Experimental Study of the Electrolysis of Silicate Melts

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Abstract

To produce oxygen from lunar resources, it may be feasible to melt and electrolyze local silicate ores.

This possibility was explored experimentally with synthesized melts of appropriate compositions. Platinum electrodes were employed, at a melt temperature of 1425 °C. When silicon components of the melt were reduced, the platinum cathode degraded rapidly, which prompted the substitution of a graphite cathode substrate. Discrete particles containing iron or titanium were found in the solidified electrolyte after electrolysis of 3 hours duration.

Electrolyte conductivities did not decrease substantially, but the escape of gas bubbles, in some cases, appeared to be hindered by high viscosity of the melt. Several key issues of the approach remain to be examined in further experimentation: electrolyte conductivity; current efficiency; separation of products; and stability of electrode and container materials.

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. A suitable chemical oxidation process is required to produce valuable molecular oxygen. Electrolysis of the oxides is a possibility. Melting available silicates and electrolyzing this melt appears particularly attractive because of the conceptual simplicity of this approach, which has been called "magma electrolysis". Its fundamentals have been studied in recent years at Washington University in St. Louis [1] [2].

Lunar raw materials for in-situ utilization are silicates that contain various amounts of other oxides such as aluminum oxide, calcium oxide, magnesium oxide, iron (Fe^{II}) oxide, titanium oxide, etc. These oxides can be molten, typically at temperatures of 1400 °C and higher, and electrolyzed, reducing metal components at the cathode,

$$Me_xO_y + 2y\ e^- \quad ----> \quad x\ Me + y\ O^{2-},$$
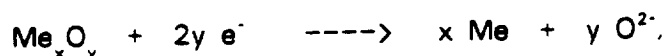
and oxidizing oxides to oxygen gas at the anode,

$$Me_xO_y - 2y\ e^- \quad ----> \quad x\ Me^{(2y/x)+} + y/2\ O_2$$
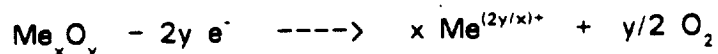
When the electrolysis is conducted to produce oxygen as the useful product of

primary interest, the melt can be partially electrolyzed and residual oxides discarded. Reduction potentials and mass transport conditions determine which metals will be preferentially reduced.

For the feasibility of "magma electrolysis" to produce lunar oxygen, we consider at this stage the following to be key issues:

(1) Electrolyte Conductivity. To maintain 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. Current efficiencies can also be affected by the oxidation of lower valent species to higher valent ones, as in the case of Fe^{II} to Fe^{III}.

(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. As high temperatures and aggressive melts are involved, materials requirements are anything else but trivial.

Work on the electrolysis of molten silicates representative of lunar resources has been performed in very-small-scale experiments at Washington University [1] [2]. Molten material suspended on a small platinum wire loop was electrolyzed, thereby avoiding problems with containment materials. Recently small crucibles of magnesium-aluminum spinel have been employed.

Some disturbing phenomena were observed in these small scale experiments. The melt resistance appeared to increase after a short time of electrolysis; retainment of gas bubbles was suspected as the main reason. In some electrolytes, gas was found trapped in the melt after its solidification, indicating relatively high viscosities and potential problems in electrolysis. It was the main goal of the present effort to see if such phenomena also exist in a somewhat larger scale and if new problems become evident.

Electrolyte Composition and Conductivity

Lunar raw material may be molten and electrolyzed in a batch mode. In such a case, the electrolyte composition changes during the course of electrolysis, which is carried to a certain point at which the residual melt is discarded. Such an approach was discussed in an earlier publication by Washington University authors [1].

