

MOLTEN OXIDE ELECTROLYSIS FOR LUNAR OXYGEN GENERATION USING *IN-SITU* RESOURCES

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Abstract

Molten Oxide Electrolysis (MOE) is a promising and laboratory-proven in-situ resource utilization technology for generating oxygen from lunar regolith simulant. Prior to this work, iridium metal was the only demonstrated suitable inert anode material, but its use had been limited to laboratory-scale testing owing to its extraordinarily high density, hardness, and cost. In the current work, electrodes fabricated from 50:50 (wt%) iridium-tungsten alloy were shown to be functional inert anodes for molten oxide electrolysis. The performance of the iridium-tungsten alloy was compared with that of pure iridium in a series of constant current electrolysis experiments under a variety of conditions, including the use of different electrolytes, cathodes, currents, and experiment durations. The iridium-tungsten alloy was also examined post-run by scanning electron microscopy and electron dispersive spectroscopy to determine its durability in the electrolyte, and to perform a preliminary survey of the nature of diffusion in Ir-M systems in support of potential development of Ir-based anode systems.

Introduction

In recent years, *in-situ* resource utilization (ISRU) – namely, ‘living off the land’ – has become the driving paradigm behind the economically viable establishment of a permanent human presence on the moon. Molten oxide electrolysis (MOE) using an inert anode is a leading candidate technology for ISRU on the moon or other predominantly hydrate-free planetary bodies because it can use un-beneficiated lunar regolith as feedstock to produce oxygen and useful metals, such as iron and silicon [1]. At the same time, it is important to note that inert anodes developed for MOE have potential significant applications on earth as well.

It has long been asserted that inert anodes for high-temperature electrolysis have significant advantages over consumable carbon anodes and would have broad applications to both established industries, such as aluminum, and to processes currently under development, including those for electrolytic production of titanium and iron [2-4]. Use of an inert anode would: 1) eliminate the emission of greenhouse gases such as CO, CO₂, and perfluorocarbons, 2)

reduce process cost and downtime by eliminating periodic anode fabrication and installation [3], 3) prevent potential contamination of a metal product by carbon dissolved from the anode, and 4) improve the theoretical energy efficiency of an electrolytic cell [5].

However, significant materials challenges have slowed the search for viable inert anode candidates. Very few single materials possess the combination of electronic conductivity, high melting point, mechanical stability, and extreme corrosion resistance to oxygen and molten oxides required of an inert anode [6-7]. Although some Cu-Ni alloys [8] and certain novel metallic ceramics [9] have shown potential at lower operating temperatures, prior to the present work, the only demonstrated inert anode material for MOE at the high temperatures (>1650°C) required by lunar regolith was pure iridium metal [10].

Unfortunately, bulk iridium is inherently limited as an engineering solution by its extreme scarcity (~0.4 ppb in the Earth's crust), high cost of processing, and limited fabrication methods due to its extreme hardness. For spaceflight applications, iridium is further limited by its extraordinarily high density (~22.6 g cm⁻³). Ultimately, it may be possible to develop a surface-engineered anode system, which uses a thin iridium coating as an active surface on a cheaper, lighter substrate. However, in preparation for such an endeavor, increased knowledge of iridium-based systems and the interfaces between iridium and other materials must be obtained.

Thus, the primary focus of this work was to use an iridium-tungsten alloy as an inert anode in a MOE reactor. A series of constant-current electrolysis experiments were performed to examine the alloy on its own merits as an inert anode and to generate important background knowledge on the physical properties of iridium-metal systems, in particular, interdiffusion at Ir/M interfaces.

Selection of Iridium-Tungsten

A number of Ir-M alloys were considered for fabrication and study, where the alloying element M came from the following groups: 1) platinum group metals (Ir, Pt, Rh), 2) high-melting/low-density metals (Ti, Zr, Hf, and Cr), and 3) refractory metals (W, Mo, Nb, Ta).

Other platinum group metals were rejected as candidates because they are also costly and dense, offering no apparent benefits over pure iridium. Alloys of iridium and high-melting/low-density metals were also unsuitable, because the minimum melting point over relevant composition ranges of each of the alloys was lower than the expected operating temperature of the cell.

Thus, the only remaining candidates were alloys of iridium and refractory metals. Due to time and resource limitations, only one of these alloys could be fabricated and tested. Based on tabulated data, the system with the highest minimum melting point, iridium-tungsten, was selected as a best-case technical solution. Since tungsten was expected to oxidize from the surface of the electrode during electrolysis, the highest melting point suggested the slowest rate of tungsten depletion, which would allow the extended testing of the material as an inert anode, and easy observation of time-dependent iridium/tungsten inter-diffusion.

Constant-Current Electrolysis Experiments

A total of six constant current experiments was conducted to determine the performance of the iridium-tungsten alloy relative to a baseline of pure iridium in two different melt compositions.

