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Title: Performance Testing of Molten Regolith Electrolysis and Transfer of Molten Material for Oxygen and Metals Production on the Moon

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Performance Testing of Molten Regolith Electrolysis with Transfer of Molten Material for the Production of Oxygen and Metals on the Moon

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Previously, we have demonstrated the production of oxygen by electrolysis of molten regolith simulants at temperatures near 1600°C. Using an inert anode and suitable cathode, direct electrolysis (no supporting electrolyte) of the molten silicate is carried out, resulting in the production of molten metallic products at the cathode and oxygen gas at the anode. Initial direct measurements of current efficiency have confirmed that the process offer potential advantages of high oxygen production rates in a smaller footprint facility landed on the moon, with a minimum of consumables brought from Earth. We now report the results of a scale-up effort toward the goal of achieving production rates equivalent to 1 metric ton O₂/year, a benchmark established for the support of a lunar base. We previously reported on the electrochemical behavior of the molten electrolyte as dependent on anode material, sweep rate and electrolyte composition in batches of 20-200g and at currents of less than 0.5A. In this paper, we present the results of experiments performed at currents up to 10 Amperes) and in larger volumes of regolith simulant (500g – 1kg) for longer durations of electrolysis. The technical development of critical design components is described, including: inert anodes capable of passing continuous currents of several Amperes, container materials selection, direct gas analysis capability to determine the gas components co-evolving with oxygen. To allow a continuous process, a system has been designed and tested to enable the withdrawal of cathodically-reduced molten metals and spent molten oxide electrolyte. The performance of the withdrawal system is presented and critiqued. The design of the electrolytic cell and the configuration of the furnace were supported by modeling the thermal environment of the system in an effort to realize a balance between external heating and internal joule heating. We will discuss the impact these simulations and experimental findings have on the design of a suitable prototype for lunar applications.

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I. Introduction

THE production of oxygen on the lunar surface and on other planetary bodies is potentially a paradigm-shifting step in the advancement of space exploration. If sustainable, such capability would greatly enhance the survivability of a permanent human presence on any planetary surface throughout the solar system. The generation of oxygen by electrolysis of the constituent oxides of most planetary rocks and soils is one promising technology under development to establish its level of feasibility for space missions. Among other electrolytic techniques, Molten Regolith Electrolysis (Molten Oxide Electrolysis applied to natural regoliths) offers the only one-step process to separate oxygen from metals by directly electrowinning the molten oxides. No salts, or fluxing agents need to be imported from Earth or manufactured as an added step resulting in greater simplicity in engineering, lower overall landed mass, and lower contamination of the produced oxygen.

The development of such technology is multi-faceted and interdisciplinary, calling for advances in materials design, electrochemical measurements techniques at high temperatures, and designs for high temperature oxidizing environments. The realization of the promise of generating oxygen in one step process from the lunar soil or any similar oxide mixture found on a planetary surface is a challenging venture. The knowledge that the process is experimentally sound from decades-old pioneering efforts^{1,2,3,4} and our own work urges us to attempt the scale-up development of the technology as a system. At its core, the effort rests on experimental research aimed at understanding the electrochemistry involved in these unique environments and evolves through the inventions of new devices to remove molten materials from the reactor, to fabricate large surface electrodes capable of sustaining long immersions in liquid metals and oxides, and to provide long-lasting containment of the molten media. This work also advances the use of multiphysics modeling in high temperature electrolysis with the goal of aiding in designing larger reactors capable of self-heating through Joule heating effects created by large currents through the melts.

II. Direct electrowinning of oxygen and metals from mineral feeds

The concept of high temperature electrolysis of oxides is used industrially in the production of Aluminum and Magnesium in which the natural oxides of these metals are selected in high purity form, dissolved in molten halide salts, and are electrolytically dissociated to electrowin molten metal as a product and oxygen as a by-product. In practice, the oxygen is evolved as carbon dioxide and monoxide through the use of carbon anodes. These technologies work remarkably well thanks to the tailored dissolution of these pure oxides in specific formulas of halide salts (cryolite in the case of aluminum production), although it is worth noting that the saturation limits of oxides in those tailor-made salts is around 4-5 wt.%.

