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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 (Fe") 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,

$$Me_xO_y + 2y\ e^- \text{ ----> } x\ Me + y\ O^{2-},$$

and to oxidize oxides to oxygen at the anode,

$$Me_xO_y - 2y\ e^- \text{ ----> } x\ Me^{(2y/x)+} + y/2\ O_2.$$

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^{II} to Fe^{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 a 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

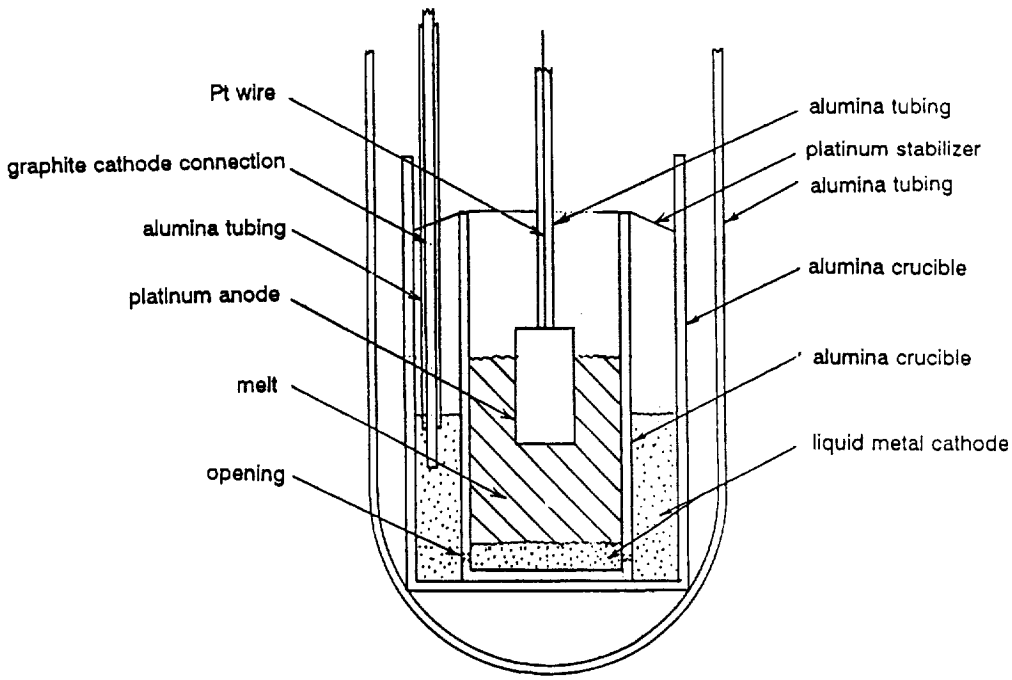

Figure 1 Experimental Arrangement to Determine Gas Anodically Produced in the Electrolysis of Molten Oxides ("Magma Electrolysis")

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/cm^2. Larger anodes were used in a few late experiments, increasing currents to 5 A and reducing nominal current density to 0.5 A/cm^2. 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 CO_2 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

