FROM OXYGEN GENERATION TO METALS PRODUCTION:
IN SITU RESOURCE UTILIZATION BY MOLTEN OXIDE ELECTROLYSIS

Deepak Khetpal, **Andrew C. Ducret, and Donald R. Sadoway***

Massachusetts Institute of Technology

For the exploration of other bodies in the solar system, electrochemical processing is arguably the most versatile technology for conversion of local resources into usable commodities: by electrolysis one can, in principle, produce (1) breathable oxygen, (2) silicon for the fabrication of solar cells, (3) various reactive metals for use as electrodes in advanced storage batteries, and (4) structural metals such as steel and aluminum. Even so, to date there has been no sustained effort to develop such processes, in part due to the inadequacy of the database. The objective here is to identify chemistries capable of sustaining molten oxide electrolysis in the cited applications and to examine the behavior of laboratory-scale cells designed to generate oxygen and to produce metal.

The basic research includes the study of the underlying high-temperature physical chemistry of oxide melts representative of lunar regolith and of Martian soil. To move beyond empirical approaches to process development, the thermodynamic and transport properties of oxide melts are being studied to help set the limits of composition and temperature for the processing trials conducted in laboratory-scale electrolysis cells. The goal of this investigation is to deliver a working prototype cell that can use lunar regolith and Martian soil to produce breathable oxygen along with metal by-product. Additionally, the process can be generalized to permit adaptation to accommodate different feedstock chemistries, such as those that will be encountered on other bodies in the solar system.

The expected results of this research include (1) the identification of appropriate electrolyte chemistries; (2) the selection of candidate anode and cathode materials compatible with electrolytes named above; and (3) performance data from a laboratory-scale cell producing oxygen and metal. On the strength of these results it should be possible to assess the technical viability of molten oxide electrolysis for *in situ* resource utilization on the Moon and Mars. In parallel, there may be commercial applications here on earth, such as new "green" technologies for metals extraction and for treatment of hazardous waste, e.g., fixing heavy metals.

Introduction

There is plenty of oxygen on the Moon to sustain life — indeed, the lunar surface is over 60% oxygen[1]. Martian soil is about 45% oxygen[2]. However, all of this is chemically bound to other elements in the form of very stable compounds. Molten oxide electrolysis is a candidate technology for exploiting local resources in order to produce breathable oxygen along with a host of valuable by-products such as silicon for use in solar cells, reactive metals for use in advanced storage batteries, and steel and aluminum for use in construction[3]. No special reagents need to be transported from earth in order to employ the technology. The only process input that needs to be furnished on site is electric power and this, presumably, can be generated either photovoltaically or by nuclear fission. Furthermore, it has been shown that molten

*Corresponding author e-mail: dsadoway@mit.edu

oxide electrolysis has potential for treating certain forms of hazardous waste produced by the metals and chemicals industries[4]. This shows that the process has the flexibility to be adaptable to different feedstocks, an attribute making it attractive for use with the resources available on the Moon or Mars.

Molten oxide electrolysis is an extreme form of molten salt electrolysis, a technology that has been producing tonnage metal for over 100 years; aluminum, magnesium, lithium, sodium, and the rare-earth metals are all produced in this manner. What sets molten oxide electrolysis apart is its ability to produce oxygen gas at the anode. No contemporary electrolytic technology can do this. Indeed, in the light of the push to reduce greenhouse gas emissions in the metals industry one of the greatest challenges for the aluminum industry is the replacement of the consumable carbon anode (which produces CO_2) with a nonconsumable anode which would produce oxygen[5]. So molten oxide electrolysis then both avoids the use of molten halide electrolytes and enables the production of oxygen gas.

