

# LUNAR PRODUCTION OF OXYGEN BY ELECTROLYSIS

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## Abstract

Two approaches to prepare oxygen from lunar resources by direct electrolysis are discussed. Silicates can be melted or dissolved in a fused salt and electrolyzed, with oxygen evolved at the anode. Direct melting and electrolysis is potentially a very simple process, but high temperatures of 1400 - 1500 °C are required, which aggravates materials problems. Operating temperatures can be lowered to about 1000 °C by employing a molten salt flux. In this case, however, losses of electrolyte components must be avoided. Experimentation on both approaches is progressing.

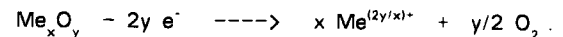
## Oxygen from Lunar Resources

Molecular oxygen may be prepared from oxides by electrolysis. In the absence of volatile oxides, solid oxides may be used. Such oxides are readily available on the lunar surface, mainly as silicates of various compositions. Lunar soil may be regarded as an already adequately comminuted raw material. Highland soils are anorthositic, feldspar-like, with compositions similar to the one given as an example in Table 1. Soils of the mare region have a more basaltic character and are represented in Table 1 by a composition indicated by Washington University authors [1] as representative.

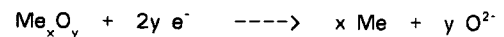
Table 1. Compositions of Lunar Soils

	Anorthositic Soil [2]	Basaltic Soil [1]
SiO <sub>2</sub>	44.9 wt%	46.2 wt%
Al <sub>2</sub> O <sub>3</sub>	27.6 wt%	12.6 wt%
FeO	5.03 wt%	17.4 wt%
TiO <sub>2</sub>	0.55 wt%	2.8 wt%
MgO	5.35 wt%	10.4 wt%
CaO	15.8 wt%	10.5 wt%
Na <sub>2</sub> O	0.39 wt%	
K <sub>2</sub> O	0.10 wt%	

In the electrolytic decomposition of the oxides, oxygen gas is produced at the positive electrode, the anode. The reaction may be formulated as follows:



Metallic components, meanwhile, are reduced at the cathode:



Various metals are reduced with different ease. Theoretical decomposition potentials for the oxides can be calculated from thermodynamic data, but they are modified as the oxides combine to mixed oxide compounds. For the major components of the oxides discussed, the following order of decreasing (more negative) cathodic deposition potential appears to exist:



To produce oxygen, the cathodic products may be of no substantial interest and may even be discarded. Silicon and aluminum, on the other hand, may be the products of major interest. Depending on the desirability to produce and collect the metals, the process may be refined to various degree [3].

Two major approaches to the electrolysis of lunar oxides are being explored: (1) a fused salt electrolysis in which the oxides are dissolved in a molten salt (flux) and (2) a molten silicate electrolysis in which the oxides are melted and the melt electrolyzed.

## Fused Salt Electrolysis

Lunar soil may be dissolved in a suitable electrolyte of molten fluorides and electrolyzed. It is important that all components added to the electrolyte are removed again from the system. In the approach envisioned by EMEC Consultants, this is accomplished by complete electrolysis (separation of some components as undecomposed oxides would also be possible). Electrolysis conditions are such that the component most difficult to reduce reacts. As this component is calcium, a cathode potential, therefore, is maintained which permits deposition of calcium; the other metals are co-reduced at the rate they reach the cathode, i.e. at the mass-transport-limited rate. This approach has, thus, been called a "calcium-plus electrolysis".

Calcium fluoride, with a very high theoretical decomposition voltage, would be a desirable electrolyte, but its melting point is high. Also metal solubilities leading to current

efficiency losses would be excessive. A mixture of calcium fluoride and lithium fluoride is preferable as electrolyte, as added lithium fluoride reduces operating temperatures. The presence of lithium fluoride, however, leads to a cathodic co-deposition of lithium which has to be recovered in an auxiliary metal separation step, presumably by vacuum distillation.

