Experimental Study of the Electrolysis of Silicate Melts

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Abstract

Melting and electrolyzing lunar silicates yields oxygen gas and potentially can be practiced in situ to produce oxygen. With the present experiments conducted with simulant oxides at 1425-1480 °C, it was ascertained that oxygen can be obtained anodically at feasible rates and current efficiencies. An electrolysis cell was operated with platinum anodes in a sealed vessel, and the production of gas was monitored. In these electrolysis experiments, stability of anodes remained a problem, and iron and silicon did not reduce readily into the liquid silver cathode.
Principles of Magma Electrolysis
Raw materials readily available on the lunar surface are generally oxides. They contain copious amounts of oxygen for potential use as propellant or for life support. Elemental oxygen can be obtained by chemical oxidation or electrochemically. Melting available silicates and electrolyzing this melt appears particularly attractive because of its conceptual simplicity. This approach has been called "magma electrolysis". Its fundamentals have been studied in recent years at Washington University in St. Louis[1,2,3].

Lunar raw materials for in-situ utilization include primarily silicates that contain various amounts of other oxides such as aluminum oxide, calcium oxide, magnesium oxide, iron (Fe²⁺) oxide, titanium oxide, etc. These silicates can be melted at temperatures of 1400 °C and higher, and electrolyzed to reduce metal components at the cathode,

\[ \text{Me}_x\text{O}_y + 2y e^- \rightarrow x \text{Me} + y \text{O}_2^-, \]

and to oxidize oxides to oxygen at the anode,

\[ \text{Me}_x\text{O}_y - 2y e^- \rightarrow x \text{Me}^{(2y/κ)^+} + y/2 \text{O}_2. \]

When the electrolysis is conducted to produce oxygen as the product of primary interest, the melt can be partially electrolyzed and residual oxides discarded, possibly along with some metallic products. Reduction potentials and mass transport conditions determine which metals will be preferentially reduced.

The selection of conditions has been discussed previously[4,5], also advantages and disadvantages of the process[6].

The feasibility of "magma electrolysis" to produce lunar oxygen rests, we believe at this stage, upon the following key issues:

(1) Electrolyte Conductivity. To obtain acceptable production rates at reasonable space-time yields and energy efficiency, the specific conductance of the molten material must be high and remain high during the electrolysis.

(2) Current Efficiency. The process must have an acceptable faradaic yield. Low current efficiencies may result from reoxidation of cathode products; metals often are soluble in molten
electrolytes and solid metallic products may become dispersed in them, then react upon reaching anode products. Current efficiencies can also be affected by the oxidation of lower valent species to higher valent ones, as in the case of Fe\textsuperscript{II} to Fe\textsuperscript{III}. The presence of two- and three-valent iron may lead to electronic conductance of the electrolyte.

(3) **Separation of Products.** Products need to be removed from the system. This applies to the oxygen gas as well as to metals that form at the cathode.

(4) **Stability of Electrode and Containment Materials.** Because high temperatures and aggressive melts are involved, materials requirements are non-trivial.

### Goal of the Present Experimentation
The experimentation focused primarily on the anodic current efficiency in the electrolysis of molten silicates: how much oxygen is actually produced? Oxygen evolved anodically was to be collected in a closed system and the production rate evaluated quantitatively. The size was to exceed that of previous small-scale approaches, in dimensions as well as production rates.

### Experimental Equipment and Procedures
The main challenge consists in capturing the oxygen quantitatively, without any losses towards the outside and without any reaction with cell parts such as metals or carbon. By designing a system with minimal overpressure and relying on ceramic components for parts exposed to high temperatures wherever possible, we succeeded to conduct experiments producing the desired information. Nevertheless, the experimentation had its difficulties and not every run was productive.

An electrolysis cell was placed in an alumina tube, as represented in Figure 1. Two alumina crucibles contained the electrolyte and the liquid metal cathode. Amounts of about 270 g silver were used for the cathode, part of this metal placed as cathode connection in the space between inner and outer alumina crucible. Four small holes were drilled in the inner containment crucible to allow current to pass. Electrical connection to the cathode metal was made by means of a shielded graphite rod. The electrolyte was contained in the inner crucible above the metal pad. A platinum sheet anode was suspended into the electrolyte.

Silver was selected as the cathode metal because of its high density, its convenient melting point (a liquid cathode substrate is preferred), and its absence in the electrolyte. A ferrosilicon cathode may eventually be used in magma electrolysis, but the employment of such a composition would have distorted some of our results because of silicon reacting with electrolyte components, mainly
Figure 1  Experimental Arrangement to Determine Gas Anodically Produced in the Electrolysis of Molten Oxides ("Magma Electrolysis")
reducing iron oxide, and cathodic current efficiencies for iron and silicon could not have been
examined.

As shown in Figure 2, the cell arrangement was placed in a sealed alumina tube which was
connected to an apparatus measuring changes in the gas volume. The cell was kept in a DELTECH
furnace at the desired temperature, typically at 1425-1460 °C. The tube protruded out of the high-
temperature furnace and was sealed on top with a stainless steel lid. Provisions were made to fill
the tube with inert gas (helium was preferred over argon or nitrogen because argon was the carrier
gas in the gas chromatographic analysis and the presence of nitrogen was used to indicate leakage
of air into the system).

