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Stability of Iridium Anode in Molten Oxide Electrolysis for Ironmaking: Influence of Slag Basicity

Hojong Kim, James Paramore, Antoine Allanore, Donald Robert Sadoway

Department of Materials Science and Engineering, MIT, Cambridge, MA, 02139, USA

Molten oxide electrolysis (MOE) is a carbon-neutral, electrochemical technique to decompose metal oxide directly into liquid metal and oxygen gas upon use of an inert anode. What sets MOE apart from other technologies is its potential environmental advantage of no greenhouse gas emissions. Therefore, the primary challenge for carbon-free molten oxide electrolysis is the development of an inert anode. In the quest for an inert anode that can sustain the aggressive conditions of the process, iridium has been evaluated in two different slags for ironmaking. The basicity of the electrolyte proves to have a dramatic effect on the stability of the iridium anode, where iridium corrosion in an acidic slag with high silica content is less pronounced than the corrosion rate in a basic slag with high calcia content.

Introduction

Electrolysis is one of the technologies investigated by the steel industry to develop a carbon-lean route that copes with potential environmental constraints on production emissions (1). The use of electrolysis to produce tonnage metal is not new for metal production industries, and several methods have been identified for iron (2,3). However, to produce liquid iron metal, only one promising way has been identified: molten oxide electrolysis (MOE). This process uses an electrical potential difference in a molten oxide electrolyte to separate the oxygen from the iron, producing liquid iron and oxygen gas, according to the general equation:

\[ 4Fe^{3+} + 6O^{2-} \rightarrow 4Fe + 3O_2(g) \] [1]

The chemical principle of MOE is similar to that of the Hall-Héroult process for aluminum production. However, the two processes are fundamentally different with regards to underlying chemistry. The most important difference is the anode reaction: the aluminum electrolysis process relies on graphite consumption to produce carbon dioxide. The aluminum process also involves fluoride-based melts and runs at 950°C.

Over the last 40 years, the primary technological challenge for the aluminum industry has been the development of an inert-anode material (4). On the path to carbon-free steelmaking by electrolysis, the primary hurdle is the development of an inert anode for the far more corrosive MOE process conditions. To underline the difficulty of such development, some of the characteristics of the MOE process investigated in this study are listed below. Highly corrosive conditions exist within the molten oxide electrolyte, and are particularly severe at the anode/electrolyte interface:
Temperatures in excess of the melting point of iron (1538°C).
High solubilizing power of a multicomponent oxide melt.
Presence of pure oxygen gas at atmospheric pressure.

Furthermore, to meet the production requirements of an industrial process, the anode must sustain high current densities, potentially exceeding 1 A.cm\(^{-2}\). Under these conditions, most metals are poor candidates due to the oxidizing atmosphere and anodic potential. More so, oxide passivation layers which would normally protect a metallic surface are dissolved by the molten oxide electrolyte, resulting in unabated oxidation of the metal (5,6).

However, these challenges are not sufficient to abandon the search for an inert anode material. There are a few exceptional metals, well known by aqueous electrochemists, which may be viable: the noble metals. Without considering the issues related to material costs or scarcity, it is of fundamental interest to study the oxygen evolution reaction using these metals in molten oxide systems. These data are a prerequisite in order to tailor new materials necessary for large scale applications, at reasonable costs, in the future.

Preliminary, small scale experiments using cyclic voltammetry, conducted by the Sadoway research group at MIT have revealed that iridium was the most promising noble metal anode material for small scale experimentation (7,8). Additionally, results from these tests suggest that the anodic current density for the oxygen evolution reaction increases with the optical basicity of the electrolyte at a given potential (7).

The molten oxide electrolytes investigated in the present study are composed of five oxides: silica, alumina, magnesia, and calcium oxide. Iron oxide (Fe\(_2\)O\(_3\)) is added in the melt at 9.1 wt\%, as raw material for ironmaking. These oxides have different acido-basic properties, at first approximation related, to the fundamental attraction between the metal cation and the oxygen anion. A scale of basicity, empirically measured as the optical basicity, is used in molten oxide chemistry to establish the properties of these oxides and their melts. It is expected, as in other media, that a melt of higher acidity will more readily dissolve basic oxides and vice-versa. Though the slag composition is chosen to guarantee a low melting temperature (below 1450°C), it is possible to use either highly acidic slags (e.g. slags with silica as a major component), or highly basic slag (e.g. slags that contain a large concentration of alkali and alkali-earth oxides). To conclusively investigate the potential of iridium as an inert anode material for MOE, a systematic investigation of its stability has been conducted as a function of the slag composition during galvanostatic electrolysis at high anodic current density.