Alternatively, the electrolysis may be conducted in a quasi-continuous mode. Fresh ore is added to an electrolyte which represents partially electrolyzed raw material. While components that reduce most easily are continuously electrolyzed, electrolyte is gradually removed from the system. This approach is represented in Figure 1.
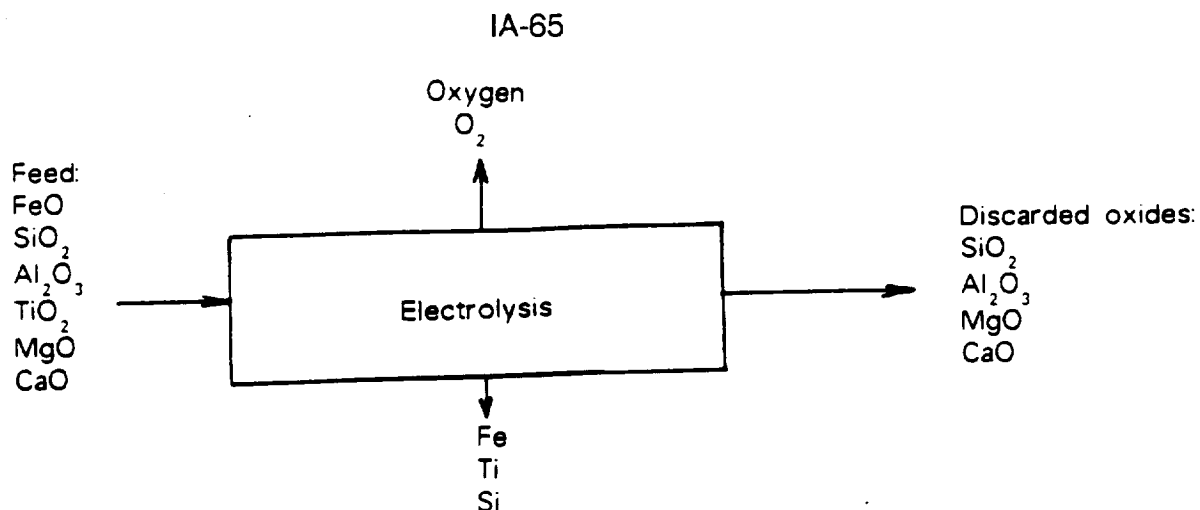
Oxygen
O_2

Feed:
FeO
SiO_2
Al_2O_3
TiO_2
MgO
CaO

Electrolysis

Discarded oxides:
SiO_2
Al_2O_3
MgO
CaO

Fe
Ti
Si

Figure 1: Continuous Electrolysis of Molten Lunar Oxides

Table 1 presents compositions that represent potential lunar raw materials: (1) a basaltic material given as typical by [1]; (2) a simulant of mare soil, as provided as MLS-1 by the University of Minnesota [3]; and (3) anorthosite considered by EMEC Consultants as raw material for the electrolysis in molten salt [4]. Table 2 gives compositions that may be expected after partial electrolysis of basaltic material, or compositions of electrolytes as they may be present in continuous electrolysis.

Electrolyte conductivities vary remarkably with composition. Haskin et al [1] give the following regression equation (for 1425 °C):

$$\ln \lambda = 5.738 - 12.6[SiO_2] - 10.0[AlO_{1.5}] - 3.7[TiO_2] + 1.89[FeO] + 0.07[MgO] - 1.25[CaO]$$

(symbols for oxides stand for mole fractions; λ in $ohm^{-1}cm^{-1}$)

Conductivity values included in Tables 1 & 2 have been calculated based on this equation.

High iron oxide contents obviously lead to relatively high conductivities. Excessive silicon contents result in low conductivities. In practice, one may expect to be operating with electrolytes of specific conductances of about 0.3 $ohm^{-1}cm^{-1}$.

Electrolysis Experiments

In our electrolysis experiments, mixtures of oxides were placed in alumina crucibles and melted in a DELTECH furnace equipped with silicon carbide heating elements. Typically, 70 g of a mixed oxide composition was used. The electrolysis was conducted between two electrodes. Platinum was used as the anode material, platinum and carbon as cathode substrate. Currents were applied at current densities approximating 0.5 A/cm². Electrolysis durations of 2-4 hours were targeted. A temperature of 1425 °C was normally maintained.