The first question was whether an Ir-W alloy could serve as an inert anode for molten oxide electrolysis. If that could be demonstrated, then of particular interest were the oxygen generating capabilities of Ir-W vis-à-vis pure iridium and the extent and nature of the physical and chemical changes occurring to the alloy under conditions of electrolysis.

Experimental Setup

Electrodes: Pure iridium and 50:50 (wt%) iridium-tungsten anodes were purchased from the Furuya Metal Co., Ltd., Tokyo, Japan which fabricated them using a powder metallurgy process of mixing, pressing, and sintering. Each anode was a solid metal cylinder, diameter of 15mm and a height of 20mm, drilled axially and connected to a long molybdenum rod electrode lead.

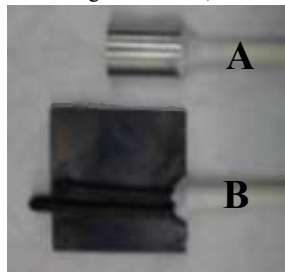


Figure 1 – A) Typical Ir or Ir-W cylindrical anode, B) Mo plate cathode.

After receipt from the manufacturer, the lead rods were dielectrically sheathed with alumina tubes and hi-purity alumina cement to protect the electrode leads from oxidation and mechanical damage (**Figure 1A**).

Since the iridium cathodes used in the first two runs proved to be too fragile, later runs used a custom-fabricated molybdenum plate cathode, which was produced by heating a molybdenum lead rod with a propane torch, and then bending the rods securely around a 30×40×0.7mm plate (**Figure 1B**).

Electrolyte: JSC-1A, a standard NASA lunar simulant, obtained from Orbitec™, was used in two of the runs. However, as demonstrated in this and previous work, oxygen

detection by gas chromatography is challenging due to parasitic back-reactions of electrolyte components. Thus, a Simplified-Composition Lunar Simulant (SCLS) was developed to allow easier comparison of Ir and Ir-W oxygen generating performance. SCLS was based on JSC-1A, with minor constituents (< 3 wt%) removed and all Fe₂O₃ replaced by an equivalent quantity of FeO (lunar regolith is Fe₂O₃-free).

Furnace Set-Up: A Mellen CD18 tube furnace with MoSi₂ elements was used for these experiments. The molten electrolyte was contained with a nested series of two crucibles and two furnace tubes and the entire apparatus was sealed from atmosphere by a custom-fabricated stainless steel cap. A schematic is shown in **Figure 2**. The electrodes were fitted through dielectric vacuum fittings in the cap and current was furnished by an Argantix 10kW DC power supply. All experiments were run at or near a cell temperature of 1575°C and under a constant flow of ultra high purity helium (600 mL/min), used as received from Airgas.

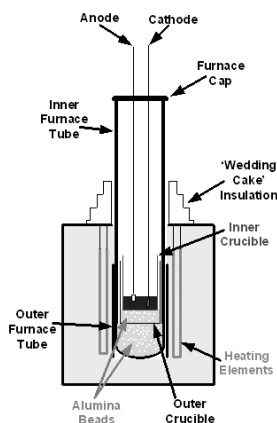


Figure 2 – Schematic of furnace setup and geometry.

Instrumentation: During the experiments, data were collected and recorded by a central computer. The composition of the furnace gas was regularly sampled by a Varian GC-4900 micro gas chromatograph; these data were correlated to electrochemical, and furnace performance data. In some runs, it was also possible to quantify O₂ production by comparing gas inflow and outflow.

The progress of electrolysis was also observed visually through a borosilicate viewing port in the cell cap; several still photographs and videos of electrolysis were recorded using a handheld digital camera.

Electrolysis

Three experiments using pure Ir electrodes were run to validate the experimental setup and provide a baseline for comparison of the runs using Ir-W under similar conditions. Next, three similar constant-current experiments were conducted using the cylindrical iridium-tungsten electrodes with the goal of running electrolysis for a variety of time-periods, including long durations of six or more hours.

In each of the six experiments, one or more current targets between 5A and 10A were set, with no attempt made to limit the voltage required to pass the target current. Only when the current could not be passed at the 30V maximum of the power supply was a below-target current used.

During electrolysis, the composition of the gas stream was measured every 2.5 minutes. The theoretical oxygen content of a 600 mL/min gas stream was calculated based on the instant current flowing through the cell. This theoretical value was compared to the measured oxygen content and used to calculate a current efficiency for the system. The measured rate was also integrated to determine the total quantity of oxygen produced in each experiment.

Post-Experiment Characterization

The iridium-tungsten anodes were sectioned using electric discharge machining and mounted in a hot isostatically pressed black resin. The samples were polished with increasingly fine grades of silicon carbide sandpaper and then examined using a scanning electron microscope, equipped with a backscatter electron detector, variable pressure capability, and an electron dispersive spectrometer. Micrographs of the samples were taken, as were a number of concentration profiles of iridium and tungsten from the surface of the electrode inwards.