**Experimental**

**Slags**

Two molten oxide slags, one acidic and one basic, were selected as supporting electrolytes. These slags were named A “high silica” and B “high calcia” respectively. Slag basicity was determined using the optical basicity scale. The composition and
properties of these slags are compiled in Table I. High purity oxide powders (99.7 wt% purity min., from Alfa Aesar and Sigma Aldrich) were mixed by manual shaking for approximately 10 minutes before loading into the crucibles. No pre-melting steps were conducted. Physicochemical properties have been evaluated from the reference textbook SLAG ATLAS (9), mostly by interpolating existing data. However, the validity of this method is not confirmed, and these data are therefore given as a first approximation. Melting points have been determined using FactSage software and database (10).

Table I. Composition (mol%) and properties of selected oxide melts at 1500° C for iron decomposition.

<table>
<thead>
<tr>
<th>Slag #</th>
<th>Slag Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (high silica slag)</td>
<td>0.606</td>
</tr>
<tr>
<td>B (high calcia slag)</td>
<td>0.753</td>
</tr>
</tbody>
</table>

Crucibles

High purity alumina (99.8 wt%, McDanel Advanced Ceramics, USA) and magnesia (99.8 wt%, Ozark Technical Ceramics, USA) straight wall crucibles (6.35 cm diameter, 14 cm height) were used as containers for acidic and basic melts, respectively. An outer molybdenum crucible served as a protection crucible to prevent damage to the furnace in case of ceramic crucible failure.

Electrodes

The anode consisted of a plate of 3 cm×1 cm×0.1 cm (total surface area of 6.8 cm²) made of high purity iridium (>99.9%, Furuya Metals, Japan). This plate was welded to a molybdenum rod (0.48 cm diameter, 91.4 cm height, American Elements, USA) that served as a current lead. The cathode was a molybdenum disk (3.81 cm diameter, 0.1 cm thickness, surface area facing the anode of 11.4 cm²), connected to a molybdenum threaded rod (same dimensions as the anode lead) by a molybdenum nut. All molybdenum rods were protected by high purity alumina tubes, and connections were protected by high purity alumina paste (Resbond 989, Cotronics Corp., USA). No mechanical or chemical pretreatment of the electrode material was applied. As the anode was held vertically above the horizontal cathode disk, the active surface for electrolysis on the anode was limited and the vertical extension of this electrode was not electrochemically active. This orientation limited the anode surface facing the cathode to 0.3 cm², which can be considered as the minimum, but realistic, surface for anodic processes.

Process Operations

The crucible and electrodes were sealed from the atmosphere and placed in a closed-one-end alumina tube (11.4 cm inner diameter, 1 m height, 99.8%, McDanel Advanced Ceramics, USA). Temperature was controlled by a furnace equipped with lanthanum chromite heating elements (Model: PVT 18/100/350, Carbolite, UK). The schematic of
the experimental set-up is shown in Figure 1. The furnace temperature controller was set to 1600 °C, at a ramping rate of 84 °C.h⁻¹. The thermocouple connected to the temperature controller was located at the outside surface of the alumina tube, leading to a process temperature of 1550 °C in the crucible zone, as determined by a separate thermal profile measurement. The gas atmosphere in the tube had a low concentration of oxygen (less than 10 ppm) due to a continuous flow of high purity argon (99.9999%, Airgas) at approximately 150 cm³.min⁻¹. Oxygen content at the gas outlet of the furnace was analyzed by an electrochemical sensor (Rapidox 3100, Cambridge Sensotec, UK).