Table 1:   Composition of Lunar Raw Materials

Component	Lunar Soil [1]	MLS − 1	Anorthite
FeO	17.4 wt%	13.40 wt%	
Fe_2O_3		2.60 wt%	
SiO_2	46.2 wt%	43.86 wt%	43.2 wt%
Al_2O_3	12.6 wt%	13.68 wt%	36.6 wt%
TiO_2	2.8 wt%	6.32 wt%	
MgO	10.4 wt%	6.58 wt%	
CaO	10.6 wt%	10.13 wt%	20.2 wt%
Na_2O		2.12 wt%	
K_2O		0.28 wt%	
P_2O_5		0.20 wt%	
λ	0.320 ohm^{-1}cm^{-1}	0.304 ohm^{-1}cm^{-1}	0.029 ohm^{-1}cm^{-1}

In initial experiments, a pair of platinum electrodes was lowered into the molten silicates. Problems were encountered as the platinum bent rather readily and the original electrode geometry was not maintained; electrodes even contacted each other in some cases. This problem was alleviated when the molten electrolyte charge was raised mechanically to the mounted electrodes rather than the electrodes lowered into the melt by hand; this was possible because the furnace bottom can be raised and lowered.

In a successful experiment, a basaltic composition was electrolyzed for 3 hours at 1 A. The cell voltage decreased from an initial 8 V to 3-4 V; no increase was observed in the initial period. The anode appeared essentially unchanged after the experiment, while the cathode was brittle. The electrolysis ran smoothly, but no obviously metallic cathodic products could be found after solidification of the electrolyte.
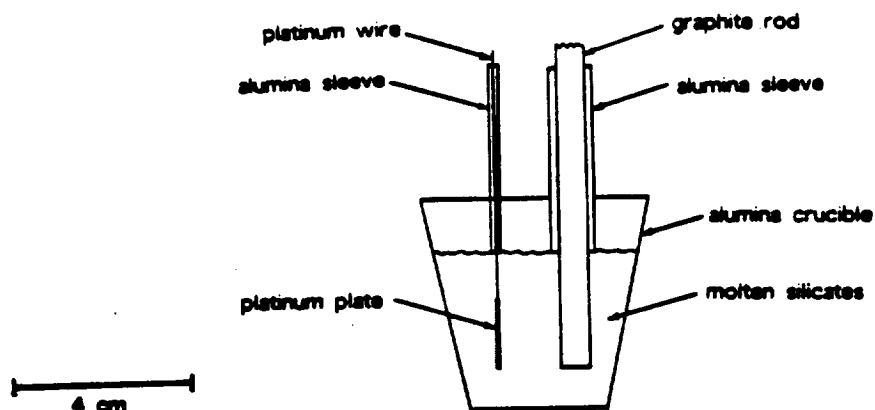
When "partially electrolyzed" compositions were used, the electrolysis could be conducted only for a short period of less than 10 minutes. The platinum cathode was attacked, presumably due to reduced silicon; electrical contact was lost.

The electrolysis could be executed successfully when a graphite cathode substrate

Table 2: Composition of Electrolytes in Continuous Electrolysis

Component	all FeO reduced	all FeO, TiO$_2$ & 50 % SiO$_2$ reduced	all FeO, TiO$_2$ & 50 % SiO$_2$ reduced; 10 % feed added
FeO	0	0	1.58 wt%
SiO$_2$	55.9 wt%	40.74 wt%	41.24 wt%
Al$_2$O$_3$	15.25 wt%	22.22 wt%	21.35 wt%
TiO$_2$	3.4 wt%	0	0.25 wt%
MgO	12.6 wt%	18.34 wt%	17.62 wt%
CaO	12.85 wt%	18.69 wt%	17.95 wt%
λ	0.073 ohm^{-1}cm^{-1}	0.286 ohm^{-1}cm^{-1}	0.313 ohm^{-1}cm^{-1}