Electrowinning of metal and oxygen from multi-oxide mixtures and particularly from natural mineral mixtures using salts as dissolving media is very limited because of the inherent low dissolving power of these salt media. Since molten halide salts are formulated to solubilize one oxide typically, their solvating performance is quite inefficient in the presence of many oxides.

The electrolysis of oxides in their own melt eliminates the obstacle of dissolution into a different electrolyte. It also allows a much more beneficial ratio of feed mass to reactor mass, an important parameter for space-bound hardware.

III. Electrochemical Measurements and Reactor Performance

Specific techniques have been developed by D.R. Sadoway's group at Massachusetts Institute of Technology to perform measurements of the electrochemical behavior of high temperature molten oxides and salts. Each measurement is the result of iterative designs in electrodes, materials combination, gas analysis and careful assembly of the components into a resistive furnace capable of reaching 1700 °C. This unique capability allows the probing of

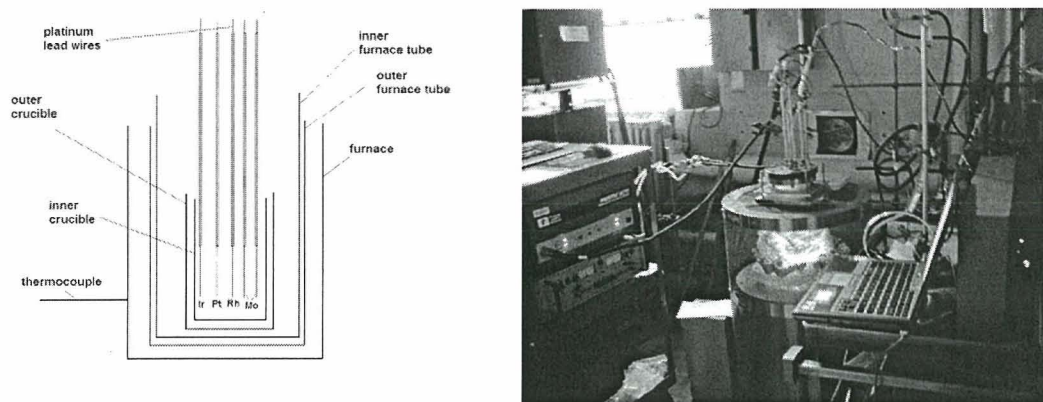


Figure 1. Schematic of electrolytic cell configuration to investigate electrochemical behaviors of various anode materials in molten oxides (left) and furnace containing the cell in operation at 1600 °C (right). The micro gas chromatograph is seen on the right of the image.

the electrochemical behavior of chemically aggressive melts and the identification of effects due to specific chemical components (Fig. 1).

The current efficiency at either electrode is defined as the portion of the current passed that is used to generate the product. The rate of production is proportional to the current efficiency according to Eq. (1).

$$rate = \frac{jA}{nF} \times Efficiency \quad (1)$$

where j is the current density, A is the surface area of the electrode, n is the number of electrons involved, and F is the Faraday constant.

At the anode, the current efficiency relates to the production of gaseous oxygen while the cathodic efficiency gives a measure of the production of metal. The direct measure of oxygen production from the anode was performed by in-line analysis of the quantity of oxygen in the gas exiting the reactor using a Varian micro-gas chromatograph CP-4900. The reactor was under a constant flow of helium during the experiment and both incoming and exiting flows were measured. Melts of various compositions have been synthesized by preparing mixtures of pure oxides to approximate the chemical composition of published lunar materials⁵. One synthetic material, labeled JSC1A and developed by Orbital Technologies Corp. with NASA⁶ was used as a recommended simulant material that also reflect the mineralogy of some basalts found in lunar mare. Chemical composition and oxidation states are the most important properties of the regolith when used as a feed for Molten Regolith Electrolysis because it is molten in superheated conditions although mineralogy will affect the melting point and viscosity in the startup of the reactor.