After 1 hour of equilibration at the target temperature of 1600 °C, the molybdenum cathode was first lowered to the bottom of the crucible. The iridium anode was then lowered until it touched the cathode, as confirmed by electrical short-circuit, and raised by 2 cm to obtain the desired anode/cathode distance. Galvanostatic electrolysis was conducted at 3.5 A, using a potentiostat/galvanostat (ParStat 2273, Princeton Applied Research) for 4 hours, the corresponding coulombic charge being 50400 C. The current density was 0.3 A.cm⁻² on the cathode and 11.7 A.cm⁻² on the anode assuming the geometric surface facing each electrode was active for electrolysis. After 4 hours of electrolysis, the anode and cathode were raised above the electrolyte to prevent back reactions during cooling, and to minimize entrained electrolyte which would hinder post-mortem analysis of electrodes.

![Figure 1. Schematic of experimental set-up (not to scale)](image)

**Figure 1. Schematic of experimental set-up (not to scale)**

**Post-mortem Analysis**

After the experiment, the system was disassembled for detailed characterization by SEM/EDX (LEO VP 438 SEM). The iridium anode was separated from its electrical lead and weighed to determine weight loss. Cross-sections of both electrodes and bulk electrolyte near the center of the crucible were obtained by cutting with a diamond saw,
mounting in thermosetting phenolic resin, and polishing using SiC paper and alumina powder down to 0.3 µm.

Results and Discussion

Constant current electrolysis

Voltage variations under galvanostatic conditions (3.5 A) are presented in Figure 2 for the two slags investigated. These results are representative of several runs for each electrolyte. The average cell voltage in high silica electrolyte is twice that measured for high calcia slag, which is in agreement with expectation based on differences in electrical conductivity data from literature. A steady-state regime is rapidly observed in the high calcia electrolyte, contrary to the silicate-based system. In the high calcia slag, the voltage is fairly constant and no fast-oscillations can be detected. In the high silica slag, after an initial increase over 30 minutes, the cell voltage slowly decreases. Several spikes are noticed in this electrolyte, as well as a small, high frequency oscillation of the cell voltage. Altogether, these observations suggest a key role for the viscosity of the electrolyte. The spikes may be related to the formation of large gas bubbles in the slag, the removal of which are hindered by the high viscosity, causing a large increase in the local electrical resistivity.

![Figure 2. Cell voltage variation during constant current electrolysis at 3.5 A in high silica (A) and high calcia (B) slag for 4 hours.](image)

The oxygen content of the outlet gas has been quantified during a separate electrolysis experiment in high silica slag, as reported in Figure 3. The classical bell-shape of the signal is related to the gradual filling of the analyzing system with oxygen, the concentration of which decreases more sharply when the current flow is stopped. The oxygen flow-rate is estimated from the total gas flow-rate and the measured composition. The total oxygen produced can thereby be obtained and compared with the coulombic charge passed during the experiment, leading to a calculated current efficiency of ~25%. The low current efficiency measurement is likely attributed to consumption of
electrolytically produced oxygen by the molybdenum crucible to form molybdenum oxide. However, such measurement shows that oxygen is produced at a significant rate on the iridium anodes such production being correlated to the current flow.

Figure 3. Composition of the outlet gas (average flow-rate of 150 cm³/min) in slag A during constant current electrolysis at 3.5 A for 1 hour.

Macroscopic Observations

The shape of the anode changes significantly after electrolysis in the high calcia slag, whereas no noticeable changes were observed for the iridium anode used in the high silica melt. The vertical dimension of the iridium anode in high calcia was reduced by approximately 1 mm. The weight loss of the anode is 20 times higher in the high calcia melt than in the high silica, as exemplified in Figure 4 (these estimations are minimum values as slag may be attached to the iridium anodes after electrolysis). It is also shown that this loss is not directly proportional to the electrolysis time in the high calcia melt. The recovered cathodes from both electrolytes contain significant deposit, made partly of metallic and oxide materials. A dendritic product was also observed on the cathode from the high calcia electrolyte.

