

**ELECTROCHEMICAL PROCESSING IN MOLTEN SALTS:  
FROM “GREEN” METALS EXTRACTION  
TO LUNAR COLONIZATION**

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**Abstract**

Electrochemical processing in molten halides is the basis for a suite of reduction technologies (both electrolytic and metallothermic) for the extraction of metals, including aluminum, magnesium, lithium, titanium, tantalum, and neodymium. The development of advanced materials for reactor components has made it possible to conceive of new chemistries and reactor designs that were previously thought to be industrially inviable. This has stimulated research directed at environmentally benign (“green”) processes for metals extraction and *in situ* generation of breathable oxygen by electrolytic decomposition of lunar regolith.

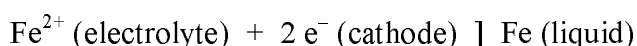
## INTRODUCTION

In a wide variety of metallurgical settings electrochemical processing in molten salts is attractive because these melts offer expanded ranges of operating temperature and chemical reactivity as compared to those available in other reaction media. Today the state of the art includes (1) production of primary metal by electrolytic extraction, e.g., aluminum, magnesium, lithium (and all the alkali metals), and the rare earth metals (yttrium and the lanthanons), (2) production of primary metal by metallothermic reduction, e.g., tantalum, titanium, magnesium, and calcium, (3) metal purification by electrorefining, e.g., titanium, and (4) electrodeposition of coatings, e.g., tantalum (and many other refractory metals). Many of these processes have been in use for more than a hundred years. Drivers for change are economic and regulatory. Existing molten salt processes strive to become more efficient in their use of energy and reagents so as to improve profitability while at the same time reducing emissions. It is the position of the author that in the 21<sup>st</sup> century, provided that carbon-free generation of electrical energy becomes widespread, thermochemical technologies such as carbothermic reduction will be displaced by new electrochemical technologies. In parallel, the development of advanced materials for reactor components has made it possible to conceive of new chemistries and reactor designs that were previously thought to be industrially inviable. This paper examines several possibilities in this regard.

## MOLTEN OXIDE ELECTROLYSIS

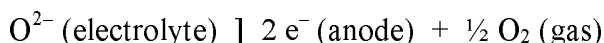
Imagine a process in which metal oxide feedstock is converted to metallurgical-grade liquid metal and oxygen gas. Molten oxide electrolysis is such a process. An extreme form of molten salt electrolysis in which the electrolyte is not a molten halide but rather a molten oxide, molten oxide electrolysis in conjunction with carbon-free generation of electricity would usher in the era of sustainable metallurgy. Specifically, new technologies based upon electrochemical processing in molten oxides have the potential to (1) improve existing electrochemical technologies, (2) displace thermochemical technologies, and (3) innovate in the field of hazardous waste treatment.

Figure 1 shows how iron and oxygen might be produced by the proposed technology [1]. The reactor depicted is an electrolytic cell, a device that causes electrical energy to do chemical work. This occurs by the transfer of electrical charge between two electrodes across an ionically conducting liquid (electrolyte). The electrolyte in this case is a multicomponent solution consisting of iron oxide and other oxides, such as silica, alumina, magnesia, and calcia. The cathode is a pool of molten iron at the bottom of the cell. At the interface of liquid metal and electrolyte, the electrochemical reduction of iron occurs according to the following reaction:



The origin of the  $\text{Fe}^{2+}$  is the iron oxide feed, which has dissolved in the molten oxide electrolyte and dissociated to form  $\text{Fe}^{2+}$  cations and  $\text{O}^{2-}$  anions. The liquid iron produced is instantly incorporated into the metal pool without the need for mass transport to another site within the cell. Thus, as the reaction proceeds, the depth of the iron pool increases. The solid member forming the floor of the cell and also acting as current collector must be made of a material that is chemically inert in contact with molten iron and also is a good electronic conductor. Materials satisfying these requirements include certain electronically conducting oxides and refractory hard metals, as well as thermally graded materials such as “cold fingers”

around which iron has frozen. At the top of the cell is the anode, which acts as the current feeder. The anode must be chemically inert with respect to both oxygen gas and the molten oxide electrolyte. Evolution of oxygen occurs according to the following reaction:



The source of  $\text{O}^{2-}$  is the iron oxide feed which has dissolved and dissociated in the molten oxide electrolyte. The anode functions as an electron sink, and the product oxygen gas evolves as bubbles on the surface of the anode and floats to the surface of the melt. Candidate anode materials include electronically conducting oxide and metals protected by an oxide film on the surface [2]. The sidewall consists of electrolyte frozen against a shell made of refractory brick. This is the electrolytic equivalent of skull melting, and is precisely the condition in a modern Hall cell producing tonnage aluminum. Feed consisting of iron oxide is added to the cell from the top. The process is continuous. Periodically, metal is siphoned from the cell.

What about the engineering aspects of the reactor depicted in Figure 1? At 1800 K, the standard free energy of formation of FeO is 159 kJ/mol [3] which via the Nernst equation gives a standard decomposition potential of 0.825 V. In practice, molten salt electrolysis cells operate at about 2 to 2½ times theoretical voltage in order to surmount kinetic barriers and to supply adequate energy to keep the electrolyte molten by Joule heating [4], so we can expect the cell in Figure 1 to operate at about 2 V. The current will be set at a value governed by the thermal balance of the cell: the current must exceed a minimum level in order to generate adequate Joule heat to keep the electrolyte molten. Given the thermal and electrical properties of molten salts, it turns out that the threshold of thermal sustainability is 1 kA. In one hour, such a cell would produce 1.04 kg iron and 0.30 kg oxygen or 0.23 standard cubic meters oxygen. Current densities in molten salt cells are on the order of 1 A/cm<sup>2</sup>, although in molten oxides substantially higher values (~ 5 A/cm<sup>2</sup>) may be sustainable. This means that the anode would be on the order of 30 cm in diameter, immersed in the electrolyte to a depth of 1 cm. This translates into a rather compact device with a small footprint. Productivity scales linearly with these dimensions. In other words, to double the production of oxygen one would double the anode area and hence double the current through the cell; voltage remains unchanged. The oxygen produced at the anode bubbles through the electrolyte and rises to the top of the cell for collection. Molten iron is harvested by siphon. All that is required to sustain productivity is iron oxide (about 1.4 kg/hr) and electric power (2 kVA).

The advantages of molten oxide electrolysis include the following:

- \* few unit operations – minimal chemistry to prepare feedstock and cell produces liquid metal ready for subsequent processing
- \* chemically flexible – cell can be used to produce different metals depending upon feedstock
- \* carbon-free & halide-free – most environmental problems stem from the combination of carbon and a halogen which is pervasive in today's molten salt electrolyses
- \* oxygen the main by-product – environmentally friendly and commercially valuable
- \* viable at small tonnage – attractive from an investment standpoint
- \* scalable – productivity increases with active electrode area: adding to existing facilities is simple compared to issues facing a thermochemical reactor whose productivity is proportional to its volume
- \* proprietary – patents have issued.

## **“GREEN” METALS EXTRACTION**

What metals are candidates for molten oxide electrolysis? Titanium, chromium, various ferroalloys, neodymium, and uranium come to mind. Far off in the future perhaps we might even dare to suggest electrolytic steelmaking! Indeed, the reaction from the American steel industry has been not unfavorable. In a speech delivered at MIT almost seven years ago, Thomas J. Usher, then President of the U.S. Steel Group stated his interest in “... new technology which will eliminate the production of CO<sub>2</sub> which is the unavoidable result of using carbon... Through the American Iron and Steel Institute, we have therefore encouraged the National Science Foundation and other agencies to support Don Sadoway’s work as a modest investment towards the steel technology which may be required to match the long term needs of the industrial ecology.”