The current efficiency obtained for an iron-free melt during electrolysis at 1600 °C is shown in Fig. 2. The melt composition is that of JSC1A material without the iron oxides. Sodium and iron oxides are the first elemental oxides to be electrolytically reduced by the process. This result shows that nearly all the current passing through the melt is utilized to discharge oxygen anions at the anode when the iron has been reduced.

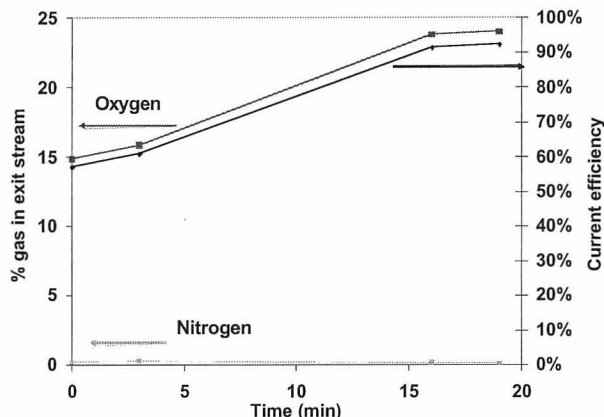


Figure 2. Anodic current efficiency from direct measurements of oxygen generated during electrolysis at 1600 °C from an oxide melt of chemical composition of JSC1A simulant without iron oxides.

The presence of iron in melts of lunar regolith simulants was found to have profound effects on the current density in the electrolyte by contributing electronic conduction. While this has the effect of increasing overall conduction, it is a parasiting effect that lowers the overall current efficiency at the anode. This translates into less oxygen produced for a given current value in melts containing iron oxides.

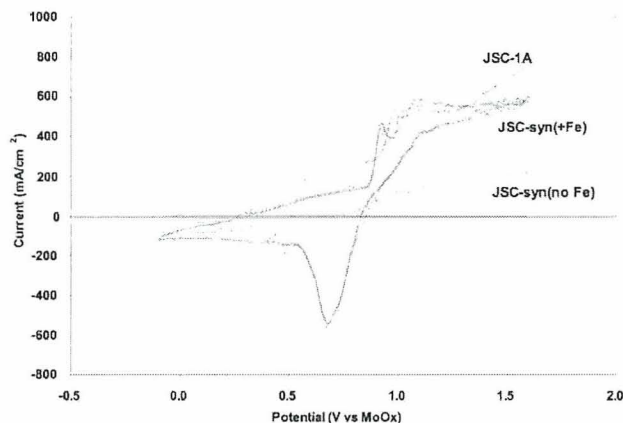


Figure 3. Effect of iron in oxide electrolytes on the current density.

The development of any technology involving chemical reactions must rely on a thorough understanding of these processes and engage in a continuing data collection in that area. In our case, the investigation of the electrochemistry involved in a requisite and has resulted in several discoveries that directly impact our technology development. The structure of oxide melts is the subject of many investigations⁷ because of their role as primary feeds in metal productions and glass making as well as their central place in many geochemical studies and planetary science. These disciplines provide very useful concepts that describe these melts and a wealth of data over temperature ranges that are typically slightly lower than the operating temperature of our work. The MIT laboratory has developed a measure of the availability of oxygen anions in the melt based on the concept of optical basicity used in glassmaking⁸. Duffy and Ingram proposed optical basicity to quantify the acid-base properties of oxides and glasses⁹. The value of optical basicity for an individual oxide can be calculated from refractive index and optical bandgap measurements, reflecting the electronic state of the oxide ion (ion polarizability). The very adaptable chemistry of oxygen allows the formation of oxides in which the chemical bonding ranges from strongly electrovalent (CaO, Na₂O) to covalent (eg, P₂O₅) or metallic (eg, TiO)¹⁰. As a result, ionicity is a feature of basic