Microscopic observations

Cathode. Though not the primary interest of this specific study, the cathode product has been observed and analyzed in detail, as exemplified in Figure 5. Both melts lead to a similar deposited product shape, but the overall composition determined by EDX changes significantly: the high silica slag product has a composition of Fe₀.₄₈Mo₀.₅₂ (Figure 5a), while the high calcia melt product also contains iridium, the composition being Fe₀.₄₉Ir₀.₂₃Mo₀.₂₈ (Figure 5b). In both case, the oxygen content is lower than the detection limit of the EDX analysis system, qualitatively proving the efficiency of the process to separate the oxygen from metal cations. On the high calcia cathode, EDX confirms the
dendrites identified by the naked eye do contain iridium, the dendrite formation being due to iridium deposition below its melting temperature (Figure 5c).

![Graph showing weight loss of iridium anode](image)

Figure 4. Weight loss of iridium anode, reported to the total geometric surface area, in both electrolytes as a function of electrolysis time at constant current (3.5A).

The presence of the iron/molybdenum alloy on the cathode is clearly related to the cathode substrate miscibility with the electrochemically obtained liquid metal. Furthermore, the presence of iridium is an important indication of the instability of the anode in the high calcia electrolyte: the possibility of an electrowinning-type process cannot be dismissed. By estimating the amount of iridium found in the cathodic product, and assuming the following overall reaction:

\[
\text{Ir (anode) \rightarrow Ir}^{4+} \text{(electrolyte) \rightarrow Ir (cathode)}
\]

it may be calculated that the proposed electrowinning of the iridium consumed only \(~3\%\) of the total current passed during electrolysis. Therefore, such a mechanism could exist in this process with little effect on the cathode current efficiency.

**Electrolyte.** The characterization of the bulk electrolyte reveals that iridium metal particles are present in both systems (Figure 6a and b). The size of these particles is very small (<1μm) in the high silica slag, which hinders a quantitative and reproducible analysis of their composition by EDX. The concentration and the size of these particles are much more significant in the high calcia slag, and the iridium concentration of these particles increases closer to the anode (Figure 6c). Near the anode these inclusions have a powder-like structure. The detailed analysis of these particles is presented in Table II. There is significant contamination of the dispersed iridium metal phase with iron and oxygen. Though the oxygen signal is quantitatively underestimated, the presence of an iron oxide phase hints to the mechanism responsible for the presence of iridium metal in the bulk electrolyte. Indeed, any iridium oxide phase written here IrO₂, or cation, electrochemically produced at the anode could spontaneously react with an iron suboxide...
to convert back to iridium metal while oxidizing iron to Fe(III). The following reaction is an example of this mechanism:

\[
\text{IrO}_2 + 3\text{FeO} = \text{Ir} + \text{Fe}_3\text{O}_4 \quad (\Delta G(1600^\circ C)=-271.778 \text{ kJ.mol}^{-1})
\]  \[2\]

This spontaneous thermochemical conversion, thermodynamically favored with respect to the spontaneous decomposition of iridium oxide \((\Delta G(1600^\circ C)=-83.336 \text{ kJ.mol}^{-1})\), can also occur if gaseous iridium oxide phases are introduced in the slag. These gas phases are known to be easily produced on iridium at temperatures above 1300°C in contact with dry oxygen (11). Thermodynamic calculations have been conducted using data from HSC 6.0 Database.

Figure 5. SEM observations of the cathode after electrolysis in high silica (a) and high calcia (b,c) slags.

**Anode.** The difference in anode consumption between the two electrolytes is exhibited in Figure 7a and b, where the iridium anode in the high calcia slag shows consumption on both sides at a significant level (around 200 \(\mu\)m). This consumption leads to a wave-shaped metal surface, such morphology being potentially related to gas phase generation. The bulk of the iridium reveals fractures, but these are not an artifact of the experiment and were present in the starting material. At higher magnifications for both electrolytes (Figure 7c-d), it can be seen that the iridium is detached in the form of small clusters with a shape very close to those observed in the bulk electrolyte (see Figure 6c). In the high calcia slag the anode edge closest to the cathode (Figure 8a-b) is much thinner than the edge furthest from the cathode during electrolysis, and holds a drop of finely divided metal mixed with the oxide, possibly indicating the production of a gas phase on the high current density tip.
Data from the EDX analysis of the bulk of the anode, the particles detached from the anode (larger than 3 μm), and the drop present on the tip of the anode in high calcia (Figure 8) are gathered in Table II. In both electrolytes, the bulk analysis reveals the presence of iridium metal with background level of other oxides, iron being in a similar concentration range as the other metal cations. Interestingly, the iridium particles detached from the electrode in the high calcia slag are enriched in iron and oxygen. Their composition is similar to the particles found in the bulk electrolyte, confirming the identical nature of this material and likely the same mechanism for their generation.