was substituted for platinum. A graphite rod of 6 mm diameter was shielded by an alumina tube above the melt and exposed to the electrolyte as the cathode. The simple arrangement is shown in Figure 2. The cell resistance decreased by about a third during the course of a two-hour electrolysis. Some melt, however, flowed over the top of the crucible, most likely indicating hindrance in the discharge of the anode gas from the melt into the gas phase above the melt.

platinum wire — graphite rod — alumina sleeve — alumina sleeve — alumina crucible — platinum plate — molten silicates

4 cm

Figure 2: Electrolysis Arrangement with Graphite Cathode

The cell of one experiment was cut into two halves after solidification following termination of the experiment. The cross section is shown in Figure 3. It shows the alumina crucible (1), the carbon cathode (2), the thin platinum sheet anode (3) and the electrolyte (4). Voids probably formed on solidification. Marks from the cutting with a diamond-studded saw blade are visible.
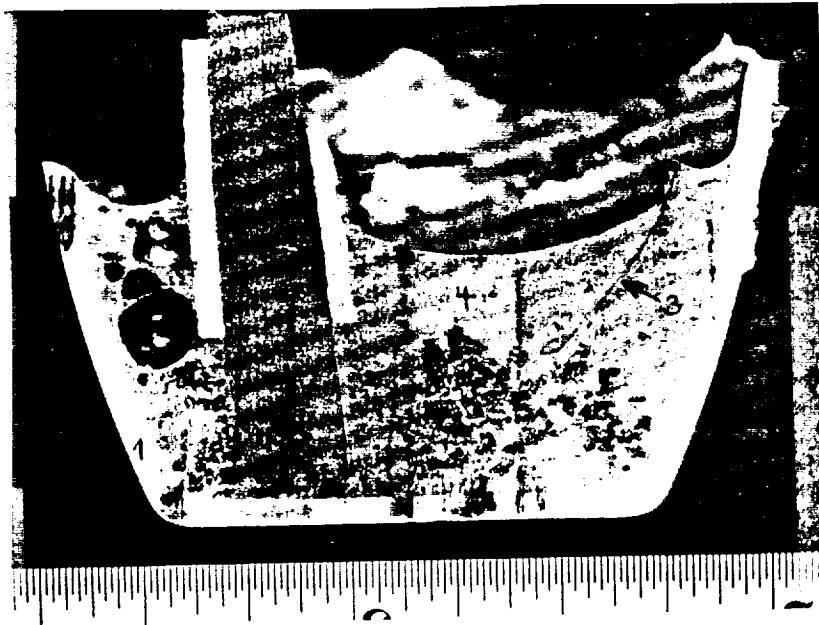