oxides and covalency is that of acidic ones. Oxide melts are typically represented as polymeric fluids in which the oxide specie associate and dissociate continuously. The availability of oxygen anions to participate in the electrochemical reactions and thus become gaseous oxygen at the anode depends on the speciation of the melt, i.e. the nature of the molecular ions that constitute the melt. The complex melts formed from lunar materials (rocks and soils) are dominated by oxides of silicon and are ionic liquids by definition. The description of the ionic specie making up the melt is important: silicon as a dominant species polymerizes and thus populates the melt with SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_{10}^{8-}$ which coexist with O^{2-} and cations such as Ca^{2+} , Al^{3+} , Fe^{2+} . The silicon oxide anions and the free oxygen anions are sources of oxygen available for gaseous evolution at the anode but only the oxygen anions discharge at the anode. The creation of these anions is in constant flux depending on the complex equilibria between the oxygen-bearing anionic specie and cations; thus it is not possible to measure the concentration of O^{2-} as source of available oxygen. The MIT team has proposed that optical basicity is a concept that provides a measure of the total available oxygen-containing molecular anions as a function of the composition of the oxide melt. Because the property is a measure of the type of bonding of these oxides, it expresses the ability of a multicomponent oxide melt to provide oxygen ions to discharge at the anode to form gaseous oxygen. The optical basicity of the melt, Λ_{melt} is defined as follows:

$$\Lambda_{\text{melt}} = \frac{\sum_i x_i n_i \Lambda_i}{\sum_i x_i n_i} \quad (1)$$

where x_i is the mole fraction of oxide i ; n_i is the number of oxygen per mole of oxide i ; and Λ_i is the basicity of oxide i .

The work done by Gmitter and Sadoway shows the strong correlation between the calculated optical density of a melt of a given composition and the expected current density that the melt can support during electrolysis (Fig. 4). The same calculations were performed using lunar oxide compositions published in the Lunar Sourcebook for various regoliths collected at the various Apollo landing sites. Figure 5 shows that the values of optical density for these locations are relatively close to each other; this suggests that Molten Regolith Electrolysis would achieve similar oxygen production efficiencies at any of the known lunar landing sites, which is not the case for other oxygen-producing techniques that are more sensitive to oxide chemical compositions.

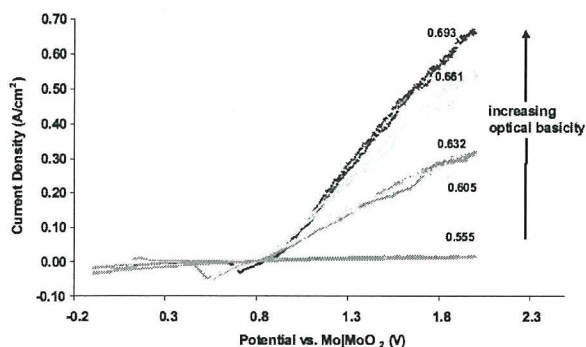


Figure 4. Current densities sustained in oxide melts of different optical basicities (Ir anode)

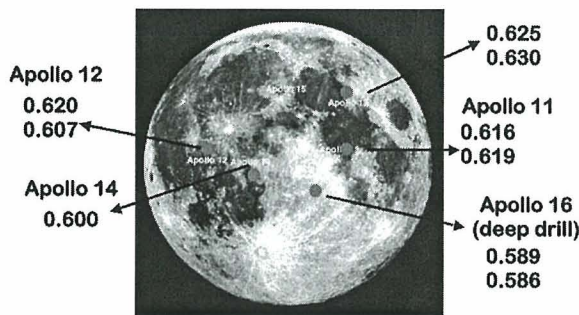


Figure 5. Optical basicities calculated for known lunar regolith compositions.