Figure 1 shows how iron and oxygen might be produced by the proposed technology[4]. The electrolyte in this case is a multicomponent solution consisting of iron oxide and other oxides, such as silica, alumina, magnesia, and calcia. All of these oxides are highly abundant in the lunar regolith[1] and Martian soil[2]. The cathode is a pool of molten iron at the bottom of the cell. At the interface of liquid metal and electrolyte, the electrochemical reduction of iron occurs according to the following reaction:

$$Fe^{2+} \text{ (electrolyte)} + 2 \text{ e}^- \text{ (cathode)} \rightleftharpoons Fe \text{ (liquid)} \qquad [1]$$
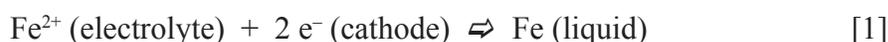
The origin of the Fe^{2+} is the iron oxide feed, which has dissolved in the molten oxide electrolyte and dissociated to form Fe^{2+} cations and O^{2-} anions. The liquid iron produced is instantly incorporated into the metal pool without the need for mass transport to another site within the cell. Thus, as the reaction proceeds, the depth of the iron pool increases. The solid member forming the floor of the cell and also acting as current collector must be made of a material that is chemically inert in contact with molten iron and also is a good electronic conductor. Materials satisfying these requirements include certain electronically conducting oxides and refractory hard metals, as well as thermally graded materials such as "cold fingers" around which iron has frozen. At the top of the cell is the anode, which acts as the current feeder. The anode must be chemically inert with respect to both oxygen gas and the molten oxide electrolyte. Evolution of oxygen occurs according to the following reaction:

$$O^{2-} \text{ (electrolyte)} \rightleftharpoons 2 \text{ e}^- \text{ (anode)} + \tfrac{1}{2} O_2 \text{ (gas)} \qquad [2]$$
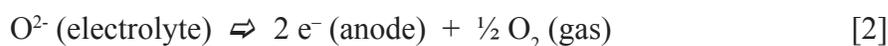
The source of O^{2-} is the iron oxide feed which has dissolved and dissociated in the molten oxide electrolyte. The anode functions as an electron sink, and the product oxygen gas evolves as bubbles on the surface of the anode and floats to the surface of the melt. Candidate anode materials include electronically conducting oxide and metals protected by an oxide film on the surface[6]. The sidewall consists of electrolyte frozen against a shell made of refractory brick. This is the electrolytic equivalent of skull melting, and is precisely the condition in a modern Hall cell producing tonnage aluminum. Feed consisting of iron oxide is added to the cell from the top. The process is continuous. Periodically, metal is removed from the cell by siphoning.

What about the engineering aspects of the reactor depicted in Figure 1? At 1800 K, the standard free energy of formation of FeO is -159 kJ/mol[7] which via the Nernst equation gives a standard decomposition