Oxygen is evolved at the anode as a gas. Some electrolyte components evaporate into this gas but may be retained by process feed through which the off-gases are bled, similar to the recovery of fluorine values in the fume treatment of commercial aluminum production. Traces of sulfur dioxide may remain with the oxygen and should not affect the performance of the oxygen as propellant. It may be possible to obtain oxygen feasible for life support by simple reevaporation of liquefied oxygen.

The envisioned molten salt electrolysis process is summarized in Figure 1. Experiments on the process are being conducted at EMEC Consultants.

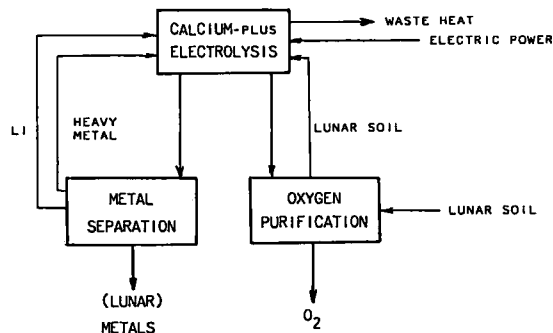


Figure 1. "Calcium-plus Electrolysis" to Produce Oxygen

#### Molten Silicate Electrolysis

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 2.

A cell design for such an electrolysis, with a molten silicon-iron cathode, has been suggested by McCullough and Mariz [4].

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

$$\ln \lambda = 5.738 - 12.6[\text{SiO}_2] - 10.0[\text{AlO}_{1.5}] - 3.7[\text{TiO}_2] + 1.89[\text{FeO}] + 0.07[\text{MgO}] - 1.25[\text{CaO}]$$

( $\lambda$  in  $\text{ohm}^{-1}\text{cm}^{-1}$ ; symbols for oxides stand for mole fractions).

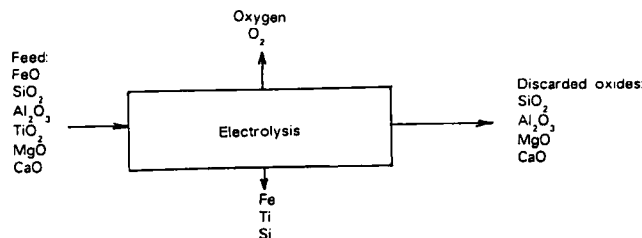


Figure 2. Continuous Electrolysis of Molten Oxides

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

So-called "magma electrolysis" experiments have been conducted and reported by L. A. Haskin and his co-workers at Washington University. They gathered essential basic data on the electrolyte properties and electrolyzed small molten charges suspended in platinum wire loops. Recently, experiments were conducted in small spinel crucibles. EMEC Consultants started investigations using alumina crucibles, a platinum anode and a graphite cathode. Cathodic deposits will be examined and several anode candidates and other materials tested in future work.

#### Comparison of Two Direct Electrolysis Approaches

In one approach, the silicates are dissolved in molten salt solvents and electrolyzed. In the other approach, the lunar ore is melted and the melt electrolyzed. Both approaches have favorable characteristics and disadvantages. A summary is given in Table 2.

Cell voltage and current efficiency determine the specific consumption of electric energy by the process. While the molten salt electrolysis is designed to operate at a cell voltage sufficient to decompose CaO, the silicate electrolysis may be conducted at lower theoretical decomposition voltages. Polarization losses are expected to be relatively low in both cases, probably below 0.25 V at anode and cathode combined. The significance of the electrolyte conductance depends to a large extent on the cell design. If one uses a liquid cathode, an anode-to-cathode distance is likely to measure at least 2 cm. Ohmic losses also depend on the current density -- assumed at  $0.6 \text{ A/cm}^2$  -- which, on the other hand, determines the productivity of the cell, along with the faradaic current efficiency.