IV. Development of inert electrodes

The environment created in a molten oxide electrolytic reactor is extraordinarily challenging for materials used in containing the molten materials and those chosen as electrodes to support the electrochemical reactions. The anode must have a melting point well above the operating temperature of 1600 °C, be highly resistant to the attack of aggressive oxide melts, resist high temperature oxidation from the gaseous oxygen formed at its surface, while displaying high electrical conductivity. The resistance to oxidation is a critical criterion for the use of the technology on lunar or other planetary missions; the formation of volatile oxides of the material would deplete the anode material over time and force frequent and costly replacements of the anodes, and add another process step to dissociate the oxides formed thus negating many of the advantages of the technology. The selection of an anode material also includes the evaluation of the material in terms of its electrochemical activity in the melt; the higher the activity, the better the anode efficiency is. Other considerations play a role as well such as cost of the material, and the ability to machine and fabricate items of complex shapes. The making of high temperature coatings of refractory metals for inert anodes is under investigation but the cost of fabrication is a barrier to its implementation in this effort so far. Figure 6 shows measured activities for several candidate materials to be used as inert anodes.

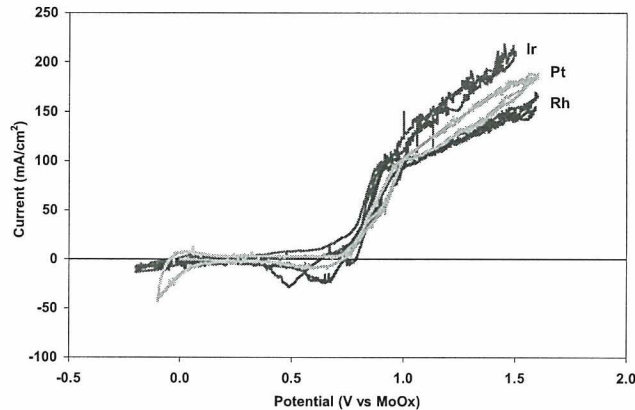


Figure 6. Relative activity of candidate electrode materials.

Through much iteration of designs and fabrication techniques, we have developed several geometries of anodes. The use of innovative welding techniques has yielded a set of anodes with surface areas of the order of 10-20 cm² by assembling elements and minimizing wasteful machining of expensive materials such as iridium or other platinum-group metals (Fig. 7). Such anode has performed very well in initial electrolysis experiments under currents of several Amperes.

The selected materials for use as cathode and cathode current collector must possess similar properties while surviving a different environment. While they must also display a high melting point well above the operating temperature, and be good electrical conductors at temperature, they must contend with the extraordinarily solvation power of molten iron and Fe-Si alloy formed at the cathode by electrolytic reduction of the oxides. The cathode collector must also resist high temperature oxidation above the oxide melt. Such constraints have resulted in the selection of several materials among which Molybdenum, that has not fared well enough when immersed in molten iron (Fig. 7).

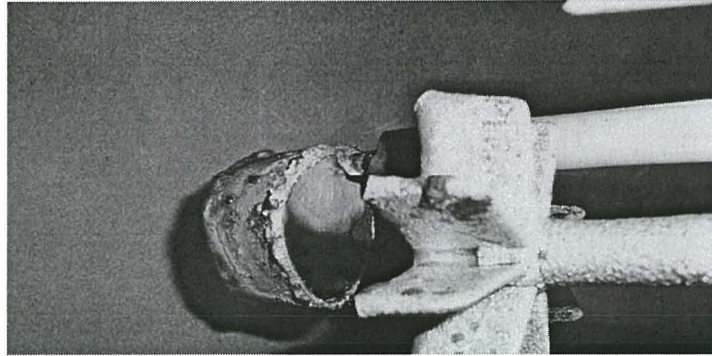


Figure 7. Wagon-wheel shape anode of Iridium (60 cm²) and cathode collector of Molybdenum after electrolysis test passing currents of 10 A.

V. Withdrawal of Molten Materials

The production of metals in molten form at the bottom of the reactor requires that this mass be removed at intervals. Similarly, the melt accumulates over time after multiple loads of fresh regolith are added to the reactor. These mass changes change the composition of the melt, the interelectrode gap, and the melt depth thus requiring adjustments of these values by regular withdrawals of molten materials. The development of this technology as part of the development of an integrated Molten Regolith Electrolysis system is done in partnership with D. M. Stefanescu from the Department of Materials Sciences and Engineering at Ohio State University and is reported in details elsewhere¹¹.