potential of 0.825 V. Although, strictly speaking, there is no formal relationship between the value of the decomposition potential (a *thermodynamic* quantity) and the value of the steady-state voltage in an industrial cell operating under conditions of controlled current, molten salt electrolysis cells (aluminum, magnesium, etc.) are observed to operate at about 2 to 3 times theoretical voltage in order to surmount *kinetic* barriers associated with the electrode reactions and to keep the electrolyte molten by Joule heating[8]. Accordingly, we can expect the cell in Figure 1 to operate at about 2 to 3 V. The value of the current will be governed by the thermal balance of the cell: the current must exceed a minimum level in order to generate adequate Joule heat to keep the electrolyte molten. Given the thermal and electrical properties of molten salts, it turns out that the threshold of thermal sustainability is 1 kA. In one hour, such a cell would produce 1.04 kg iron and 0.30 kg oxygen or 0.23 standard cubic meters oxygen. Current densities in molten salt cells are in the vicinity of 1 A cm^{-2}. This means that the anode would be on the order of 30 cm in diameter, immersed in the electrolyte to a depth of 1 cm. This translates into a rather compact device with a small footprint. Productivity scales linearly with these dimensions, i.e., to double the production of oxygen one would double the anode area and hence double the current through the cell; voltage remains unchanged. The oxygen produced at the anode bubbles though the electrolyte and rises to the top of the cell for collection. Molten iron needs to be periodically harvested, and this is typically done by siphon. All that is required to keep the oxygen coming is iron oxide (about 1.4 kg h^{-1}) and electric power (2 to 3 kVA).
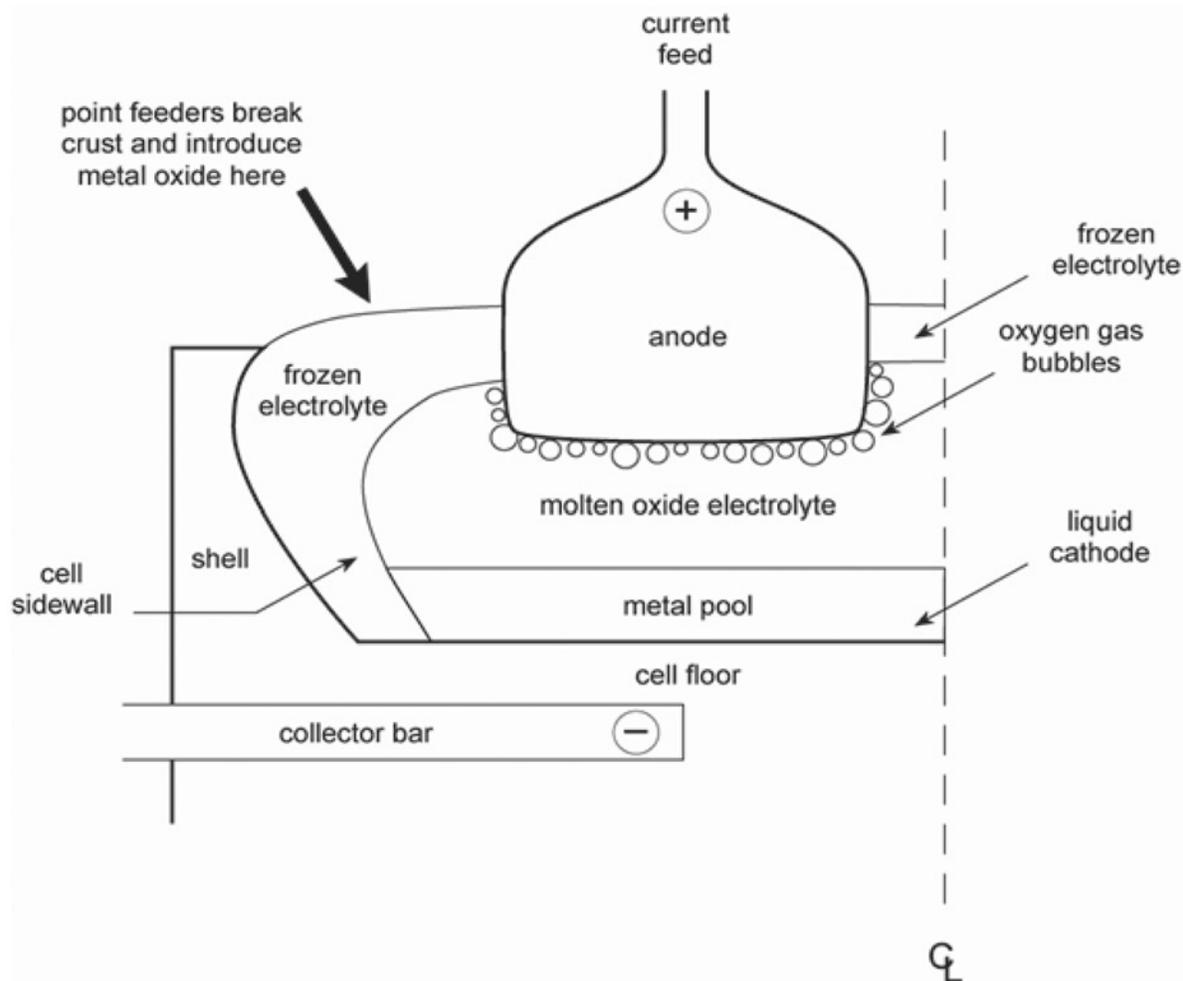
Figure 1. Schematic of cell for the production of oxygen by molten oxide electrolysis.

Accurate knowledge of the electrical properties of molten salts is paramount in the design of industrial electrolytic cells because joule heating of the electrolyte is central to establishing the thermal balance of the reactor. Accordingly, the electrical conductivities and transference numbers were measured for various FeO - CaO - MgO - SiO$_2$ systems.

Experimental

The experimental conditions have been described elsewhere. Electrical conductivity was measured by the coaxial-cylinders technique which was invented in this laboratory[9]. For sample preparation and other experimental details the reader is directed to the paper by Schiefelbein and Sadoway which reports the electrical conductivity measurements of several melts in the CaO - MgO - SiO$_2$ system[10]. Transference numbers were measured by stepped-potential chronoamperometry following the procedure described in the paper by Fried, Rhoads, and Sadoway[11].