Figure 3: Cross Section of Crucible after Experiment

A cross section of the electrolysis cell prepared after the experiment was examined by scanning electron microscopy. Figure 4 shows the interface between the graphite cathode and the solidified electrolyte. No distinct metal coating on the graphite surface is indicated, although the analytical results represented in Figure 5 revealed at position 1 a somewhat higher titanium content than in the electrolyte. Particles that appear to be metal, however, were found dispersed in the electrolyte phase. Essentially pure iron was indicated at location A, essentially pure titanium at location C, while titanium with minor amounts of silicon and iron was indicated at location B. Calcium, aluminum, silicon, iron and titanium all were present in the electrolyte (position D), presumably as oxides. Evidently the electrolysis was not conducted much beyond the reduction of iron and titanium components.
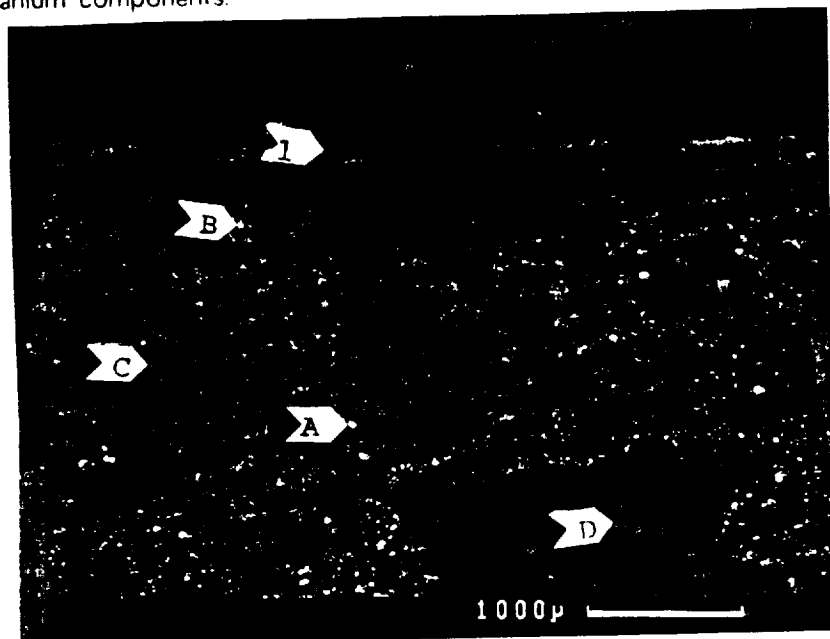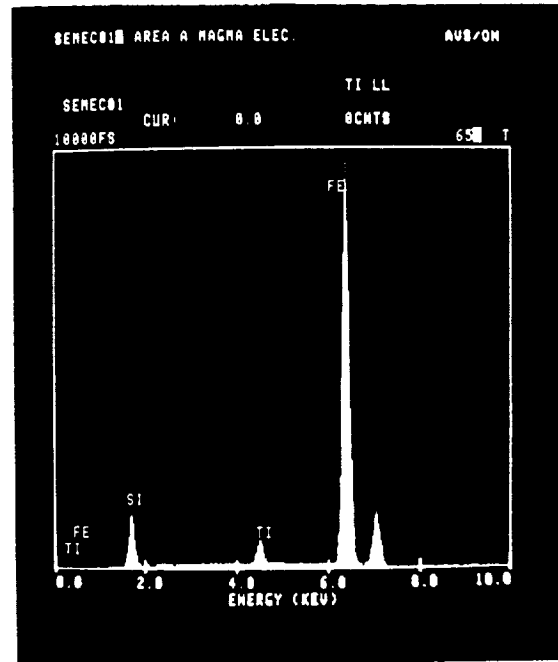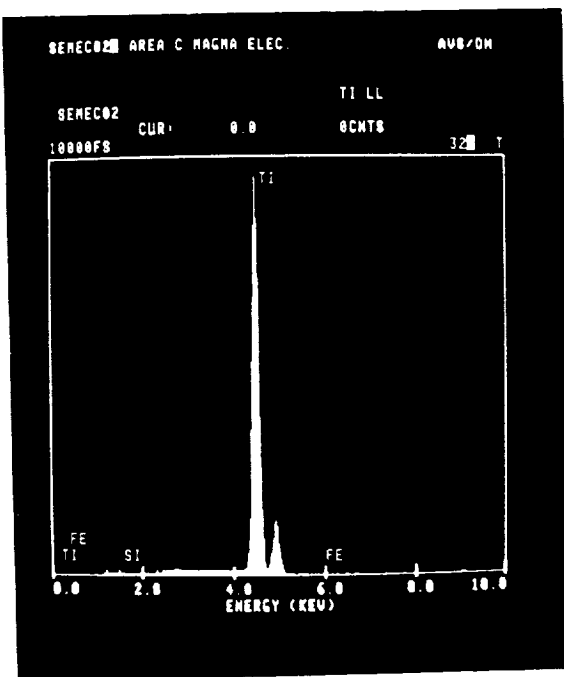
Figure 4: Scanning Electron Microscopic Image of Solidified Electrolyte After Electrolysis
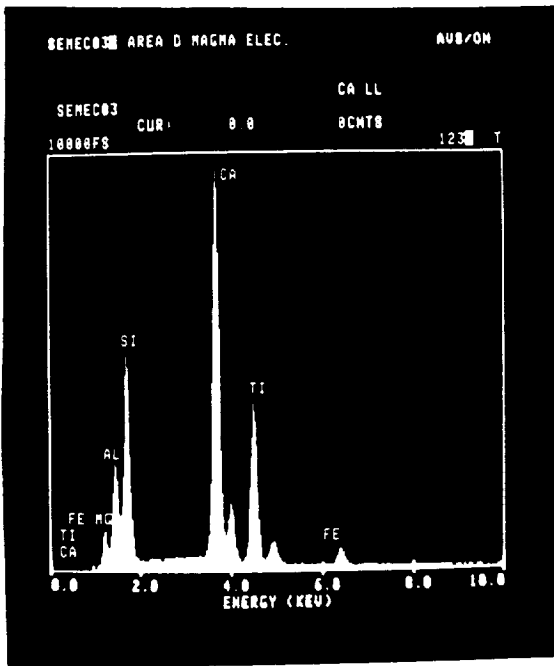
electrolyte, area D

