ and $H_3PO_4W_{12}O_{36}$ lay in close proximity to each other so that columbic forces draw them close to each other.

The dielectric material produced for the device consists of a porous paste. Once CO_2 was allowed to permeate the material, the pH begins to increase from acidic to basic, and $H_3PO_4W_{12}O_{36}$ begins to break apart into small WO_2 and WO_3 molecules, along with H_3PO_4 , and H_3PO_4 molecules and ions. Once the smaller molecules such as WO , WO_2 , PO_4 , Na , and OH appear, they are able to pass through the interstitial spacing between the $Si_2H_{12}O_4$ molecules, toward the positive and negative charged plates of the capacitor. Neutral species simply remain within the crystal (Figure 5).

A final theoretical consideration involved identification of O_2 source. An isotope could be used which contains more neutron or proton in each of its atoms. Because $^{18}O_2$ has more mass than $^{16}O_2$, it follows a different pathway when traveling in a Mass Spectrometer. In this way, the molecule to which it was attached, or separated from, could be differentiated from other species. In addition to the information provided by isotopic analysis, thermodynamic information can also be obtained by measuring temperature changes in the reactions. The thermodynamic information can provide insight as to what reactions are favorable under standard temperature and pressure, and those that were not favored.

4.3 Experimental Design Considerations

One experiment was conducted so that the source of O_2 could be identified from either CO_2 , H_2O , or $H_3PO_4W_{12}O_{36}$. Distilled water was mixed with $^{18}O_2$. Next, CO_2 was fed into the chamber. In a control experiment, CO_2 which was not mixed with $^{18}O_2$ was fed into the chamber. Evaluation by photo spectroscopy, X Ray Diffraction and Mass Spectroscopy would then reveal the presence of $^{18}O_2$ by measuring its background presence quantity in the O_2 gas chamber and SiO_2 filter material.

As background information, human breath contains 2-3% less O_2 after exhalation. The system therefore only needs to replace that 2-3 % (Tortora and Anagnostakos, 1987). For example, a crew of seven people consumes 3,920 grams of O_2 per day (Patton and Thibodeau (2009).

For a crew to maintain health and fitness, the air must be replenished with approximately 650 grams of O_2 per day. At the same time, six people produce 10,780 grams per day of CO_2 , and this gas must also be removed. Crewmembers need O_2 at the rate of 23.3 grams per hour, and this rate is too high for biological process with limited surface area or time, as is the case for spacecraft, military aircraft and other confined spaces.

Therefore, two tasks must be completed: the design of the material, and the implementation of the material within the system. A material must be selected that can either produce O_2 during a physical or chemical process, or contain O_2 so that it can be released by a physical or chemical process.

First, a capacitor could supply energy through dissociation of molecules and generating charge by collection of ions to each side of the capacitor. Secondly, the dielectric within the

capacitor could be modified for suitable use as a CO₂ absorber, and this adsorption process could be used to release O₂ from an O₂ rich metal oxide.

Other oxides such as K₂O, and Na₂O₂ could be used, but they do not have the O₂ rich nature of H₃PO₄W₁₂O₃₆, and the material would have to be recycled numerous times in order to produce the desired amount of O₂ (560 grams), because only 32 grams of O₂ are available per mole per unit recycle time (Unpublished data, Series II modeling results, 2017).

In summary, a material and process could be developed where H₃PO₄W₁₂O₃₆ was used as a dielectric, suitably modified in order to provide O₂ and remove CO₂. Since the H₃PO₄W₁₂O₃₆ decomposition entails an exothermic reaction, so heat was produced. Since the chemical breakdown of species produces ions, and ions have charge, current was generated.

4.4 Example System Process

Below is a systematic illustration of the gas exchange process:

1. Carbon Dioxide (CO₂) entered a chamber constructed as shown in Figure 6.
The gas combines with the H⁺ ion, creating HCO₃⁻. A pH of 2.0 was used to start the reaction, based on previous literature (Keggan, 1937).
2. The pH of the system began to increase as NaOH was adsorbed, and H₃PO₄W₁₂O₃₆, composed of H₃PO₄ and W₁₂O₃₆ separated to H⁺, PO₄⁻³, and WO₃. The Tungsten molecule formed (W₁₂O₃₆) was unstable, and various species of tungsten oxide formed.

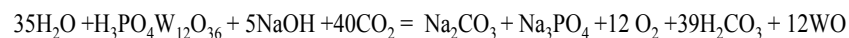
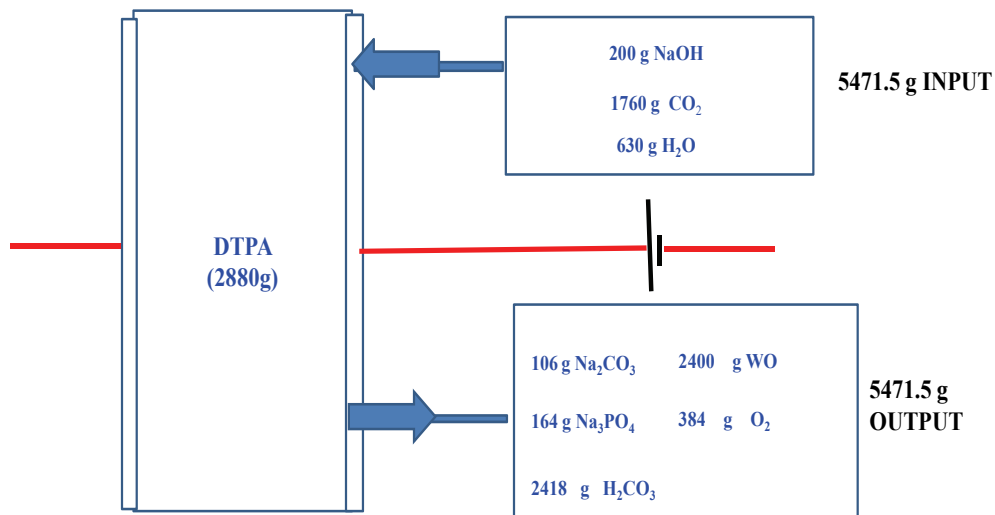
When applying a bias voltage (0.5-1.0 V) the plates, the W begins to move toward the negative cathode.

Table 1: Various species of decomposing $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ at different pH of the disassociation process.

| pH | Ionic Species |
|-----|---|
| 1.1 | $\text{PO}_4\text{WO}_{36}$ |
| 2.2 | $\text{PO}_4\text{W}_{12}\text{O}_{36}$ |
| 3.5 | $\text{PO}_4\text{W}_{12}\text{O}_{36}$, WO_3 |
| 5.4 | $\text{PO}_4\text{W}_9\text{O}_{34}$, O_2 , WO_2 |
| 8.3 | PO_4WO_3 , WO |

This particular table illustrates the pH of solution needed in order to attain some of the precursor ions needed for DTPA decomposition to WO_3 , WO_2 and WO .

DE GENERATION



RE GENERATION

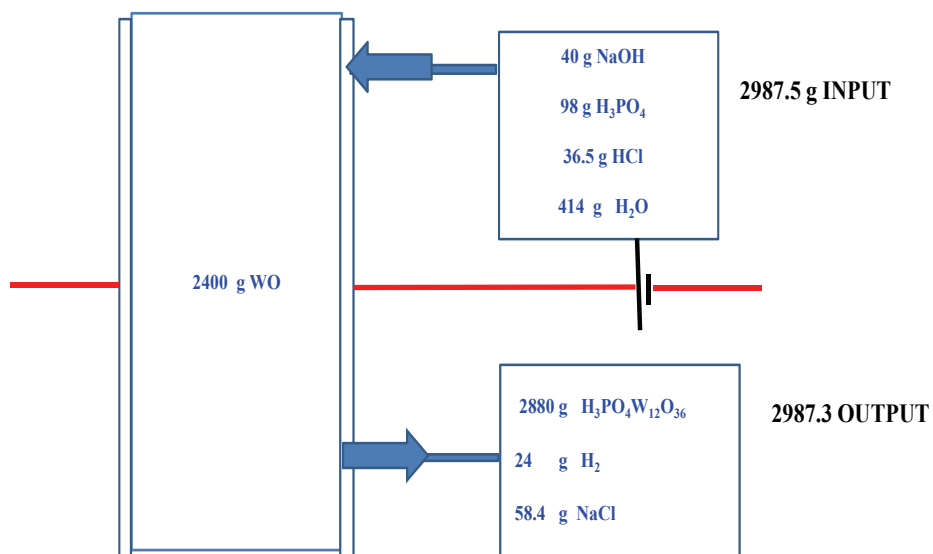


Figure 9: Illustration of the O₂-CO₂ gas exchange system in terms of mass balance. Each species produces a product and all reactants were accounted for in the closed system.

5. METHODOLOGY

5.1 Summary

A test chamber was constructed to test the functionality of DTPA material. It consisted of three components (See Figure 2). The first part allowed CO₂ gas to flow from the container to the capacitor chamber. The second part allowed CO₂ to flow into the dielectric material. The pH of the mixture increased as the reaction continued, and WO₃ forms. After depressurization O₂, the gas flowed to a gas collection chamber.

The following experiments were done chronologically in order to satisfy design requirements reported by discussions with Lockheed Martin (Lockheed Martin, telecommunication 2016). Specifically, the following experiments were completed in order to validate (or invalidate) the proposed mechanism by which H₃PO₄W₁₂O₃₆ degenerates to WO, and regenerates back to H₃PO₄W₁₂O₃₆.