Several options have been considered, ranging from tapping through the reactor walls as done in steelmaking reactors to active pumping mechanisms. Another industrial method more likely to succeed in withdrawing molten metal and oxides from the electrolysis cell is a method known in the metal casting industry as counter gravity (CG) casting.¹² In counter gravity casting a refractory tube inserted into the mold is immersed below the surface of the metal which is to be cast (withdrawn from the reactor) and vacuum is applied over the closed mold. The differential pressure between atmosphere and inside the mold causes metal to be pushed up the tube and into the mold. The technique has similarities to the one used in Aluminum-producing cells. By varying tube dimensions and pressures used this process can be made flexible to fit a wide range of requirements.

Figure 8 shows the system for withdrawing molten products from the electrolysis cell. The figure does not show equipment used for charging the cell with powdered regolith or the electrodes used for electrolysis. Basic operation consists of opening the slide gate closure, lowering the withdrawal tube into the melt and pulling a vacuum to draw material up into the mold. After withdrawal is completed the tube is removed from the melt and the slide gate is closed. Removal of the withdrawal tube from the melt in between cycles is necessitated by the corrosive action of the regolith on any potential tube materials.

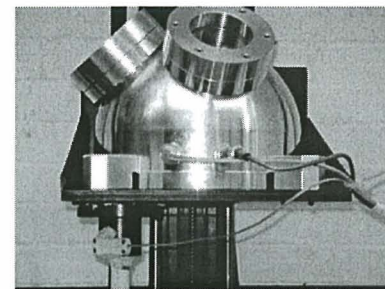


Figure 8. Pressure-driven counter gravity Molten Material Withdrawal device (Ohio State U.).

VI. Heat Transfer Modeling (Joule heating)

The current configuration and dimensions of the molten regolith electrolytic reactors forces their operation as hot-walls reactors. In fact, the oxide melt must be maintained in a superheated molten state through external heating

provided by the resistive furnace in our experiments. Such conditions place particularly severe constraints on materials used to contain both the melt, the molten metal pooling at the bottom, and the evolving oxygen. Very few materials can perform in these conditions and none of them is capable of sustaining operations of weeks or months.

The solution proposed is to configure the molten regolith electrolytic reactor into a cold-walls reactor akin to a Hall-Héroult cell used to produce Aluminum industrially (Fig. 9). The dimensions of the cell are defined to enable the reactor to heat itself via Joule heating of the melt by the electrolytic current. Such dimensioning relies on the interactions of several variables including the interelectrode gap, the electrode surface areas and the changes in the melt physical properties to achieve the proper thermal management. In the case of a Hall Héroult cell, the result is a reactor measuring tens of meters in width, with an interelectrode gap on the order of 4-5 cm and an accumulating layer of solid cryolite salt on the reactor walls that protects the structural containment.

Any attempt to determine the parametric values needed to achieve self-heating of a molten regolith electrolytic reactor would quickly become prohibitively expensive. We selected a multiphysics simulation software tool, called COMSOL Multiphysics to help solve the problem; it allows users to perform all the steps in the modeling process that include physics and equation definition, mesh generation, equation solving, visualization, and post processing. Primary results of the model are published concurrently in these proceedings showing the contribution of conduction, convection, and radiative heat transfer mechanisms on temperature profile generated within the molten regolith¹³.

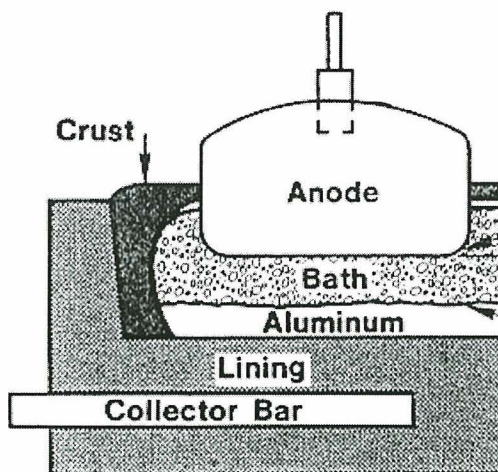


Figure 9. Schematic of a Hall-Héroult electrolytic cell for Aluminum production.