Results and Discussion

A summary with the setup and results of each experiment in this series is provided in Figure 3.

Run Duration

The goal of running extended-duration electrolysis near 6 hours was met in only one of the six experiments. In the first two runs, the iridium cathode failed early, an issue which was resolved by the introduction of a more robust molybdenum cathode. In the other four runs, electrolysis was ended by actual or imminent failure of the inner crucible, resulting from contact with the

extremely corrosive electrolyte. From these runs, it appears that durability of the Ir-W alloy anode is not currently the limiting factor for longer-duration runs of an MOE system.

<i>ID</i>	<i>Anode</i>	<i>Cathode</i>	<i>Electrolyte</i>	<i>O₂ Based Current Efficiency</i>	<i>Duration in Melt</i>	<i>Oxygen Detected by GC</i>	<i>Reason for End</i>
NASA1	Ir	Ir Plate	JSC-1A	N/A ¹	N/A ¹	N/A ¹	Cat. Failed
NASA2	Ir	Ir Cylinder	SCLS ²	70-90% @ 5A	30 min	c. 800 mL	Cat. Failed
NASA3	Ir-W	Mo Plate	SCLS ²	35-45% @ 5A	83 min	c. 350 mL	Crucible failed
NASA4	Ir-W	Mo Plate	SCLS ²	35-40% @5A 45-55@ 7.5A	125 min	c. 700 mL	Crucible failed
NASA5	Ir	Mo Plate	SCLS ²	10-120% ⁴	172 min	c. 1300 mL	Crucible failed
NASA6	Ir-W	Mo Plate	JSC-1A	c. 2% ³	352 min	c. 126 mL ³	Time goal reached

Figure 3 – Experimental matrix for series of runs. NOTES: 1) This run was aborted before any results were obtained; 2) SCLS = Simplified-Composition Lunar Simulant; 3) Very limited oxygen was detected by GC even after a long-duration run even though significant bubble evolution was observed. Parasitic oxygen-consuming reactions among components of JSC-1a are suspected; 4) Reliable current efficiency data from this run are not available due to prolonged exposure of hot molybdenum to the gas stream.

Anode Performance and Current Efficiency

Under nominal operating conditions, current efficiencies of pure iridium anodes were quite high, well in excess of 75% in the two successful iridium runs. Results also suggested that current efficiencies increased with increasing current. However, pure iridium anodes tended to show a gradual drop in current efficiency with time, which is likely related to the development of a chemical short circuit involving multivalent ionic species, most notably Fe²⁺ and Fe³⁺. It is also worth noting that the introduction of a molybdenum cathode, a potent oxygen getter at high temperatures, can severely harm current efficiencies if the metal becomes exposed to the gas stream as was the case in the NASA5 run (Figure 1, Footnote 4).

The experiments involving Ir-W demonstrated that upon depletion of tungsten at the electrode surface, iridium-tungsten is an inert anode material capable of generating significant quantities of oxygen by MOE. However, over the course of the experimental series, three main points differentiated the electrochemical performance of the two electrode materials:

- 1) Ir-W anodes tend to evolve oxygen at lower current efficiencies than seen with pure Ir anodes. The best estimates available from these runs suggest that in SCLS pure Ir is around 80-90% efficient (at the peak), while Ir-W is around 45-55% efficient. Presumably, some quantity of oxygen is being consumed by the oxidation of tungsten from the alloy anode surface.

- 2) Ir-W anodes must spend a period of time immersed in the electrolyte before their full current-passing capability is reached. In contrast, iridium electrodes can pass full current immediately. This ‘delay’ effect is likely related to the kinetics of tungsten depletion from the anode surface.
- 3) At least on the timeframes accessed by these experiments, Ir-W did not show the gradual drop in current efficiency seen with pure Ir anodes.

Alloy Performance and Iridium-Tungsten Interdiffusion

The iridium-tungsten anodes used for this analysis were used for electrolysis lasting 83 and 125 minutes (short-duration) and 352 minutes (long-duration). In these runs of less than six hours, no noticeable change in size or mass was noted in any of the iridium-tungsten anodes. Additionally, there was no decline in the oxygen generating performance over these run durations. However, each of the electrodes had entirely lost their original metallic sheen, suggesting that the expected surface tungsten depletion had occurred.

As expected, SEM and EDS analysis confirmed that the surface of the Ir-W anode was depleted of tungsten. In the ‘short-duration’ anodes, depletion depth was just over 500 μm . A thin layer (approximately 50 μm) at the surface appears ‘broken’ and has been thoroughly penetrated by electrolyte. For the long-duration anode (352 minutes), the depth of tungsten depletion was approximately 1140 μm while the ‘broken’ layer was around 100 μm thick. The data from 85 and 352 minutes scale as would be expected by the laws of classical Fickian diffusion, according to which the depth of depletion should scale with the square root of duration.