1. Sodium hydroxide and H₃PO₄W₁₂O₃₆ in solution produce Na₃PO₄, WO and water.

A sample of reactants and products were taken using a manual 10 ml pipette.

2. Samples were placed on a glass slide and air-dried at room temperature and standard pressure for 24 hours.
3. Samples were evaluated using X Ray Diffraction analysis for identification of products based on crystalline structure.
4. Samples were evaluated for molecular signature using spectro-photometry analysis.

5. Samples were evaluated using $^{18}\text{O}_2$ doped CO_2 and H_2O , to determine the source of O_2 in solution.
6. The next experiment involved a reaction between WO_3 , obtained from the $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ decomposition experiment (1), and mixed with dissolved CO_2 to produce reactants Na_2WO_4 . These samples were also sampled using a 10 pipette.
7. Samples were placed on a glass slide and dried at room temperature and standard pressure for 24 hours.
8. Samples were evaluated for structure identification using X Ray Diffraction analysis, Mass Spectroscopy, Raman Spectroscopy and Photo Spectroscopy.
9. Samples were evaluated for molecular signature based on spectral signatures.
10. At this point in the reaction, a voltmeter indicated a voltage of 0.22 volts (baseline) to 6.2 volts over a period of 16 minutes.
11. The chamber reactants began to separate according to charge.
12. Oxygen gas began to dissolve into solution.
13. A small piece of sensitive litmus paper for O_2 , was taped to the entry port of the O_2 collection chamber to detect the presence of gas.
14. Spent WO_3 was harvested from the residue of experiment (2), and placed in a 50 ml Erlenmeyer flask.
15. The sample was then titrated with H_3PO_4 and then HCl according to techniques outlined by Zhu et. al, (2003), Gouzerh and Che (2006).
16. A small aliquot of the resultant precipitate and solution was placed on a glass slide and dried to remove water at room temperature and standard pressure.

In summary, the first experiment tests the idea that dodeca tungsto phosphoric acid could be decomposed through interaction with NaOH. The second experiment illustrated that spent WO could be used to regenerate DTPA.

5.2 General Assumptions

Experiments were completed which release measured amounts of CO₂ gas to the filter material, and measured using a Pinpoint II O₂ concentration meter. Oxygen gas concentration moving into the capture container was measured after each hour CO₂ was allowed to move through the dielectric material.

An assumption was made that reactions taking place within the chamber were occurring in a homogeneous mixture, throughout time in a curvilinear manner, slowing down after availability of react ants began to diminish. The second assumption was that all of the CO₂ shall be consumed in the process, and all of the O₂ contained in the super oxide moves into solution upon decompression, The length of time (30 seconds) that the samples were mixed was assumed to provide <99% uniformity of mixing during the preparation of the H₃PO₄W₁₂O₃₆ (DTPA) and the Si₂H₁₂O₄ (TEOS). Thus, if the CO₂ absorbing material was uniformly distributed throughout the dielectric, CO₂ introduced into the dielectric would also be uniformly distributed.

A test chamber was constructed to test the behavior of the material. It consisted of three containers. Carbon dioxide gas flows from the container to the capacitor (second) chamber. In this container, CO₂ flowed and the pH of the mixture reduced by the addition of NaOH. At that time the chamber depressurizes to 0.5 atmosphere. Oxygen gas then outgased into

the third and final chamber. Other depressurization experiments were done for 0.75 atm. and 0.92 atm.

A second effort reduced the pressure below the partial pressure of O_2 , so that the gas moved into the solution as gas bubbles. Another effort tested the hypothesis that WO_3 could be recycled back to $H_3PO_4W_{12}O_{36}$ using water combined with Na_2WO_4 . This mixture was titrated with H_3PO_4 , to generate $Na_3PO_4W_{12}O_{36}$, followed by HCl to produce $H_3PO_4W_{12}O_{36}$. A test chamber was constructed to test the ability of the super oxide material to regenerate itself. It consisted of three components. The first part allowed CO_2 gas to flow from the container to the capacitor chamber. The second part allowed CO_2 to flow into the dielectric material. The pH of the mixture increased as the reaction continues, and tungsten oxide formed. After depressurization to the vapor pressure of O_2 , the gas flowed to a gas collection chamber.

5.3 Experimental Procedure: Collection of Samples

Samples taken for evaluation of CO_2 , O_2 concentration, pH temperature (ΔH), voltage and capacitance were made on an hourly basis under a set flow rates of CO_2 into the capacitor chamber. The values of each of these dependent variables are a function of time and cross sectional area.

5.4 Experimental Procedure: Preparation of Controls

Experimental controls were completed as described below.

Control 1 The first control that was prepared was a mixture of dodeca tungsto phosphoric acid and H_2CO_3 .

Control 2 The second control that was prepared was a mixture of $H_3PO_4W_{12}O_{36}$ and $Si_2H_{12}O_4$.

Control 3 The third control that was prepared was H_2CO_3 .

Control 4 The fourth control prepared was $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$.

Control 5, These controls were composed of $\text{Si}_2\text{H}_{12}\text{O}_4$.

Each of the controls were checked for O_2 . The purpose was to ensure that the sources of O_2 were not from the raw materials themselves. A small amount of $^{18}\text{O}_2$ (0.1 microliter) was introduced into each of the controls so that a background trace of the source of O_2 could be ascertained. Background O_2 levels were measured with a dissolved O_2 meter, and CO_2 were measured with a CO_2 gas meter. The $^{18}\text{O}_2$ were evaluated using mass spectroscopy techniques.

5.5 Experimental Procedure: Preparation $\text{Si}(\text{OC}_2\text{H}_5)_4$

The purpose of this experimental procedure was to prepare the inert material serving to surround the tungsten crystal with a protective hydrated layer of water. It was also to serve as adsorbent for H_2 release during the decomposition process. The gelatin material was inert and did not take part in the decomposition or recombination process itself. It also provided a degree of temperature insulation from the surrounding environment.

The matrix material tetra ethyl ortho silicate was prepared by the standard method listed below:

1. Two grams of NH_4F were added to 100 ml of distilled water.
2. Five grams of $\text{Si}_2\text{H}_{12}\text{O}_4$ and 10.0 g ethanol were mixed in a 250 ml beaker.
3. Ten grams of water and 15.0 g ethanol were mixed in another 100 ml beaker.
4. Pour the catalyst solution into the solution and stir at 200 rpm for 30 seconds.

5. A small amount of polycarbonate polymer was then added to the mixture for decreasing the viscosity material.
 6. The material was placed in a desired mold (10 cm by 10 cm by 2 mm), and stored in a desiccator at room temperature and 1 atmosphere of pressure.
 7. A solution was prepared as a 5% solution of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and distilled water, and then mixed to 15% tetra ethyl ortho silicate, in a 200-ml beaker. The speed of the mixing was set at 200 rpm for 30 seconds, in 10-second intervals, to avoid over heating the specimen.
 8. This resulting mixture above was allowed to set for 1 hour at room temperature, and kept in a desiccator to eliminate water adsorption. This solution was also mixed at 200 rpm for 30 seconds, allowing for 10 second intermissions in order to dissipate heat released during the mixing process.
- 1 In another variation, the tungsto phosphoric acid $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$) was mixed with $\text{Si}_2\text{H}_{12}\text{O}_4$ (TEOS). The operating temperature for the polymerization is 155 C, well below the melting temperature of dodeca tungsto phosphoric acid.
 - 2 A solution was prepared as a 5% solution of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and distilled water, and then mixed to 15% tetra ethyl ortho silicate, in a 200-ml beaker. The speed of the mixing was set at 200 rpm for 30 seconds, in 10-second intervals, to avoid over heating the specimen.
 - 3 This resulting mixture above was allowed to set for 1 hour at room temperature, and kept in a desiccator to eliminate water adsorption. This solution was also mixed at 200 rpm for 30 seconds, allowing for 10 second intermissions in order to dissipate

heat released during the mixing process.

5.6 Experimental Procedure: Preparation of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$

The purpose of this experiment was to verify that the chemistry used to generate $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ from WO crystals was possible. In this particular experiment, the reactants were not tested while in the chamber, but separately under laboratory conditions. This aspect of the test would eliminate possible variations due to unknown (or known) variables such as temperature, sample in homogeneity, and variations in air moisture.

For the deposition of thin films of phosphoric tungstic acid [$\text{H}_3(\text{PW}_{12}\text{O}_{40})$], 2% solution of sodium tungstate in distilled water was made in 200 ml glass beaker. The speed of the mixture rotation was kept 200 rpm for 30 seconds, with 10-second cooling intervals. After half hour, the precipitate was introduced to H_3PO_4 , as white colored precipitate formed at the bottom of the beaker [$\text{Na}_3(\text{PW}_{12}\text{O}_{40})$]. The next step was to introduce the precipitate to HCl so that the resulting precipitate results in $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$.

5.7 Experiment 1: Measurement of pH

The purpose of this experiment was to identify the change in pH of the system, because this parameter was important for predicting the different species of tungsten produced in the dielectric. The pH of the system varied between 2.0 and 9.0. During the experiment, pH values began at approximately 2.0 while the material was acidic, and rose to about 8.0 when sufficient CO_2 (as H_2CO_3) was added to become basic.

The pH of the system was measured using a Pinpoint II pH meter. The pH of the dielectric was experimentally measured at one-hour intervals during the introduction of CO₂ in the dielectric material. A pH meter probe was inserted within 1-3 mm of the dielectric.