Based on above assumptions, a specific energy consumption of 14.3 kWh per kg  $\text{O}_2$  produced is calculated

Table 2. Characteristics of Direct Electrolysis Approaches

	<u>Fused Salt Electrolysis</u>	<u>Molten Silicate Electrolysis</u>
Temperature *	1,000 °C	1,425 °C
Electrolyte conductance *	1.5 ohm <sup>-1</sup> cm <sup>-1</sup>	0.3 ohm <sup>-1</sup> cm <sup>-1</sup>
Ohmic voltage loss **	0.8 V	4.0 V
Decomposition voltage	sufficient to reduce calcium ( $V_{\Delta G_{CaO}} = 2.58 \text{ V}$ )	sufficient to reduce silicon ( $V_{\Delta G_{SiO_2}} = 1.58 \text{ V}$ )
Polarization losses *	0.25 V	0.25 V
Total cell voltage	3.6 V	5.8 V
Current efficiency *	85 %	75 %
Estimated consumption of electric power	14.3 kWh per kg O <sub>2</sub> produced	26.0 kWh per kg O <sub>2</sub> produced
Theoretical minimal energy consumption	12.06 kWh per kg O <sub>2</sub>	9.1 kWh per kg O <sub>2</sub> (calculated for SiO <sub>2</sub> )
Completeness of electrolysis	all components of feed must be electrolyzed	partial electrolysis permitted
Separation of cathode products	liquid cathode probably a necessity	not required, but reoxidation of suspended solids by oxygen may be a problem
Electrolyte losses	fluorides recovered by adsorption on cell feed	none
Recovery of electrolyte constituents from cathode products	requires an auxiliary process step	not required
Stability of materials (anodes, container, conductors)	stability problems similar to terrestrial processes	environment particularly aggressive due to high temperature
Resource selectivity	not selective	possibly some selectivity due to material stability requirements

\* approximate and/or estimated values

\*\* projected based on current density of 0.6 A/cm<sup>2</sup> and interelectrode distance of 2 cm

for the molten salt electrolysis, 26.0 kWh/kg for the silicate electrolysis. The second figure, however, would be reduced to approximately the lower value if one would succeed in reducing the interelectrode distance to 1 cm for the silicate electrolysis.

The necessity to conserve all electrolyte components is a severe handicap for the molten salt process. It leads to the requirement of additional process steps such as the treatment of the cathode product.

Materials problems exist for both oxygen production processes discussed here, although they are compounded at the high temperatures of the molten silicate approach.

Such problems are not entirely new, as the lack of ideal materials is largely responsible for the relatively low energy efficiency of the commercial aluminum smelting process. Research on oxygen-evolving anodes to replace the carbon anodes in aluminum production is in progress [5] [6] [7] [8].

It is premature to assess one of the two approaches as more promising than the other. Only further investigations of the process details will clarify the magnitude of problems and the viability of envisioned solutions. On the near term, the study of anode candidates for both process variants appears particularly appropriate.

### Other Approaches

Ilmenite reduction with hydrogen is practiced in the Carbotek process [9]. This process includes an electrochemical step, as the water produced by the reaction of hydrogen with ferrous oxide is electrolyzed. An electrolysis at high temperatures is proposed but has not been explored in Carbotek's experimental work.

### Required Process Development

There does not appear to be a clearly favored process to produce lunar oxygen at this time. All approaches discussed above include unconventional process elements with various degree of uncertainty regarding their technical feasibility. Additional research is required. Materials stability problems need to be addressed. In particular, a suitable anode for the evolution of oxygen needs to be identified. Such work is in progress at EMEC Consultants.

Although conceptual work has progressed, more such work is needed. After investigating the chemistry of individual process steps, their demonstration on the bench scale shall be planned. It is estimated that 8 to 12 years of additional work will be required before a successful pilot demonstration may be undertaken [10]. Time periods for the development of new processes or process variants in terrestrial extractive metallurgy, which is directly related to the discussed approaches, are considerable. Time and effort necessary to develop a lunar oxygen extraction process should not be underestimated.

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