## **OXYGEN GENERATION ON THE MOON AND MARS**

Metals are not the only product of interest. Space colonization will require *in situ* resource utilization in order to support human habitation. Specifically, space pioneers will need a readily accessible supply of oxygen. It turns out that there is plenty of oxygen on the Moon and on Mars: the lunar regolith is over 60% oxygen [5] while martian soil is about 45% oxygen [6]. However, all of this is chemically bound to other elements in the form of very stable compounds. Molten oxide electrolysis has the potential to generate oxygen from locally available resources on the Moon and on Mars. No special reagents need to be transported from earth in order to employ the technology. The only process input that needs to be furnished on site is electric power which, presumably, can be generated photovoltaically.

## **TECHNICAL BARRIERS AND RESEARCH NEEDS**

What are the technical barriers to molten oxide electrolysis? First, the molten oxides of many of the metals of interest exhibit electronic conductivity and thus are unsuitable for use as electrolytes. Secondly, to sustain oxygen evolution a carbon-free anode material must be found. Thirdly, the database is inadequate.

To address the electrolyte issue a major research effort on a par with what accompanied the molten salt breeder reactor must be mounted to reveal the underlying science if we are to be able to proceed with deterministic process design. Much of the research would entail basic property measurements, e.g., phase diagrams, vapor pressure, density, viscosity, surface tension, and most importantly, electrical conductivity. The latter is arguably the most important property of the electrolyte as it determines the thermal balance of the cell. Obtaining accurate values of the electrical conductivity of a molten oxide at temperatures sometimes exceeding 1500°C is not trivial. Recent work in this laboratory has shown that on the strength of the invention of a new technique for measuring the electrical conductivity of a liquid, it is possible to take accurate data under very hostile conditions [7]. Furthermore, the electrical properties of the melt can be tailored by the control of composition [8].

To address the anode issue requires attention to the attendant materials science. In previous work directed at identifying a carbon-free anode for use in the electrolytic production of aluminum, the author has developed a methodology for solving such materials problems [9,10]. These materials selection criteria should be adaptable from the molten fluoride chemistry of aluminum smelting to the molten oxide chemistry of the present paper.

## **TREATMENT OF HAZARDOUS WASTE**

In the context of waste treatment, electrolysis in molten oxides is a process offering the prospect of changing the valence of dissolved heavy metals while making pure oxygen gas as the main by-product. Laboratory tests conducted at a temperature of 1550°C on chromate sludge dissolved in a melt composed of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{MgO}$  have confirmed electrochemical production of oxygen on a carbon-free anode [11]. It may even be possible to win chromium metal from solution. If the process can be generalized to treat other forms of hazardous waste containing heavy metals, the commercial importance will be significant. The most important technical barriers remain the same as above: electrolyte chemistry and anode selection.

## **SUMMARY AND CONCLUSIONS**

What can be said in general about trends in the metals industries vis à vis molten oxide electrolysis? In the opinion of the author, environmental concerns will prompt a shift from thermochemical approaches to electrochemical approaches. We see evidence of this today in the magnesium industry where new electrolytic capacity is being installed to process feedstock derived from ore bodies that historically were processed by metallothermic reduction, e.g., Noranda has chosen to electrolyze chlorinated serpentine tailings [12]. If this trend is coupled with carbon-free generation of electricity, the result will be “greener” metallurgy. The second point is that the transitional technologies will play an uncertain role. This is largely due to the fact that the metals industry is very conservative owing to the very high capital costs associated with technology. For example, it has been roughly 25 years since a major new technology for producing aluminum was installed: the Alcoa smelting process. There can be no denying that the Alcoa smelting process was an engineering achievement with its bipolar electrode array, fluoride-free electrolyte, and negligible carbon consumption rate. Yet the plant proved to be an economic failure and was ultimately closed, even though the electrolysis step was 30% more efficient than the Hall cell. So on the heels of such an experience the metals industry is going to be very loathe to make major changes. Even so, we recognize that attaining sustainable metallurgy requires major technological adjustment— a paradigm shift. Conservative management is afraid to spend money on risky technology, and impatient policy makers and government officials want to force dramatic changes in the emissions profile of the metals industry. This juxtaposition represents a great opportunity. Whether we consider incremental changes in current technology or radical innovation, the future looks bright for molten salts.

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