The arrangement was assembled at room temperature. Before electrolysis was started, it was
brought to the desired temperature. After melting of the metal and oxides, thermal equilibrium was
established. Electrolysis was initiated and changes of the gas volume in the sealed system
determined, using a burette and a leveling device. Gas samples could be taken for analysis.

Currents applied were normally about 2 A. With a platinum sheet anode of 1.5 cm x 1.0 cm,
immersed 1.0 cm into the electrolyte, the nominal anodic current density was 1 A/cm². Larger
anodes were used in a few late experiments, increasing currents to 5 A and reducing nominal
current density to 0.5 A/cm². At the current of 2 A, 0.6 g oxygen would be produced pr hour at 100
% faradaic current efficiency. This corresponds to a volume of 2600 ml at 1425 °C or 456 ml at 25
°C. The targeted duration of a single experiment was usually 6 hours.

While the measurement of gas volume changes was the main indication for oxygen production,
additional information was obtained from an analysis of the gas. A sample was collected, at the end
of the experiment, in a gas sampling device and submitted to the Pittsburgh Applied Research
Corporation for analysis. Complete mixing of the gas contained inside and outside the high-
temperature vessel and a value for the total gas volume were assumed to calculate the amount of
oxygen produced. Corrections were made for the formation of CO₂ by reaction with the graphite
of the cathode connection and for the penetration of air, as indicated by the presence of nitrogen.
In some cases, escape of helium from the gas mouse after sampling was suspected, this problem
being alleviated by switching from a plastic to a glass device.

Cathodic current efficiencies based on metallic products collected in the silver cathode were also
Figure 2  Experimental Arrangement to Determine Gas Anodically Produced in the Electrolysis of Molten Oxides ("Magma Electrolysis")
determined. Following solidification of the melt, the metal was physically separated from the alumina crucibles and remaining electrolyte. The metal then was remelted and sampled with a quartz tube. Samples were analyzed, again, by the Pittsburgh Applied Research Corporation.

Selection of Electrolytes

Experiments were performed with four electrolyte compositions:

1. Minnesota Lunar Simulant, MLS-1
2. Composition B, selected to represent a steady state electrolyte; partially electrolyzed basaltic ore (composition proposed by Haskin and Colson as representative), with all the iron oxide and 50 percent of the silicon oxide reduced, then 10 percent of fresh ore added (Fe\textsubscript{3}O\textsubscript{4} was substituted for FeO)
3. Composition C, free from iron oxide, representing an aluminosilicate slag composition remaining as electrolyte according to Haskin and Colson, minor constituents not considered
4. Cryolite, Na\textsubscript{3}AlF\textsubscript{6}, with 10 % Al\textsubscript{2}O\textsubscript{3} added; used for comparison purposes; electrolysis at 1000 °C

The compositions are given in Table 1. While MLS-1 was used as received from the University of Minnesota, the other combinations were synthesized from commercially available chemicals.

Table 1. Composition of Electrolytes

<table>
<thead>
<tr>
<th>Component</th>
<th>MLS-1 (A)</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>43.86 wt%</td>
<td>41.25 wt%</td>
<td>37.08 wt%</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>13.68 wt%</td>
<td>21.36 wt%</td>
<td>18.64 wt%</td>
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<tr>
<td>FeO</td>
<td>13.40 wt%</td>
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<td></td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>2.60 wt%</td>
<td>1.58 wt%</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>6.32 wt%</td>
<td>0.25 wt%</td>
<td>16.52 wt%</td>
</tr>
<tr>
<td>MgO</td>
<td>6.68 wt%</td>
<td>17.62 wt%</td>
<td>27.77 wt%</td>
</tr>
<tr>
<td>CaO</td>
<td>10.13 wt%</td>
<td>17.95 wt%</td>
<td></td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>2.12 wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>0.28 wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>0.20 wt%</td>
<td></td>
<td></td>
</tr>
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</table>
Experimental Results
The experimental results are summarized in Table 2.