Results and discussion

Figure 2 shows the effect of FeO on the electrical conductivity of the solvent melt designated S1, the composition of which is 24.59% CaO, 26.15% MgO, 49.26% SiO$_2$ on a molar basis. Figure 3 shows a similar variation observed in a binary system (48.53 % CaO and 51.47 % SiO$_2$). It is clear from the figure the value of electrical conductivity increases as the concentration of FeO increases. Figure 4 shows the isothermal variation of electrical conductivity at 1425ºC. Conductivity scales with FeO content on a molar basis. This indicates that FeO donates charge carriers that are highly mobile in comparison to what is already present in the solvent melt. We speculate that these carriers are electronically conductive, as evidenced by Figure 5 which shows the electronic transference number rising in tandem with the molar concentration of FeO.

The isothermal variation in electrical conductivity with composition for a multi-component melt is expected to follow

$$\sigma = \sum_i X_i \, \mu_i \, z_i^{\,2}$$

[3]

where σ is electrical conductivity, X_i is the mole fraction of component i, μ_i is the mobility of component i, and z_i is the net charge of i. Lumping all coefficients exclusive of X_i and assuming negligible interaction between solutes in a multicomponent melt, one can perform a multivariate regression analysis to get a first order estimate of the effect of any given solute on the conductivity of the solution. Figure 6 shows the result at 1425ºC for the set of melts investigated in this study. The effect of FeO is seen in two places. Along with CaO and MgO, FeO donates ionic charge carriers and, unlike the alkaline-earth oxides, FeO also contributes electronically conductive carriers as expressed by the coefficient with a value of 2.326, more than twice that of CaO and MgO. Note that the coefficient associated with SiO$_2$ has a negative value, -0.192, which is in keeping with the fact that SiO$_2$ does not contribute charge carriers, but instead reduces their population by forming covalent bonds with them.