During the experiment, a total of 24 measurements of pH were taken. The gas CO₂ was introduced into the system so that the number of anions and cations increase or decrease. This change was reflected as the negative of the log of the hydrogen ion concentration.



Figure 10: The instrument used to evaluate the pH within the dielectric material.

5.8 Experiment 2: Measurement of Dielectric Constant

The purpose of this experiment was to identify the amount of current that was produced during the break down of the super oxide to WO and other components. In addition, measurement of the dielectric during the introduction of CO₂ and also regeneration of the WO to DTPA were also obtained in order to further understand the temporal nature of the super oxide breakdown and formation. One critical question to be answered was whether the breakdown and or reformation

proceeded in a linear, curvilinear, or logarithmic pace. The answer to this question would provide insight as to the longevity of the system, and its potential use as an energy source.

The capacitance and voltage of the capacitor chamber was measured by connecting the top and bottom of the capacitor (which were each aluminum wafers) to the respective leads of a digital multimeter (voltmeter). The value of capacitance and voltage of the capacitor chamber was measured as a function of time, in this particular case, one hour, since the pH of the system was measured on an hourly basis. Since CO₂ was continuously introduced into the system, the number of anions and cations increased or decreased, thus changing the totals charge on each conductive film. Since the charge changed, so do the voltage and capacitance of the system.

The procedure for measuring the dielectric constant of the material involved these steps.

1. The first is connecting the top and bottom aluminum film of the device to the positive and negative terminals of a voltmeter.
2. The top aluminum film of the dielectric was assigned to the positive lead of the voltmeter and the negative lead was connected to a variable resistor. The assembly made was an RC circuit.
3. At periodic (1 hour) intervals, the voltmeter was checked after the setting on the voltmeter was re-zeroed.
4. The variable resistor was set to a bias 1000 milliohm for hours 1 to 5, and 10 milliohm for hours 6 to 12, and 24 total hours. Based upon previous test runs and the O₂-CO₂ curve, the volume of O₂ generated at the beginning of the reaction was larger, generating more current. So, a larger resistance was used in order to reduce the surge in current.

5. Figures 4 and 8 illustrate the device. The chamber was built not only as a depressurizeable chamber but a capacitor as well. This allows the unit to be capable of collecting and electrical charge on the aluminum wafers, as well as adsorbing CO₂ and releasing O₂. These charges accumulated when the introduction of CO₂ into the gelatin induced a break-up of the super oxide (H₃PO₄W₁₂O₃₆). Separated ions were H⁺, PO₄⁻³, HCO₃⁻, Na⁺, and Cl⁻. The actual charge collected upon the plates was measured using a standard voltmeter (Figure 2).
6. The capacitance of the unit was measured using a voltmeter. The capacitance can also be calculated using the relation

$$C = \epsilon k A/d, \quad (9)$$

where ϵ was the electrical permeability constant, k was the dielectric constant of the material, A was the cross sectional area of wafer and d was the distance between the wafers, or the thickness of the dielectric material (dodeca tungsto phosphoric acid-tetra ethyl ortho silicate. See Figure 11 below.

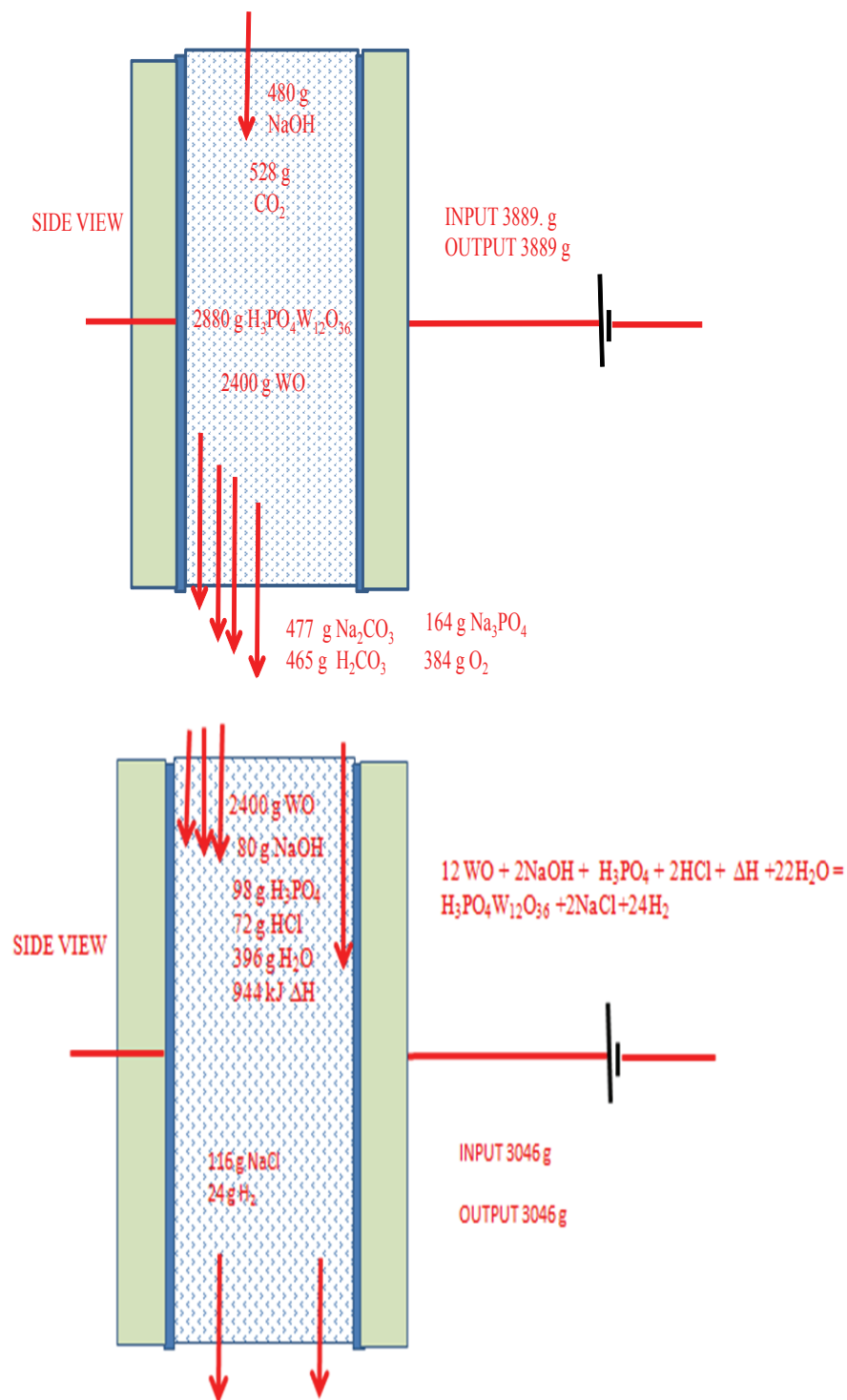


Figure 11: Schematic illustration of capacitor chamber for separation of ions. Dielectric constants were measured before and after introduction of CO₂, and during ion collection on each plate.

The arrows indicate the direction and quantity of ions, reactants and products that enter and leave the chamber. In addition, a global equation is was included to illustrate the general chemical processes, which occur within the chamber. Both degeneration of DTPA and regeneration of DTPA could be seen in the diagram (Figure 9).

5.9 Experiment 3: Measurement of Heat Capacity

The purpose of this experiment was to determine how much heat was produced during the breakdown of the dielectric material. In addition, measurement of the amount of heat needed for reformation of the crystal was also an important parameter. The results of this experiment would determine whether the system could function as a tri-use system- CO₂-O₂ gas exchange, electrical current, and heat exchanger. The dielectric constant varied between 1.98 to 10.55, but occasionally peaked between 92 to 101.0. It cannot be determined why the dielectric constant peaked intermittently throughout the experiment. It was assumed to be related to the formation of gas pockets within the dielectric.

The release of heat from the successive exothermic reactions benefits the system. There are two reactions that were exothermic in nature. The first is the breakdown of the superoxide DTPA into components H₃PO₄ and WO₃, which essentially was the breakdown of the dodecahedron complex. Theoretical calculations from reaction-modeled data suggest that approximately 844 kJ per mole material was released during the decomposition reaction.

An exothermic reaction involved the addition of NaOH with the H₃PO₄W₁₂O₃₆ (DTPA) to produce Na₂PO₄, Na₂WO₄, and H₂O. This reaction produces about 844 kJ/mole of heat, and

increase the temperature of 1 gram of material from 30 C to 80 C in approximately 10 minutes. The heat generated was measured by obtaining a small sample of dielectric and observing the temperature change of a small 1-gram sample. During the CO₂ adsorption process, the temperature within the device chamber was also measured by thermocouple attached to the conductive plates of the filter.

1. A Styrofoam container of suitable size (larger than the capacitor chamber, about 15 cm by 15 cm by 15 cm) was used to contain the capacitor chamber during the experiment. A thermocouple was used to measure the temperature at successive (hourly) intervals of the super oxide decomposition and regeneration experiment.
2. A Sigma Aldrich thermocouple was inserted into one of the portholes of the capacitor chamber and sealed using Teflon tape.
3. Measurements of temperature were taken before the CO₂ was introduced into the chamber, and at hourly intervals thereafter.
4. Temperatures of the reaction were calculated using the relation:

$$\Delta H = m_{cp} \Delta T \quad (10)$$

These experiments described the physical characteristics of the system. Further experimentation and spectroscopy methodologies can identify the chemical nature of the system.