A micrograph of a representative Ir-W anode cross-section, clearly shows several bands near the electrode surface which may correspond to the increasingly tungsten-poor phases seen on an iridium-tungsten phase diagram (**Figure 4**).

More quantitatively, EDS elemental analysis was used to determine the iridium and tungsten concentration profiles near the surface of the electrodes. Figure 5 contrasts the profiles for the short and long-duration electrodes. While the short-duration profile shows an essentially smooth trend from surface to interior, the long duration profile shows several distinct features, and not a Gaussian error function as would be expected for simple diffusion. Both sets of data correspond closely to a depth of around 0.5 mm, which suggest that this is a steady-state profile for this region. The long-duration profile then diverges, being largely flat from a depth of 0.5 to 0.8 mm (over compositions from 25 to 30% tungsten) and then showing a nearly linear trend to the original 50-50 composition over depths of 0.8 to 1.1 mm (**Figure 5**).

Computer modeling using Matlab’s *pdepe* function to solve Fick’s Second Law suggests that such a profile occurs when there is a region of intermediate composition with a higher diffusion coefficient than either extreme. Based on this simple model, it is suggested that the diffusion coefficient in the intermediate composition of 25-30% tungsten is on the order of $4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, while the diffusion coefficient on either side is about $4\text{-}5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, an order of magnitude lower. In terms of future design of iridium systems, the fact that there exists an intermediate composition layer with a higher diffusion coefficient suggests alloy compositions that may improve system durability.

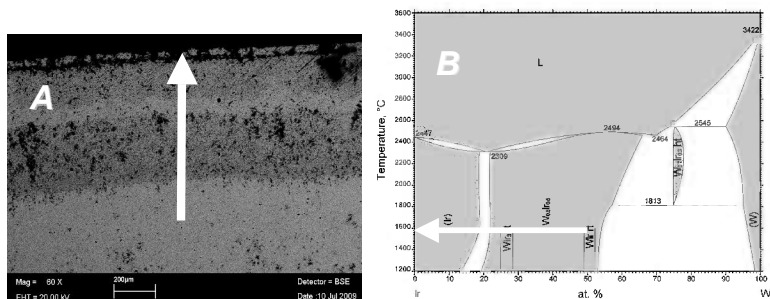


Figure 4 - A) SEM micrograph showing banding at surface of anode. The arrow corresponds to that in Part B of this figure. **B)** Ir-W phase diagram with operational temperature and relevant compositions marked by arrow

In any case, the development of depletion layers with non-trivial metallic interdiffusion coefficients strongly suggests that a conductive diffusion barrier, such as a tungsten carbide layer, would be necessary for the long-term performance of any inert anode system involving iridium/tungsten interfaces for molten oxide electrolysis.

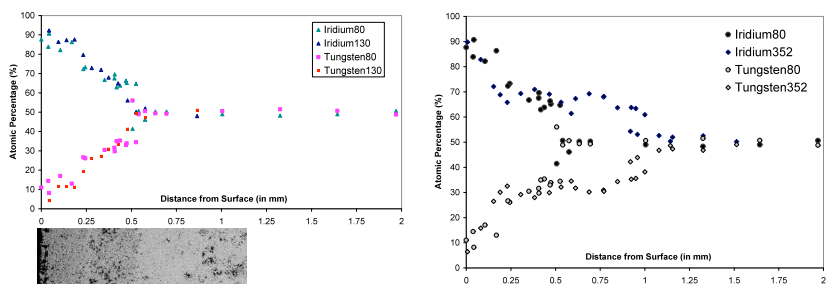


Figure 5 – Iridium-tungsten profiles for runs of various lengths. The figure at left compares two short-duration runs with banding seen in a SEM micrograph of the anode surface. The graph at right is a comparison of profiles for long and short duration runs.

Conclusions

Iridium-tungsten alloy (50-50 wt%) has been confirmed as an inert anode material for oxygen generation by molten oxide electrolysis. The oxygen generating capabilities of this material are generally good, but still somewhat inferior to pure iridium, particularly in terms of current efficiency, a ‘delay’ period before maximum current, and durability in molten oxides. SEM and EDS analysis generated diffusion data for various solid phases of the Ir-W system, providing insight into alloy compositions that may maximize the lifetime of Ir-M alloys in molten oxides. In the specific case of Ir-W, it was demonstrated that while the bulk material is substantially

stable over the time scales accessed (<6 h), a diffusion barrier will almost certainly be required to ensure the long-term performance of any anode system using Ir-M interfaces.

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