The measurements made in this work compare favorably to those reported by Haskin et al.[12] insofar as the isothermal variation of conductivity with composition at 1425ºC. However, as a data set the values reported by Haskin et al. are systematically about 40% greater in magnitude than those reported in the present study. This, we believe, may be attributable to their use of the ring technique which suffers from the fact that the current path is a function of the electrical properties of (i) the melt under investigation and (ii) the electrodes (9).
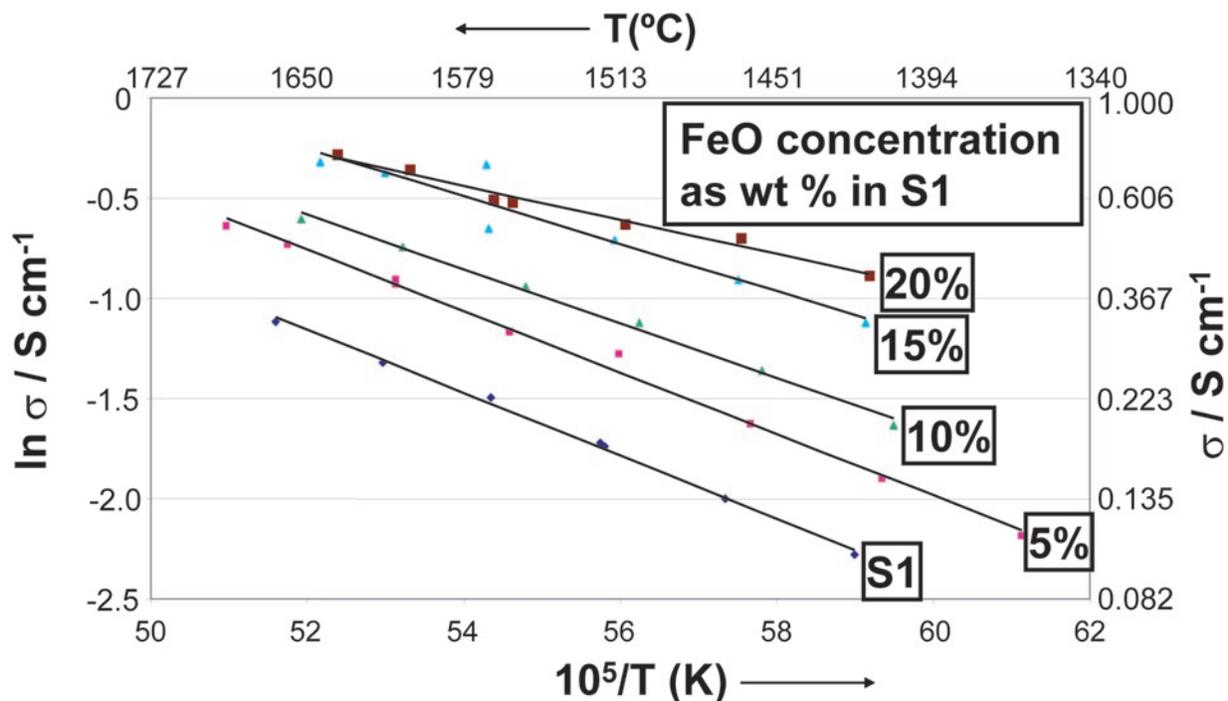
Figure 2. Variation of electrical conductivity with temperature and composition. Composition S1 is 24.59% CaO, 26.15% MgO, 49.26% SiO_2 on a molar basis. The concentration of FeO is given in weight per cent.
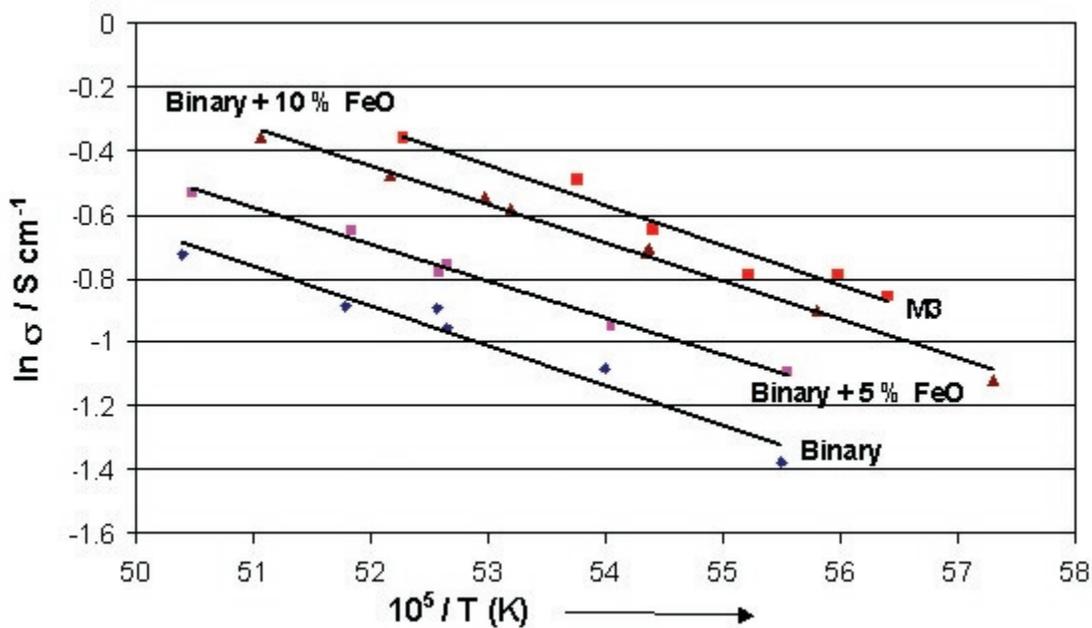
Figure 3. Variation of electrical conductivity with temperature and composition. Composition M3 is 46.03 % CaO, 13.78 % MgO, 40.19 % SiO_2 on a molar basis, binary refers to 48.53 % CaO and 51.47 % SiO_2. The concentration of FeO is given in weight per cent
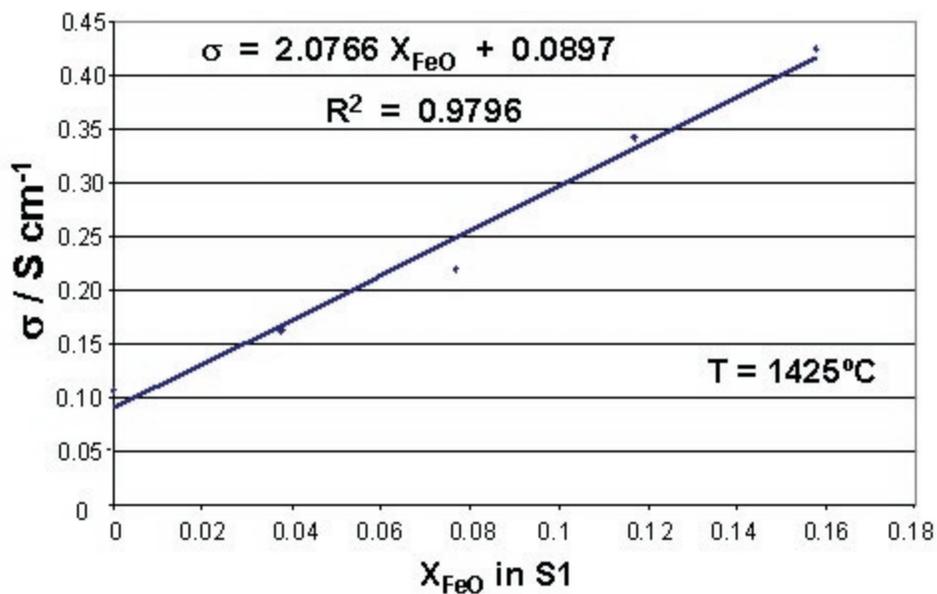
Figure 4. Isothermal variation of electrical conductivity with concentration of FeO.
T =1425ºC.
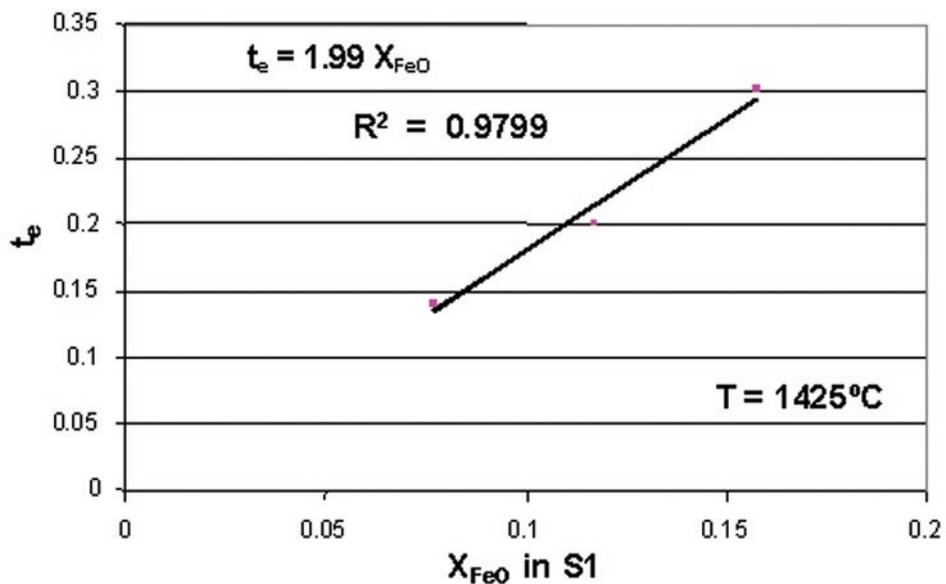
Figure 5. Isothermal variation of electronic transference number, t_e, with concentration of FeO.
T = 1425ºC.