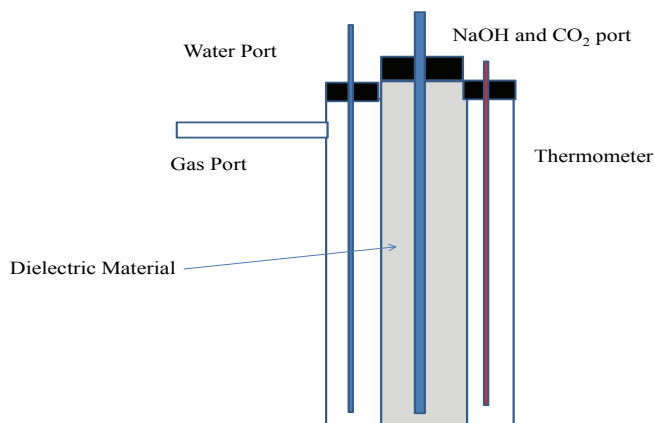


Figure 12: Illustration of Calorimetry set up to measure the temperature change during decomposition and recomposition of DTPA or WO.

The figure just above illustrates the experimental set up used to identify the heat output of the decomposition system. Theoretically, the same system could be used to identify the amount of heat needed for regeneration, but not presented herein.

5.10 Experiment 4: Measurement of O₂ Concentration

The concentration of O₂ in the system was measured using a Pinpoint II O₂ meter. The concentration of O₂ was measured by placing a probe immersed in water. The concentration of the gas was measured on an hourly basis, to coincide with the measurement of pH.

Measurements were completed on an hourly basis just before the addition of a small (50-100 ml) water to the filters. In order to correct for error created by drift, the meter was turned off and on before the measurement. The drift could be as much as 2-3 mg/ml.

For O₂ tracing experiments with ¹⁸O₂, distilled water with the isotope were added instead of distilled water. The same amount of water (50-100 ml) was added periodically at one hour intervals just before measurement.

5.11 Experiment 5: Measurement of CO₂ Concentration

The concentration of CO₂ in the system was measured using a Pinpoint II CO₂ meter connected to the CO₂ supply valve. Values were measured in increments of one hour, and recorded for statistical analysis. Measurements were completed on an hourly basis just after addition of a small (50-100 ml) water to the filters, as maintenance, to ensure integrity of the gelatinous state.

During each measurement, the Pinpoint II meter was zeroed so that drift from static charge could be eliminated. This was done by pressing the reset button of the device. The instrument provided consistent measurements during the experiment, having a repeatability rate of 7 out of 10 measurements.

For O₂ tracing experiments using gas with ¹⁸CO₂, a sample of the gas provided by Sigma Aldrich Chemical Company was connected by T valve to the experimental assembly. Approximately 1 ml per 100 ml of CO₂ gas from the non-tracer CO₂ source was added during a test run. It was assumed that natural ¹⁸CO₂ in the non-tracer CO₂ source was below the amount of ¹⁸CO₂ introduced.

5.12 Experiment 6: Decomposition of H₃PO₄W₁₂O₃₆

The objective of this experiment was to determine the characteristics and properties of the decomposition process of H₃PO₄W₁₂O₃₆, (DTPA). Four specific answers to the following questions were sought. One question was -what were the products from the decomposition

process. Another question was- how much CO_2 could be consumed in the process. A third question was- how much O_2 could be produced from the process. Finally, where does the O_2 come from- the crystal itself, or the CO_2 adsorbed by the dielectric.

The steps taken to decompose the super oxide, listed below:

1. A small amount of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, (DTPA) was placed in a 200 ml beaker.
2. To this powder, 100 gm of distilled water was added.
3. Approximately 50 ml, 100 ml, and 200 ml CO_2 , at a ratio of 3 moles of gas to 1 mole of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ was introduced to the powdered water. The same step was completed for $^{18}\text{CO}_2$ in a later experiment.
4. A sufficient amount of CO_2 was added to the solution to increase the pH from 2.0 to 8.0. Sampling was monitored using a pH meter.
5. The CO_2 entry port was closed and the exit port for O_2 was opened. Apply a small vacuum to the exit port to initiate O_2 flow to create 0.5, 0.75, and 0.92 atm. pressure. The collection chamber was modified and sealed using Teflon tape with the O_2 concentration probe inserted into the chamber.

For the illustration of the experimental set up, see Figures 4 and 8.

5.13 Experiment 7: Regeneration of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$

The question of whether the DTPA could be regenerated was explored. The molecule dodecatungsto phosphoric acid could be regenerated using a process proposed by Keggin (1937), but this process needs to be verified. In addition, the reactants and products of the system need to be identified and quantified in order to build a reactor chamber for space applications. These reactants are CO_2 , H_2O and $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$. The products are O_2 , Na_2CO_3 , Na_3PO_4 , H_2CO_3 and

WO. Carbon Dioxide serves to raise the pH to disassemble the DTPA, each of the carbonates serves to remove the carbon from the system, and the DTPA itself serves as the source of O₂.

The steps taken to regenerate the super oxide, listed below:

1. A small amount of WO₃ powder was added to a 200 ml beaker. This powder was mixed with 100 grams of distilled water.
2. A small amount (50 mg) of Na₃WO₃ was mixed with the WO₃ and H₂O mixture.
3. To this mixture, about 30 ml of H₃PO₄ was added, until Sodium Phospho-Tungstate- Na₃PO₄W₁₂O₃₆ precipitated.
- 4 The sample was then decanted, and added to a few drops of HCl so that (H₃PO₄W₁₂O₃₆) could precipitate.

5.14 Experiment 8: Tracking O₂

A desirable objective was to know what the source of O₂ was for the regenerated H₃PO₄W₁₂O₃₆. Using an isotope molecule such as ¹⁸O₂, the concentration of O₂ was measured before and after the processes of degeneration of H₃PO₄W₁₂O₃₆.

The amount of ¹⁸O₂ was determined using Mass Spectroscopy and Raman Spectroscopy, and comparing the spectral signatures to those reported in literature. (Filipescu et. al., 2012). The experimental set up used was the same for evaluation of CO₂ and O₂ gas adsorption and production.

Four samples were taken in order to evaluate the samples using Mass Spectroscopy, Photo Spectroscopy and Raman Spectroscopy. These were stored under the same conditions as samples without addition of ¹⁸O₂. See Figure 4 for an illustration of the experimental set up.

5.15 Experiment 9: X-Ray Diffraction

Figure 12 illustrates the instrument used to collect X Ray Diffraction data.

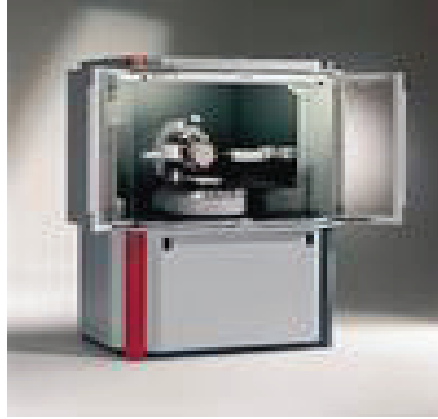


Figure 13: A Bruker X ray Diffraction Instrument.

The principle of operation of X Ray Diffraction could be summarized as a process where a sample interrogated with electrons generates secondary electrons. This tube contains a tungsten or metallic filament. The heated filament generates electrons that move through a collimator (a hole in a piece of metal) and strike the electrons of atoms in the sample. When the excited atom's electrons relax to a lower energy state, a characteristic energy was produced, captured and analyzed. This energy characterized the material.

Specifically, the sample was prepared by using a razor blade to orient the sample on a polyethylene wafer substrate.

1. The material was placed on a polyethylene wafer for X Ray Diffraction analysis.

The sample z elevation was corrected (using a screw) for the position needed to interrogate the sample.

2. The sample was placed on an X Ray Diffraction platform, the powder moved to the center of the platform using a razor blade. The sample z elevation was corrected (using a screw) for the position needed to interrogate the sample.

5.16 Experimental 10: Photospectrometer Measurements

A Bosh and Lomb photo spectrometer was used to collect information on the concentration of WO_3 , H_3PO_4 , $\text{W}_{12}\text{O}_{36}$, PO_4 and NaOH based on reflected light. A set of controls were necessary in order to identify the different peaks.



Figure 14: A Bosh and Lomb Portable Spectro Photometer Used to Identify W, P, Na and other Minerals in the Sample.

1. Standard aliquots of WO_3 , DTPA, H_3PO_4 , and NaOH were prepared to 0.1N concentrations of each reactant. If the absorbance was above the range reported for the spectra of the sample, the solution was diluted to bring the concentration to the range that the instrument was capable of measuring. A distilled water solution was used as a control. The faces of the sample containers were wiped with ethyl alcohol.

2. The instrument was turned on and placed in sample container. Standards were treated in the same manner. Place filter in slot for light path obstruction.
3. At intervals, the samples were rechecked remove drift from the system.

5.17 Experiment 11: Raman Spectroscopy Sample Preparation and Tests

This particular objective involves the thermodynamic characterization $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, CO_2 and H_2CO_3 . After a sequential amount of time (1 hour), a sample were obtained for Raman Spectroscopy evaluation. A set of controls (pure $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and H_2CO_3 solution) were also prepared as a 0.1 N solution. In addition, each sample was duplicated for tracer O^{18} analysis. This procedure provided spectral information of where the O_2 is coming from – the CO_2 or water.