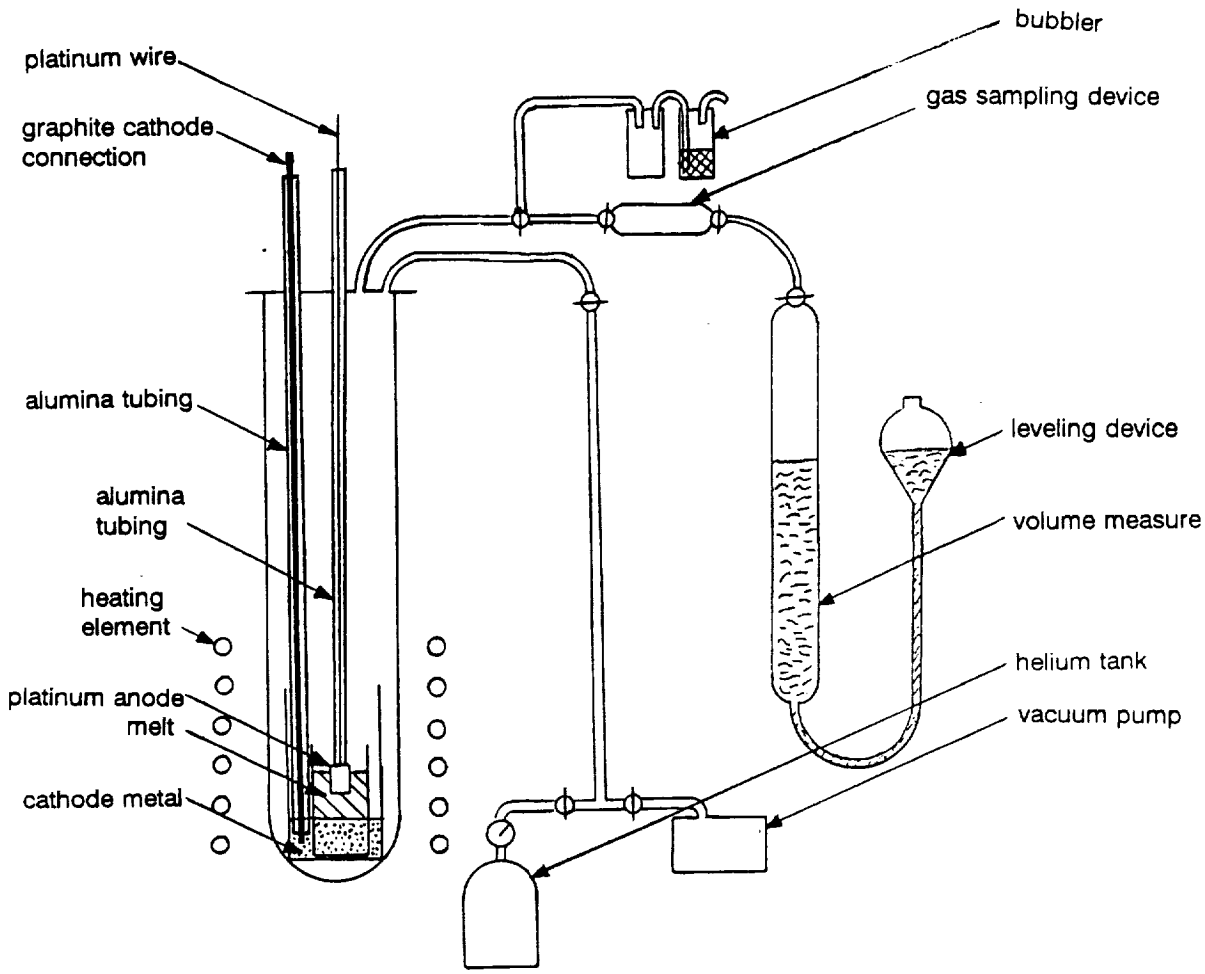

Figure 2 Experimental Arrangement to Determine Gas Anodically Produced in the Electrolysis of Molten Oxides ("Magma Electrolysis")

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[5]; partially electrolyzed basaltic ore (composition proposed by Haskin and Colson[7] as representative), with all the iron oxide and 50 percent of the silicon oxide reduced, then 10 percent of fresh ore added (Fe_3O_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[1], minor constituents not considered

(4) Cryolite, Na_3AlF_6, with 10 % Al_2O_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

Component	MLS-1 (A)	B	C
SiO_2	43.86 wt%	41.25 wt%	37.08 wt%
Al_2O_3	13.68 wt%	21.36 wt%	18.64 wt%
FeO	13.40 wt%		
Fe_2O_3	2.60 wt%		
Fe_3O_4		1.58 wt%	
TiO_2	6.32 wt%	0.25 wt%	16.52 wt%
MgO	6.68 wt%	17.62 wt%	27.77 wt%
CaO	10.13 wt%	17.95 wt%	
Na_2O	2.12 wt%		
K_2O	0.28 wt%		
P_2O_5	0.20 wt%		

Experimental Results

The experimental results are summarized in Table 2.

Table 2. Summary of Experimental Results

Expt	Electrolyte	Duration	CE by Volume	CE by O_2 %	CE by Metal	Anode Results
3-01	A	2hr 5min	3.2%	---	---	no change
3-02	C	6 hrs	30.9%	---	---	small chg
3-03	C	6hr 12min	42.2%	---	19.1%	1/3 gone
3-05	B	6 hrs	27.7%	---	---	destroyed
3-08	C	5hr 30min	20.1%	14.7%	63.7%	1/3 gone
3-09	cryolite	2hr 45min	64.3%	---	59.0%	no change
3-10	cryolite	3hr 40min	105.9%	---	112.0%	no change
3-11	A	6 hrs	0.0%	---	---	no change
3-12	B	2hr 10min	76.5%	78.6%	39.7%	destroyed
3-13	C	1hr 18min	0.0%	---	---	----
3-15	C	5hr 30min	49.0%	77.6%	56.3%	2/3 gone
3-16	B	2hr 29min	71.1%	112.8%	82.1%	destroyed
3-17	C	4hr 58min	21.9%	10.3%	42.6%	1/4 gone
3-18	B	2hr 12min	70.7%	105.3%	90.6%	destroyed
3-19	B	2hr 42min	75.2%	67.3%	57.3%	destroyed
3-20	B	1hr 40min	52.5%	37.4%	---	destroyed

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 % Faradaic 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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