$$\sigma = 0.27104 - 0.192*SiO2 + 2.326*FeO + 0.879*MgO + 1.072*CaO$$
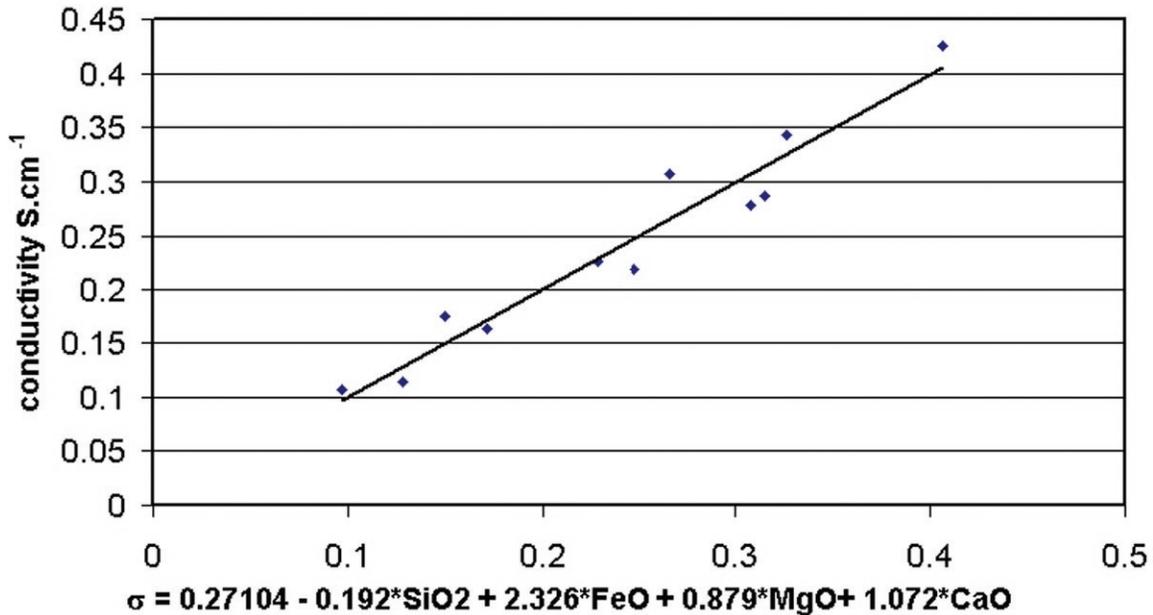
Figure 6. Isothermal variation of electrical conductivity with melt composition at 1425 °C.