The Raman measurements were acquired at ambient conditions with an *alpha 300 RAS* WITec confocal Raman system, using the 532 nm excitation of a Nd:YAG laser. An acquisition time of 10s for each spectrum and a 20X objective lens with a $\text{NA} = 0.40$ was used in all experiments.

During the third or fourth cycle a small amount of the dielectric material was harvested in order to evaluate it using Raman Spectroscopy. Approximately 5-10 grams were removed from the sample before, during and after the test. Multiple trial runs were completed for statistical consistency.



Figure 15: Illustration of a typical Raman Spectrometer.

The samples were placed in the spectrometer by first establishing a baseline. Next, the sample was placed in the sample holder. The sample was then interrogated using selected wavelengths based on previous literature (Filipescu et. al. 2012). Sample spectra were then acquired for analysis. Samples were evaluated courtesy of Manciu, (2017).

5.18 Experiment 12: Mass Spectroscopy Sample Preparation and Tests

This particular objective involves the thermodynamic characterization $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, CO_2 and H_2CO_3 . After a sequential amount of time (1 hour), a sample was obtained for Mass Spectroscopy evaluation. A set of controls (pure $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ and H_2CO_3 solution) were also prepared by dilution in 10 ml distilled water. Another sample was prepared using 1 ml distilled water with $^{18}\text{O}_2$ (0.1 N) solution.

During the third or fourth cycle a small amount of the dielectric material was harvested in order to evaluate it using Raman Spectroscopy. Approximately 5-10 grams were removed from the sample before, during and after the test. Multiple trial runs were completed for statistical consistency.



Figure 16: Illustration of Mass Spectrometer unit (Courtesy Triton Instruments).

The spectrometer prepared for $^{18}\text{O}_2$ and blank samples were tested to establish baseline levels of the isotope. A total of 6 samples with varying amounts of $^{18}\text{O}_2$ in H_2O were evaluated using the instrument. Samples of NaOH , Na_2WO_4 , $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, and WO were interrogated for analysis (Courtesy University of Texas Mass Spectroscopy Laboratory, 2017).

5.19 Experiment 13: Effectiveness of Pressure Drop to Remove Dissolved O_2 .

The objective of this experiment was to determine whether pressure reduction below the partial pressure of O_2 would be sufficient to release the gas from the dissolved state in solution. The reaction would be similar to the reaction between NaOH and its co – reactant NaMnO_4 . The partial pressure of O_2 at atmosphere depends was measured to be approximately 0.2 atmospheres.

Assuming that O_2 is removed from DTPA and O_2 is chemically exchanged into hydroxyl ions in solution, a reduction in pressure of the chamber below the partial pressure of O_2 should result in an outgas of O_2 from the system. The concentration of the gas, and the rate at which it

is released from solution, can be measured by using a CO₂ and O₂ concentration meter connected to the CO₂ outlet and O₂ inlet containers.

5.20 Experiment 14: Super Oxide Regeneration from Tungsten Products

The objective of this experiment was to identify the validity of using WO to produce H₃PO₄W₁₂O₃₆. In order to accomplish effort, other reactants were needed. These were H₃PO₄, HCl, and NaOH. Approximately 80 grams of NaOH were needed in order to form the precursor Na₂WO₄. This precursor was needed in order to form H₃PO₄W₁₂O₃₆.

It should be noted that the chemistry involving Na₂WO₄ was not fully understood, but since the process does work, and provides DTPA as a product without significant energy or material resources, the chemistry was selected for the system process.

The tungsten super oxide was regenerated from the addition of NaOH, made from hydrolysis of water, NaCl. In addition, Na₂WO₄ was made by adding NaOH to NaCl and PO₄WO₃ ions. This solution was then titrated using H₃PO₄ and HCl.

6. RESULTS AND DISCUSSION

6.1 Summary

The following data was collected in this investigation: The data was arranged in the order of chronological development during the investigation. The experiments were completed at least 3 times in order to achieve statistical repeatability to a confidence level of 0.92, and a variance of 1.2 %.

- 1 pH range for the DTPA decomposition process (Experiment 1).
- 2 Dielectric constant variation during the DTPA decomposition process (Experiment 2).
- 3 Specific Heat Capacity data for the DTPA decomposition process (Experiment 3).
- 4 Measurement of O₂ concentration during DTPA decomposition (Experiment 4).
- 5 Measurement of CO₂ concentration during DTPA decomposition (Experiment 5).
- 6 Experimental and modeled data for DTPA decomposition (Experiment 6).
- 7 Experimental and modeled data for DTPA recomposition (Experiment 7).
- 8 Experimental data for tracing source of O₂ during recomposition (Experiment 8).
- 9 Experimental data for X Ray Diffraction tests (Experiment 9).
- 10 Experimental data for Photo spectroscopic tests (Experiment 10).
- 11 Experimental data for Raman Spectroscopy tests (Experiment 11).
- 12 Experimental data for Mass Spectroscopy tests (Experiment 12).
- 13 Experimental data for pressure data- outgas dissolved O₂ (Experiment 13).
- 14 Experimental data for DTPA (H₃PO₄W₁₂O₃₆) recycling from WO (Experiment 14).

Each of these experiments were completed for both degeneration of DTPA and regeneration of DTPA from WO. All experiments were conducted under standard temperature and pressure, except for the O₂ outgas experiment (Experiment 14). A summary of the properties of the reactants and state properties such as temperature, and dielectric constant can be seen in Table 2. Comparisons were made between experimentally obtained values and modeled values. Values from literature were also presented where available.

Table 2: This table of data was obtained from mass balance experiment. Data were compared to predictions using modeling Series II Molecular Modeling, and data from previous investigations.

| Parameter | Experimental | Modeling | Literature |
|---|--------------|----------|------------|
| Dielectric Constant H ₃ PO ₄ W ₁₂ O ₃₆ | 13.34 | 11.53 | 12.5 |
| Temperature Increase | 5 C | 7.2 C | N/A |
| Reactant NaOH gm | 250 gm | 312 gm | N/A |
| Reactant CO ₂ gm | 1760 gm | 1769 gm | N/A |
| Products Na ₂ CO ₃ gm | 470.32 gm | 477.0 gm | N/A |
| Products O ₂ gm | 576 gm | 642 gm | N/A |

6.2 pH Data (Experiment 1)

The data shows that higher pH values of the dielectric material, increase the volumetric amount of O_2 produced, and also increase the amount of CO_2 removed from the air. The increase of temperature also appears to have the same effect on CO_2 adsorption and O_2 generation.

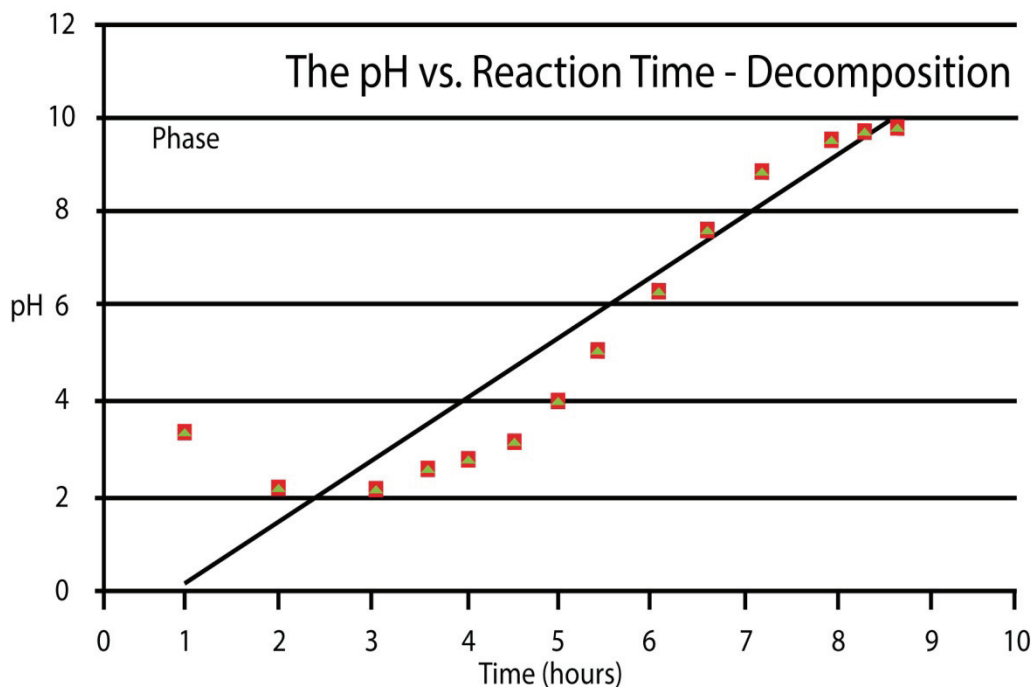


Figure 17: Relationship between pH and time for the decomposition phase of the system

6.3 Dielectric Constant Data (Experiment 2)

The dielectric constant data were obtained by obtaining samples from the filter material and placing them on a small capacitor (aluminum plate) arrangement. The voltages obtained during CO_2 adsorption were compared to the dielectric constant and voltage data obtained for CO_2 introduction. Data presented in the table below were also compared to modeled predictions.

Table 3 Summary of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ properties using Ceres II modeling compared to accepted values calculated by experimentation.

| Property | Ceres II | Experimental |
|---------------------|------------|--------------|
| Electronegativity | 2.43 | 2.46 |
| Crystal Structure | Body Cubic | Body Cubic |
| Dielectric Constant | 10.75 | 9.78 |

The data listed in Table 3 illustrates the basic information produced from a preliminary modeling effort using Ceres II Chemical Modeling software. Other properties were determined such as bond length, reaction kinetics and possible species produced, based on Gaussian statistics. However, the important parameters for this study were listed in the table above.