Table 2. Summary of Experimental Results

<table>
<thead>
<tr>
<th>Expt</th>
<th>Electrolyte</th>
<th>Duration</th>
<th>CE by Volume</th>
<th>CE by O₂ %</th>
<th>CE by Metal</th>
<th>Anode Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-01</td>
<td>A</td>
<td>2hr 5min</td>
<td>3.2%</td>
<td>---</td>
<td>---</td>
<td>no change</td>
</tr>
<tr>
<td>3-02</td>
<td>C</td>
<td>6 hrs</td>
<td>30.9%</td>
<td>---</td>
<td>---</td>
<td>small chg</td>
</tr>
<tr>
<td>3-03</td>
<td>C</td>
<td>6hr 12min</td>
<td>42.2%</td>
<td>---</td>
<td>19.1%</td>
<td>1/3 gone</td>
</tr>
<tr>
<td>3-05</td>
<td>B</td>
<td>6 hrs</td>
<td>27.7%</td>
<td>---</td>
<td>---</td>
<td>destroyed</td>
</tr>
<tr>
<td>3-08</td>
<td>C</td>
<td>5hr 30min</td>
<td>20.1%</td>
<td>14.7%</td>
<td>63.7%</td>
<td>1/3 gone</td>
</tr>
<tr>
<td>3-09</td>
<td>cryolite</td>
<td>2hr 45min</td>
<td>64.3%</td>
<td>---</td>
<td>59.0%</td>
<td>no change</td>
</tr>
<tr>
<td>3-10</td>
<td>cryolite</td>
<td>3hr 40min</td>
<td>105.9%</td>
<td>---</td>
<td>112.0%</td>
<td>no change</td>
</tr>
<tr>
<td>3-11</td>
<td>A</td>
<td>6 hrs</td>
<td>0.0%</td>
<td>---</td>
<td>---</td>
<td>no change</td>
</tr>
<tr>
<td>3-12</td>
<td>B</td>
<td>2hr 10min</td>
<td>76.5%</td>
<td>78.6%</td>
<td>39.7%</td>
<td>destroyed</td>
</tr>
<tr>
<td>3-13</td>
<td>C</td>
<td>1hr 18min</td>
<td>0.0%</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3-15</td>
<td>C</td>
<td>5hr 30min</td>
<td>49.0%</td>
<td>77.6%</td>
<td>56.3%</td>
<td>2/3 gone</td>
</tr>
<tr>
<td>3-16</td>
<td>B</td>
<td>2hr 29min</td>
<td>71.1%</td>
<td>112.8%</td>
<td>82.1%</td>
<td>destroyed</td>
</tr>
<tr>
<td>3-17</td>
<td>C</td>
<td>4hr 58min</td>
<td>21.9%</td>
<td>10.3%</td>
<td>42.6%</td>
<td>1/4 gone</td>
</tr>
<tr>
<td>3-18</td>
<td>B</td>
<td>2hr 12min</td>
<td>70.7%</td>
<td>105.3%</td>
<td>90.6%</td>
<td>destroyed</td>
</tr>
<tr>
<td>3-19</td>
<td>B</td>
<td>2hr 42min</td>
<td>75.2%</td>
<td>67.3%</td>
<td>57.3%</td>
<td>destroyed</td>
</tr>
<tr>
<td>3-20</td>
<td>B</td>
<td>1hr 40min</td>
<td>52.5%</td>
<td>37.4%</td>
<td>---</td>
<td>destroyed</td>
</tr>
</tbody>
</table>

IA-100
Current efficiencies ranging from 52 to 76 percent were obtained with composition B, a composition representing projected electrolyte composition in a cell operating at steady state. These values are quite respectable for a molten salt electrolysis of this scale. Gas volume changes appeared to be the more reliable indicator, although some reasonable agreement was generally obtained in experiments in which a glass sampling vessel had been used (polymer vessels were used in Experiments # UoA-3-16 & 18, which probably led to excessively high oxygen concentrations due to escape of helium). Electrolysis of composition B normally could be maintained for less than 3 hours, however, as the platinum anode was destroyed.

Current efficiency based on metal products was equally high, reaching 90 percent in one case. It is remarkable, however, that neither iron nor silicon were found in the silver cathode metal after electrolysis; the aluminum content corresponded to 81.3 % current efficiency, the magnesium content to 9.3 %. Evidentially there was no problem with evaporation of magnesium, as is being reported by Haskin and Colson 3.

With the iron-free electrolyte, composition C, anodic current efficiencies ranged from 20 to 49 percent. Appreciable silicon deposition, corresponding to 33 and 19 % Faradic efficiency, was only observed in two cases. Anodes lasted better in this electrolyte, although the experiments usually also had to be terminated before reaching the full 6 hours.

Anode deterioration appeared to be minimal when electrolyzing MLS-1. In this case, oxygen evolution was practically zero, probably due to the high iron oxide content which led to a different anodic reaction.

In the runs with cryolite at 1000 °C, gas current efficiencies of 64 and 106 % were obtained, values consistent with expectations, considering chemistry and accuracy of the method. Platinum anodes remained intact during the electrolysis duration of 2.75 and 3.67 hours, respectively.

**Synopsis**
Anodic production of oxygen at adequate current efficiencies was demonstrated for conditions representative of envisioned processing. High iron oxide content in the electrolyte appeared to reduce current efficiency drastically.

Contrary to expectations, iron was never found in the cathode silver, silicon only in exceptional
cases. These metals probably were reduced but remained suspended in the electrolyte. At moderate concentrations, this did not seem to affect anodic current efficiencies.

Stability of the platinum anode was unsatisfactory in all cases yielding good anodic current efficiencies. Functioning of a cathode containing iron and silicon should be studied in future efforts. A major future thrust, furthermore, should address the stability of anodes.

Acknowledgements
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References
3Colson, R.O. and L.A. Haskin. Oxygen and iron production by electrolytic smelting of lunar soil (this report).