References

1. Haskin, L., and Warren, P. "Lunar Chemistry," in Lunar Sourcebook, Chapter 8, Heiken, G.H., Vaniman, D.T., and French, B.M., Editors, p. 357, Cambridge University Press, Cambridge (1991).
2. Rieder, R., Economou, T., Wanke, H., Turkevich, A., Crisp, J., Bruckner, J., Dreibus, G. and McSween, H. Y., Science, vol. 278, 1771-1774 (1997).
3. Sadoway, D. R., Journal of Materials Research 10, 487-492, (1995).
4. Sadoway, D. R., in Metals and Materials Waste Reduction, Recovery and Remediation, Liddell, K. C., Bautista, R. G., Orth, R. J., Editors, p. 73, TMS, Warrendale, PA (1994).
5. Aluminum Association, Inert Anode Roadmap: A framework for technology development, Washington, DC: Aluminum Association, Inc. (1998).
6. Sadoway, D. R., inventor, Massachusetts Institute of Technology, Assignee, "Electrolytic production of metals using consumable anodes," U.S. patent no. 5,185,068, February 9 (1993).
7. Chase, M.W., Davies, C.A., Downey, J.R., Frurip, D.J., McDonald, R.A., and Syverud, A.N., JANAF Thermochemical Tables, 3rd edition, part II, American Institute of Physics, Inc., New York (1986).
8. Jarrett, N., in Tutorial lectures in electrochemical engineering and technology, Alkire, R. C., Beck, T. R. and Chin, D.-T., Editors, p. 27, American Institute of Chemical Engineers, New York (1981).
9. Schiefelbein, S. L., Fried, N. A., Rhoads, K. G. and Sadoway, D. R., Review of Scientific Instruments 69, 3308-3313, 1998. (1998).

10. Schiefelbein, S. L. and Sadoway, D. R., Metallurgical and Materials Transactions B, vol. 28, 1141-1149 (1997).
11. Fried, N. A., Rhoads, K. G. and Sadoway, D. R., Electrochimica Acta 46, 3351-3358 (2001).
12. Haskin, L.A., Colson, R.O., Lindstrom, D.J., Lewis, R.H., and Semkow, K.W., in The Second Conference on Lunar Bases and Space Activities of the 21st Century, Mendell, W.W., Editor, p. 411, NASA Conference Publication 3166, Houston, Texas, (1992).