Tungsten oxide could be quantified and identified using the chamber as a capacitor. The charge that was generated, was directly proportional to the concentration of each species- WO_3 , WO_2 , W_2O_6 , and W_4O_6 . The species WO_2 , W_2O_6 , and W_4O_6 were intermediate species, and do not exist in solution long. (< 1 nanosecond), because modeling data suggests that the species were unstable thermodynamically. The two diagrams below illustrate a shift in the position of WO_3 depending on whether CO_2 was introduced into the system or not. Both the position and the magnitude of the peaks were changed between the control and the sample. An interesting plot showing the sample regenerated (WO_3) to $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ resembles the original control. The question remains as to where the source of O_2 is from- the water, the CO_2 , or both.

6.4 O₂ Gas Production Data (Experiment 3)

The rate of production for O₂ was slightly smaller than that of CO₂ adsorption into the dielectric material. The cause for this particular system characteristic could be attributed to higher activation energies needed in order to release the O₂.

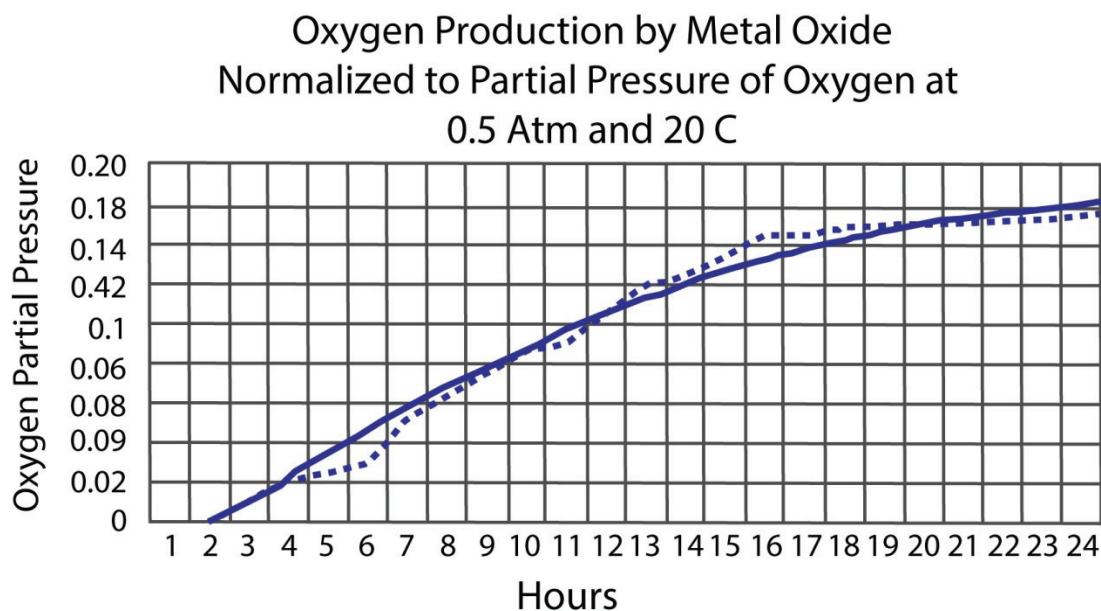


Figure 18: The rate of O₂ production as a function of the partial pressure applied to the dielectric chamber.

Figure 17 illustrates the rate at which O₂ becomes available upon decomposition of H₃PO₄W₁₂O₃₆. Based on the curve, O₂ becomes available immediately, rising linearly with time for 10-12 hours, and then levels off for the remaining 24 hours.

The data listed in Table 3 illustrates the basic information produced from a preliminary modeling effort using Ceres II Chemical Modeling software. Other properties can be determined from modeling using the software, such as bond length, reaction kinetics and possible species produced, based on Gaussian statistics. However, the important parameters for this study were listed in the table above.

Tungsten oxide was quantified and identified using the chamber as a capacitor. The charge that was generated, appeared to be directly proportional to the concentration of each species- WO_3 , WO_2 , W_2O_6 , and W_4O_6 . The species WO_2 , W_2O_6 , and W_4O_6 were intermediate species, and do not exist in solution long. (< 1 nanosecond), because modeling data suggests that the species were unstable thermodynamically.

6.5 CO_2 Gas Consumption Data (Experiment 3)

Tables 4 and 5 below show how much CO_2 was consumed during Tests 1 and 2, during which O_2 was generated by the filters within the chamber. The CO_2 adsorption rate was compared to the weight increase by the filter material, and the concentration increase in the O_2 collection flask. Each measurement was repeated 2-3 times to maintain confidence in statistical repeatability. In this particular set of tests, statistical repeatability were set at 0.9 confidence level and a Range Difference of 3% between measurements.

Table 4: Sample data from Tests 1 and 2 illustrate the concentration increase in O₂, the increase of mass in the filter, and the amount of CO₂ released into the chamber.

| Test/Parameter | O ₂ (mg/l) measured | Filter Mass (mg) | CO ₂ released into chamber (mg/l) | Range |
|-----------------|-----------------------------------|------------------|---|-------|
| Test 1 (1 hour) | 2.42 | 0.303 | 2.645 | 0.078 |
| Test 2 (1 hour) | 2.53 | 0.154 | 2.657 | 0.027 |

6.6 DTPA Decomposition Experiment (Experiment 6)

Table 5: Sample data from Tests 1 and 2 illustrate a comparison between the amounts of WO that can be harvested from decomposition from DTPA.

| Test/Parameter | DTPA (mg) | WO (mg) | Amount NaOH added (mg) | Range |
|-----------------|-----------|---------|------------------------------|-------|
| Test 1 (1 hour) | 6.95 | 7.04 | 8.45 | 0.09 |
| Test 2 (1 hour) | 6.81 | 7.034 | 8.79 | 0.224 |

The amount of WO produced from the decomposition reaction appeared to be 6.95 mg per hour, but the rate decreased after 12 hours of reaction time. The Range Difference was slightly higher at 0.224. More tests should be completed in order to reduce the Range Difference, and increase the confidence level.

6.7 DTPA Re composition Experiment (Experiment 7)

Table 6: Sample data from tests 1 and 2 illustrate the amount of DTPA that can be harvested from WO. The WO was the same sample that was harvested from the DTPA decomposition experiment illustrated in Table 5.

| Test/Parameter | WO (mg) | DTPA (mg) | Amount Na ₂ WO ₄ added (mg) | Range |
|-----------------|---------|-----------|---|-------|
| Test 1 (1 hour) | 7.00 | 5.94 | 4.55 | 1.06 |
| Test 2 (1 hour) | 7.00 | 6.22 | 4.57 | 0.78 |

In this particular experiment the Range Difference between samples were smaller. More tests should be completed in order to increase the confidence level of the tests.

6.8 Trace O₂ Test (Experiment 8)

Table 7: Illustration of presence of ¹⁸O₂ isotope in DTPA during decomposition to WO, and recomposition of WO to DTPA.

| Test/Parameter | ¹⁸ CO ₂ (mg) | ¹⁸ H ₂ O (mg) | Amount NaOH (mg) | Amount in DTPA (mg) | Amount in WO (mg) | Range |
|----------------------------------|---------------------------------------|--|------------------------|---------------------------|-------------------------|-------|
| Test 1 (1 hour) Decomposition | 10 | 10 | 5 | 0.91 | 0.83 | 0.08 |
| Test 2 (1 hour) Recomposition | 10 | 10 | 5 | 0.443 | 1.02 | 0.577 |
| Test 1 (1 hour) Decomposition | 5 | 5 | 5 | 0.915 | 0.844 | 0.071 |
| Test 2 (1 hour) Recomposition | 5 | 5 | 5 | 0.445 | 1.00 | 0.555 |

The small values give rise to large percentage differences. The variance difference presents the difference between the highest and lowest values. The amount values were calculated from the Raman and XRD spectra obtained in subsequent tests.

6.9 XRD Data (Experiment 9)

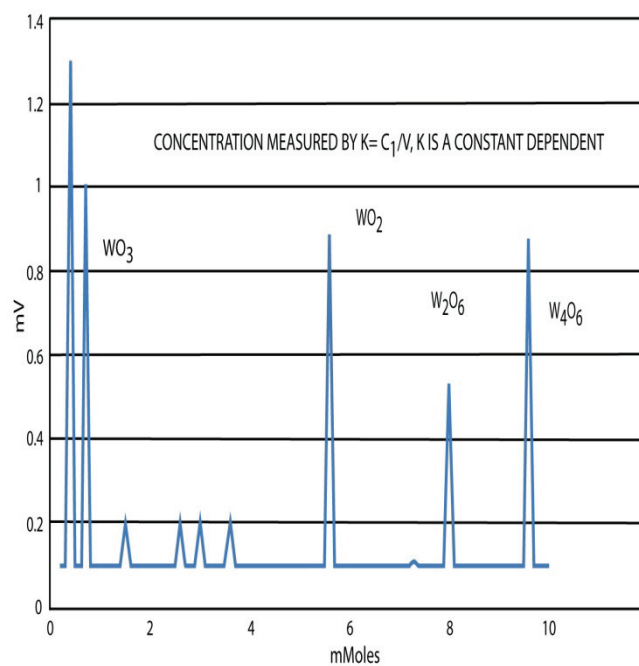
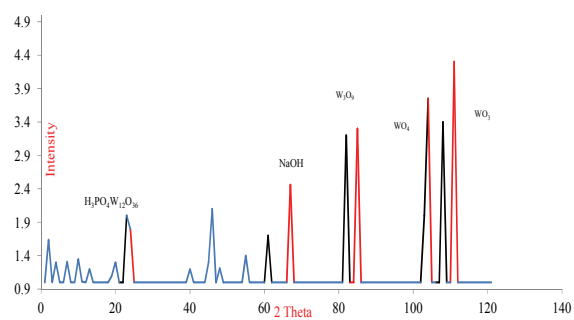
Below is a summary of data collected using X Ray Diffraction Spectroscopy. Tables 8a and 8b illustrate the comparison between the H₃PO₄W₁₂O₃₆ that was decomposed for O₂ production. The peaks centering about 22 theta, 32 theta, are the most prominent peaks. These peaks correspond well to the peaks from the virgin sample of H₃PO₄W₁₂O₃₆. Thus, the method used to reconstruct DTPA appeared effective in regenerating the material once it is spent.