The increase of the corrosion rate for iridium in highly basic electrolyte may be related to iridium speciation, e.g. in aqueous electrolyte where iridate ions are expected to form in basic environment, leading to iridium dissolution (12). However, because of the fairly complex molten oxide matrix used here, the iridium anode corrosion mechanism must be placed into the context of free oxygen chemistry, together with other cations from the melt. For example, calcium iridate may be formed in high-calcia slag, leading to a potential corrosion reaction of the iridium anode (13):

\[
\text{Ir} + \text{Ca}^{2+} + 3\text{O}^{2-} = \text{CaIrO}_3(s) + 4\text{e}^- \quad (E=0.91 \text{ V}/\text{Fe})
\]  

\ solutio

\[ \text{[3]} \]
Figure 7. SEM observations of iridium anode after electrolysis in high silica (a, c) and high calcia (b, d).

Table II. Average chemical analysis (at%, on 3 to 10 spots) of iridium composition in each slag phase measured by SEM/EDX.

<table>
<thead>
<tr>
<th>Element</th>
<th>High silica slag (Slag A)</th>
<th>High calcia slag (Slag B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iridium anode (bulk)</td>
<td>Iridium particle near anode</td>
</tr>
<tr>
<td>O</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Mg</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Al</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Si</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td>Ca</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Ir</td>
<td>92.1</td>
<td>87.8</td>
</tr>
</tbody>
</table>
Furthermore, iridium metal can be unstable in presence of oxygen at high temperature, possibly leading to its sublimation, possibly by the following reactions:

\[
\begin{align*}
\text{Ir} + \text{O}^{2-} & = \text{IrO(g)} + 2\text{e}^- \quad (E=2.38 \text{ V/Fe}) \quad \text{[4a]} \\
\text{Ir} + 2\text{O}^{2-} & = \text{IrO}_2(g) + 4\text{e}^- \quad (E=1.50 \text{ V/Fe}) \quad \text{[4b]} \\
\text{Ir} + 3\text{O}^{2-} & = \text{IrO}_3(g) + 6\text{e}^- \quad (E=0.92 \text{ V/Fe}) \quad \text{[4c]}
\end{align*}
\]

The formation of the highly stable iridium solid oxide, \(\text{Ir(IV)}\), cannot be dismissed, written as:

\[
\text{Ir} + 2\text{O}^{2-} = \text{IrO}_2(s) + 4\text{e}^- \quad (E=1.27 \text{ V/Fe}) \quad \text{[5]}
\]

Finally, oxygen evolution (according to 6) is the only desired reaction for an MOE inert-anode:

\[
2\text{O}^{2-} = \text{O}_2(g) + 4\text{e}^- \quad (E=0.75 \text{ V/Fe}) \quad \text{[6]}
\]

Altogether, our findings support a fundamental role of the chemistry of the electrolyte on the iridium stability, and only reactions (3) and (4c) should directly be favored with respect to (6) in highly basic slag in which concentrations of \(\text{O}^{2-}\) and \(\text{Ca}^{2+}\) are higher.
Cell voltages are evaluated considering a constant cathode reaction used as reference 
\((\text{FeO}+2e^- \rightarrow \text{Fe}^0 + \text{O}_2^-)\) and an anodic reaction as written in equations, using Gibbs energy 
of the stoichiometric compounds compiled in HSC Database

Conclusion

Iridium is seen as a candidate for oxygen evolution study in molten oxide electrolyte
only in acidic slags. Our results reveal that corrosion is dramatically increased in high-
calcia slags, under similar process conditions. This study points out several chemical and 
electrochemical reactions that must be taken into account to develop an inert anode 
material based on iridium for molten oxide electrolysis, of which the slag composition is 
seen to be of crucial importance.

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