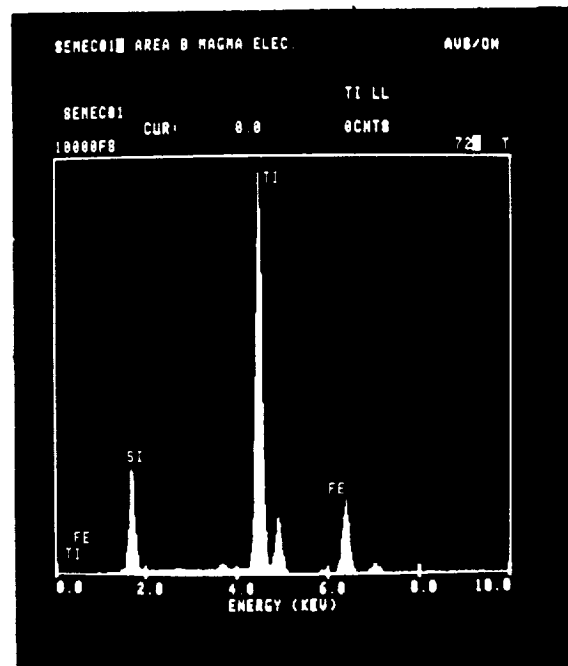particle, area A

particle, area C

particle, area B

Figure 5: EDX Spectra for Sample of Figure 4

Summary of Observations and Conclusions

The electrolysis of molten silicates could be performed smoothly between platinum electrodes if the iron oxide content was relatively high. When silicon was reduced, substitution of a graphite cathode was necessary because the platinum cathode disintegrated.

No substantial conductivity increase in the initial phase of electrolysis was observed. The cell voltage, on the contrary, showed a tendency to decline with time, possibly due to the growth of reduced species from the cathode.

Rising of the electrolyte level, presumably due to hindered discharge of anodically formed gas bubbles from the melt, was observed in electrolytes with low iron oxide content. Trapped gas bubbles could be observed in the solidified electrolyte after conclusion of the experiment.

Products with high iron and titanium content were identified, although the analytical technique did not permit the distinction between the presence of metal or oxide. Not much silicon was found in apparent metallic particles; the reduction of titanium seems to occur preferentially. The reduction of iron, the oxidation of Fe^{II} at the anode and the reoxidation of reduced metals by anodic products require further investigations.

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