Table 8a&b: X Ray Diffraction data for various species of Tungsten. These samples were evaluated before interaction between NaOH, CO₂, and H₃PO₄W₁₂O₃₆. They are the controls.

| Species | Intensity (mV) | 2θ |
|-------------------------------|----------------|--------|
| WO | 1.92 | 20.35 |
| WO ₂ | 0.95 | 45.50 |
| WO ₃ | 1.50 | 68.05 |
| W ₂ O ₆ | 0.83 | 109.95 |

| Species/Time (hour) | H ₃ PO ₄ W ₁₂ O ₃₆ | NaOH (2θ) | WO (2θ) |
|---------------------|--|-----------|---------|
| 0 | 13.43 | 2.96 | 211.96 |
| 5 | 954.23 | 64.24 | 88.30 |
| 12 | 1177.92 | 92.99 | 25.80 |
| 24 | 2243.78 | 111.67 | 10.02 |

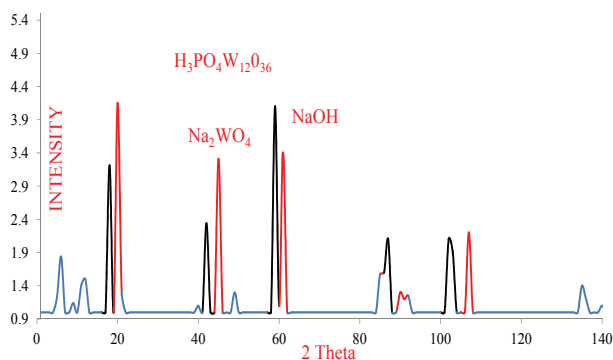
Table 8 above shows 2 theta estimations of species DTPA, WO, and NaOH during recomposition and decomposition processes for selected times during the process. These data were estimated by from X Ray Diffraction spectra peaks.



| Species | Intensity (mV) | 2 Theta Position |
|-------------------------------|----------------|------------------|
| WO | 2.10 | 23.35 |
| WO ₂ | 2.21 | 47.15 |
| WO ₃ | 3.32 | 69.25 |
| W ₂ O ₆ | 4.32 | 111.03 |

Figure 19: Diagram Illustrating the Positions and Concentrations of WO_3 after Introduction to CO_2 .

The species of tungsten, WO_2 , W_2O_6 and W_2O_6 appeared in the sample after introduction to CO_2 . After introduction to CO_2 , these species begin to disappear. Each species has a distinct 2θ position as well.



| frequencies | Intensity (mV) | 2θ |
|------------------------|----------------|-----------|
| WO | 4.50 | 19.98 |
| WO_2 | 5.36 | 43.94 |
| WO_3 | 7.01 | 66.03 |
| W_2O_6 | 8.32 | 107.65 |

Figure 20: Regenerated sample of WO_3 , Spent DTPA After Introduction to CO_2 .

In Figure 20 there were peaks that appeared to have shifted to the right in the spectra. These peaks were the tungsten oxide species and the NaOH. Changes the pH, began to change DTPA to WO and other tungsten species. In addition, the phosphate species began to dissipate on the left.

The first stage in the process consisted of the introduction of CO₂ into an aqueous solution of dodeca tungsto phosphoric acid. The pH of the system at this stage ranged between 1.4 and 2.3. The amount of heat generated at this stage was reported as 134.53 joules, and a voltage produced of 1.54 volts. During the following 1.5 hours, the pH increased from 2.3 to 10.9.

Heat was released during decomposition, and the heat calculated from the temperature increase, initial mass and cp measured was 846 joules. The voltage increases from 1.54 volts to 2.33 volts in the same time span. Approximately 70 % of the total O₂ released by the reaction occurred within the first 1.5 hours, with the remaining 30% released during the remaining 22.5 hours

6.10 Photo Spectroscopy Data (Experiment 10)

Table 9: Illustration of presence of WO and DTPA during decomposition (test1) and recomposition (test 2) using photo spectrometry. Spectral ranges used were between 400 nm and 900 nm).

| Test | WO mg | DTPA mg | Range |
|------------------------|-------|---------|-------|
| Test 1(decomposition) | 5.88 | 6.30 | 0.57 |
| Test 2 (recomposition) | 6.45 | 6.53 | 0.08 |

The Range Difference of each test was acceptably small, and an 8.8 % difference between the decomposition and recomposition value. Thus, 8.8 % in WO of the sample material remains missing. For DTPA, the percent missing material was calculated at 3.3%. More sample tests would reduce the error in statistical sampling.

6.11 Raman Spectroscopy Data

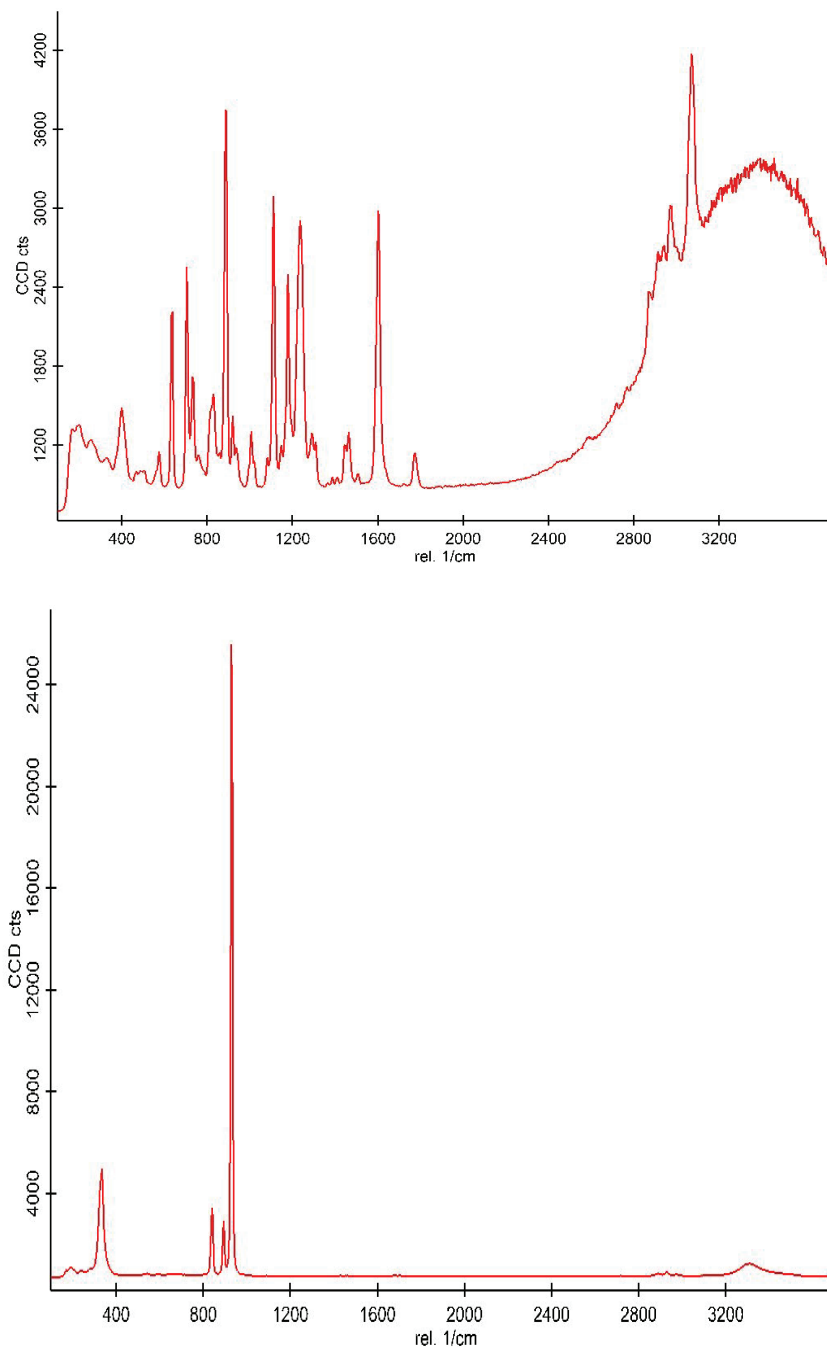


Figure 21: Raman Spectroscopy of species Na_2WO_4 , WO_3 , and $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$.

The peaks illustrated in Figure 21 represent the species WO_3 , Na_2WO_4 , and $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$. These spectra were obtained for samples which were not introduced to $^{18}\text{O}_2$ in H_2O . A comparison to

the spectra of from the sample introduced to $^{18}\text{O}_2$ in H_2O , indicated a shift in the positions of $^{18}\text{O}_2$ to non- $^{18}\text{O}_2$ samples to the right, for about 2-4 $1/\text{cm}$ units. A possible cause for this shift could be the addition of the $^{18}\text{O}_2$ to the sample within the crystal.