Electrical and heat transfer physics were coupled to model heat generation within the electrolytic cell due to the electrical current (Joule heating) applied to the cell to generate gaseous oxygen. Fluid dynamics was also coupled to model fluid motion within the molten regolith induced by the variation of melt density with temperature; the fluid motion within the molten regolith was modeled to study the generation of free convection heat transfer within the molten regolith. The modeling effort has progressed to include three heat transfer modes (conduction, convection and radiation between selected surfaces (Fig. 10) and enables us to understand the contributions of each mode and those of various reactor components.

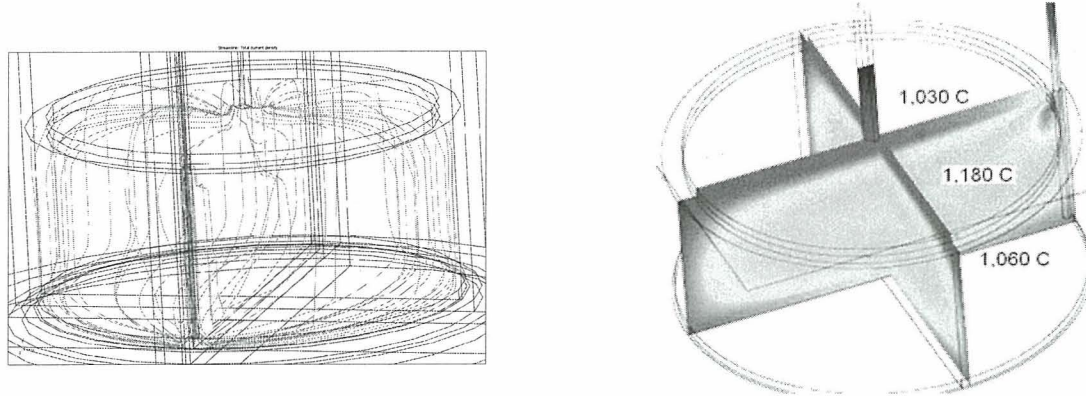


Figure 10. Lines of current through a molten regolith electrolysis cell (left) and corresponding melt temperatures generated by Joule heating (right). The anode is outline as a disc-shape plate at the top of the volume electrically connected by its central lead; the cathode collector runs vertically along the side to the disc-shape cathode at the bottom of the volume.

VII. Conclusions

Significant advances have been realized towards the understanding and development of a molten regolith electrolytic reactor capable of passing currents on the order of several Amperes to generate gaseous oxygen from lunar regolith simulant materials. Our most recent results have demonstrated the ability of currents approaching 5 A using Iridium inert anodes fabricated by innovative welding techniques. Electrochemical measurements coupled with gas analysis have revealed the operational limitations of the cell as well as specific features of the electrochemistry at play. Iron in different oxidation states was found to have a parasiting effect by decreasing the anodic current efficiency (oxygen production) while increasing the current density by electronic conduction. On the other hand, current efficiencies near 100% have been observed once iron is depleted from the melt by reduction into metal. This suggests that an entire batch of regolith could be processed at an average 94% current efficiency yielding 35% of the available oxygen contained in the soil. Materials limitations prevent the operation of the reactor at higher temperatures than 1600 °C required to extract more oxygen. At present, a stand-alone Molten Materials Withdrawal device is being assembled for testing, and will ultimately be integrated with the electrolytic reactor. We have initiated work on a comprehensive thermal model of the reactor using a multiphysics solver to define the design parameters of a self-heating cell able to sustain its molten components through Joule heating. Such a cell is considered to be the ultimate solution to enable the deployment of this technology on the lunar surface to support a lunar infrastructure with oxygen and metal alloys.

VIII. Acknowledgments

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