6.12 Mass Spectroscopy Data

Table 10: Illustration of Mass Spectroscopy for various species with and without the molecule $^{18}\text{O}_2$

| Species | m/Z without $^{18}\text{O}_2$ | m/Z with $^{18}\text{O}_2$ |
|--------------------------|-------------------------------|----------------------------|
| CO_2 | 0.022 | 0.0225 |
| Na_2WO_4 | 0.049 | 0.053 |
| H_2O | 0.009 | 0.011 |
| WO_2 | 0.036 | 0.039 |
| WO | 0.0333 | 0.0335 |

Table 10 illustrates mass spectrograph data of a sample of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ crystal decomposed to WO , and WO_2 . The trend illustrated in the table suggests that $^{18}\text{O}_2$ present in the H_2O was transferred to the NaOH , Na_2WO_4 , and Na_2CO_3 , since the ratio increased for these species. In addition, since the $^{18}\text{O}_2$ was originally in enriched water, that the O_2 in the was transferred from the water within the crystal.

Based upon the difference of values in the table, $^{18}\text{O}_2$ from CO_2 were transferred to WO_3 and $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ crystals, but the amount was less than 1% by weight. This suggests that O_2 transfer from CO_2 is possible.

Oxygen isotope ratios were measured from 50% by volume water samples. Water from the

isotopically doped samples were diluted with an equal proportion of natural abundance water. 1ml of diluted water sample was pipetted into 12ml glass vials and were purged with a 3000 ppm mixture of CO₂ in helium. Samples were prepared at 40°C for 12 hours. Oxygen 18 values were measured using CO₂ equilibration with a Thermo Scientific Gas Bench II and a Thermo Scientific MAT253 isotope ratio mass spectrometer (IRMS). Measured ¹⁸O values of CO₂ gas from IAEA-SMOW, IAEA-GISP and calibrated to generate a ¹⁸O calibration curve.

6.13 Pressure Drop Data (Experiment 13)

Table 11: Illustration of pressure drop and amount of O₂ harvested

| DECOMPOSITION REACTON | Pressure Drop | O ₂ Concentration |
|-----------------------|---------------|------------------------------|
| Test 1 (10 hours) | 0.5 atm | 589 grams |
| Test 2 (10 hours) | 0.92 atm | 458 grams |

6.14 Experimental Recycling from Spent WO (Experiment 14)

Table 12: Thermodynamic properties of selected species during reformation of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ from WO. The quantities of each species were calculated from calculated values of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$, O_2 , and CO_2

| Reaction | $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ | NaOH | WO |
|----------|---|--------|--------|
| Species | mg/ml | mg/ml | mg/ml |
| Initial. | 2880.00 | 98.34 | 205.11 |
| 1 hour | 1103.53 | 88.23 | 153.95 |
| 5 hour | 534.34 | 105.32 | 175.43 |
| 10 hour | 201.34 | 115.34 | 179.53 |
| 15 hour | 0.002 | 203.32 | 184.54 |

An important feature illustrated in Table 14 is that spent WO can be used to re-build a DTPA molecule. Experimentation completed in previous experiments (Experiment 7 illustrated that chemically, WO can be used to construct DTPA, but experiment 14 illustrates that used WO can be used as well.

7. CONCLUSTIONS

7.1 Summary

The chemical procedure developed by Karavolos (Patent Application # 62191167 2015) appears to be effective in breaking down $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ acid to WO and other products. Further investigation using Spectrophotometric, Raman Spectroscopy, and Mass Spectroscopy further validate the process by verifying the presence of specific intermediate species in samples.

Data collected with this device illustrated a significant improvement in CO_2 collection efficiency and O_2 release rate. Using the bench top test, 2-3 percent of CO_2 was not captured. Oxygen release increased by as much as 90 %, owing to the increased surface area.

The system can be regenerated as well (Tables 14,15). In addition, the method design was such that the O_2 released comes from the H_2O within the DTPA crystal. This entails a significant innovation t that was currently not available with current technology, unless a significant amount of energy was consumed.

Another key design feature in this process involved the use of products from other system sources to produce consumable products, limiting the use of fresh water needed for human consumption. Na_3PO_4 and NaOH were used to produce Na_2WO_4 , which in turn was used in conjunction with H_3PO_4 and HCl to produce $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$. The first stage in the process consists of the introduction of CO_2 into a gelatinous colloid of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$. The amount of heat generated at this stage was measured at 834.53 joules, and an average voltage of 1.54 volts was produced.

In experiment 1, during the initial 1.5 hours, the pH increased from 2.3 to 10.9. An average of 834 joules was produced during the DTPA decomposition over a 24 hour period. Approximately 70 % of the total O₂ released by the reaction occurred within the first 1.5 hours, with the remaining 30% released during the remaining 22.5 hours. The total amount of O₂ released was 846 grams.

Another key experiment (14) illustrated that WO could be regenerated back to dodeca DTPA. This part of the process, regeneration, required energy (944 kJ/mole), based upon measured temperature increase, a measured cp and known mass sample. ure 16).

Key data from this investigation illustrate important products present given specific reactants in DTPA to WO, and WO to DTPA reactions. These products and reactants are present in Raman Spectroscopy, X Ray Diffraction Spectra and Photo Spectroscopic data. Spectral data illustrates a shift in the position of WO₃ depending on whether CO₂ was introduced into the system or not (the control). Both the position and the magnitude of the peaks were changed between the control and the sample.

A regenerated sample of WO that was introduced to ¹⁸O₂ suggests that O₂ released from the sample originated within the water trapped within the DTPA crystal itself. A small percentage of this O₂ may have come from exchanges of O₂ between CO₂ and H₂O itself. More testing should reveal a more definitive answer.

Modeled results of the Gibbs Free Energy and calculated reaction constant K indicate that the decomposition reactions occur exothermically, while the recombination reactions endothermically. The exothermically released energy from the decomposition of $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ could be used to satisfy some of the energy needed to initiate regeneration.

One noticeable feature of the process is that the initial rate of reaction appears to be almost exponential, decreasing to a linear or curvilinear rate at the end of a 24 hour period. This trend appears to be true for free phosphates as well as bicarbonates.

7.2 Experimental vs. Modeled Data

The experimentally collected data agrees with the theoretically predicted thermodynamic values predicted by Ceres II and Spartan Chemical Modeling Software. Based upon the X Ray Diffraction data, a significant portion of the O_2 used to re oxygenate WO_3 comes from the original CO_2 dissolved in the water. This conclusion is deduced from the fact that very little O^{18} , which is from water, appears in the final product.

7.3 Final Thoughts

In summary the experimental observations revealed by this research are that the $\text{H}_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ (DTPA) could be broken down by using a strong base, such as NaOH . In addition, the DTPA can be regenerated using HCl , NaOH , H_3PO_4 , and WO_3 . An important characteristic of this technique demonstrates that a comparable amount of O_2 shall be released for human daily consumption.

Secondly, the interaction of NaOH with the super oxide generates electrical charge, and heat, which can also be harvested for future use within the system. Finally, reconstruction of the super oxide requires the use of chemicals such as Na_2WO_4 , HCl, and H_3PO_4 . Sodium tungstate could be prepared using WO_3 , titrated with H_3PO_4 NaOH, and HCl. The chemical components HCl and NaOH can be prepared from water and other biological waste processes.

Experimental evidence suggests that the process produces about 576 grams of O_2 , and removes about 1760 grams of CO_2 , the proposed process could be used as a CO_2 - O_2 gas exchange mechanism, having the advantage over current systems by using waste products from other systems to produce consumables. In addition, a small amount of material (about 1 kg) produces sufficient O_2 for one person per day. The method also utilizes a novel method of removing CO_2 , and simultaneously removing carbon in the process. This process removes carbon as carbonates, which can be re-utilized in other systems (plant growth). Finally, the system produces a suitable amount of heat and electrical current to supplement other systems.

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CURRICULUM VITA

Mr. Angelo Karavolos began his career as a medical officer in the Medical Corps of the U.S Air Force. During his tenure as a bioenvironmental and aerospace engineer, Mr. Karavolos developed a fiberglass nose cone, a first for the Air Force Research Laboratory. In addition, he developed a small device for removing cancerous tissue using a carbon prepreg thin rod. He served as the lead bioenvironmental engineer for the TITAN IV SRMU project, and participated in the Space Shuttle Recovery Team at Edwards AFB CA. During the remaining tenure in the military, Mr. Karavolos served in a variety of operational capacities in the National Guard Reserves. In the interim between serving in the military and his pursuit of graduate work, he began a consulting company developing aerospace technology for applications in outpatient health care, homeland defense and space physiology. He has won awards such as the Ross McFarland Graduate Fellowship Award, the NASA Space Grant Fellowship Award, and authored four patents in materials engineering. He also inspired the formation of two companies which develop technology for astrobiology and space systems. His PhD dissertation was the culmination of work initiated during his Space Grant Fellowship, involved the development of a material which adsorbs carbon dioxide and releases consumables such as oxygen, heat, and electrical charge. Other technologies designed were a textile material for space suit applications, and an identification method for micron sized gas bubbles in tissue. Mr. Karavolos currently acts as the chief technology officer for De Astris Generation LLC, and lives in Houston TX with his wife Diane Karavolos.

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