# ELECTRICAL CONDUCTIVITY AND TRANSFERENCE NUMBER MEASUREMENTS OF FeO - CaO - MgO - $SiO_2$ MELTS

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## ABSTRACT

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. Molten oxides have been named candidate electrolytes for prospective high-temperature electrochemical processes. In particular, Sadoway has speculated on the utility of producing a variety of metals by direct electrolytic reduction of their oxides dissolved in a suitable molten oxide solvent. In this vein, the electrical conductivities and transference numbers were measured as a function of FeO concentration in the FeO - CaO - MgO - $SiO_2$ system. The dominant effect of FeO addition is to render the melt electronically conductive in proportion to the concentration of FeO.

**Keywords:** oxygen generation, electrical conductivity, transference number, electrolysis

## 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 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:

$$\mathrm{Fe}^{2+}\ (\text{electrolyte})\ +\ 2\ \mathrm{e}^{-}\ (\text{cathode})\ \ \text{Ð}\ \ \mathrm{Fe}\ (\text{liquid}) \qquad [1]$$

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:

$$\mathrm{O}^{2-}\ (\text{electrolyte})\ \ \text{Ð}\ \ 2\ \mathrm{e}^{-}\ (\text{anode})\ +\ \tfrac{1}{2}\ \mathrm{O}_2\ (\text{gas}) \qquad [2]$$

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$^{-1}$ (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).

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 as a function of FeO concentration in the FeO - CaO - MgO - $SiO_2$ system.

## 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. It is clear from the figure the value of electrical conductivity increases as the concentration of FeO increases. Figure 3 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 4 which shows the electronic transference number rising in tandem with the molar concentration of FeO.

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).

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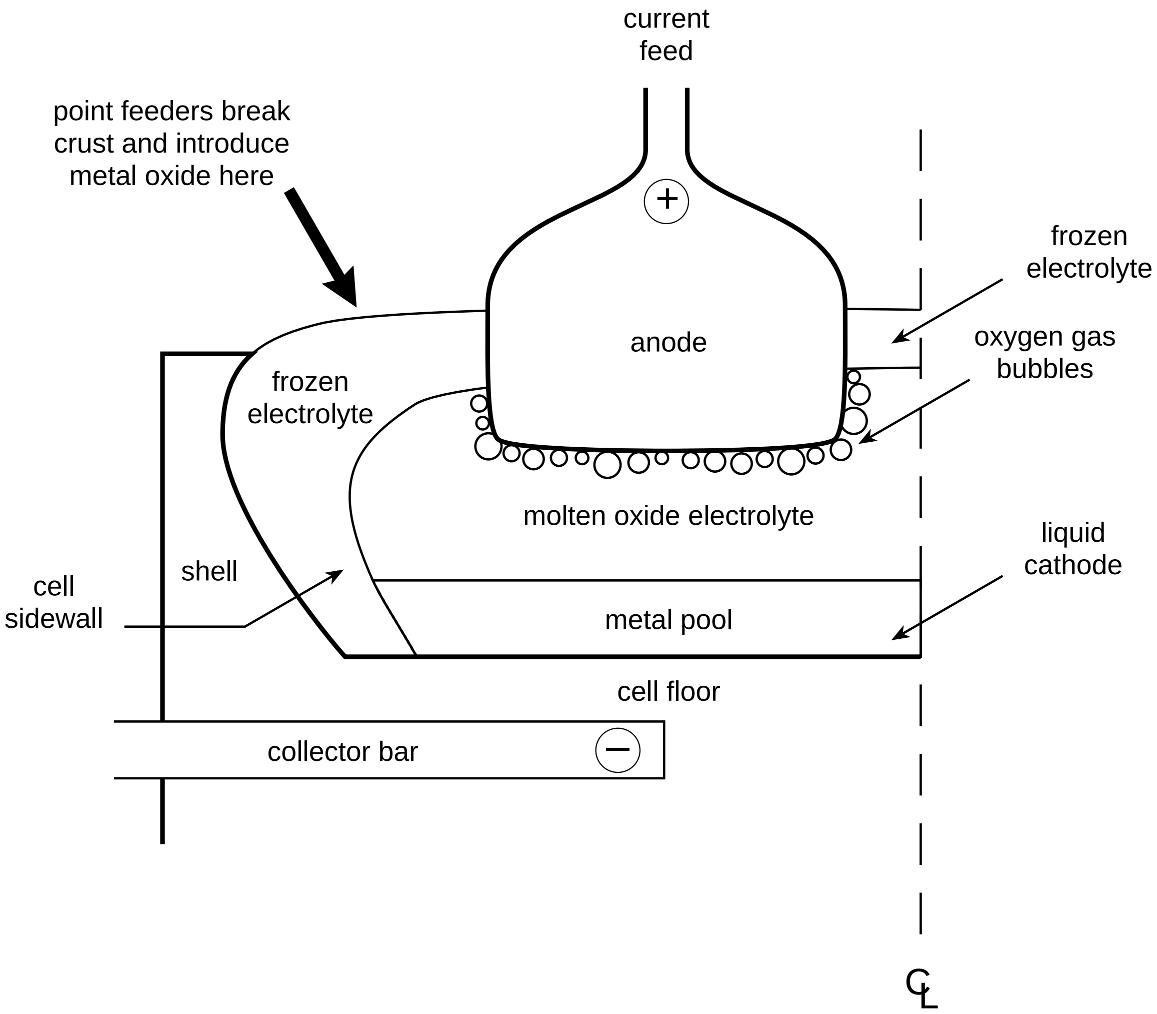

Figure 1. Schematic of Cell for the Production of Oxygen by Molten Oxide Electrolysis.

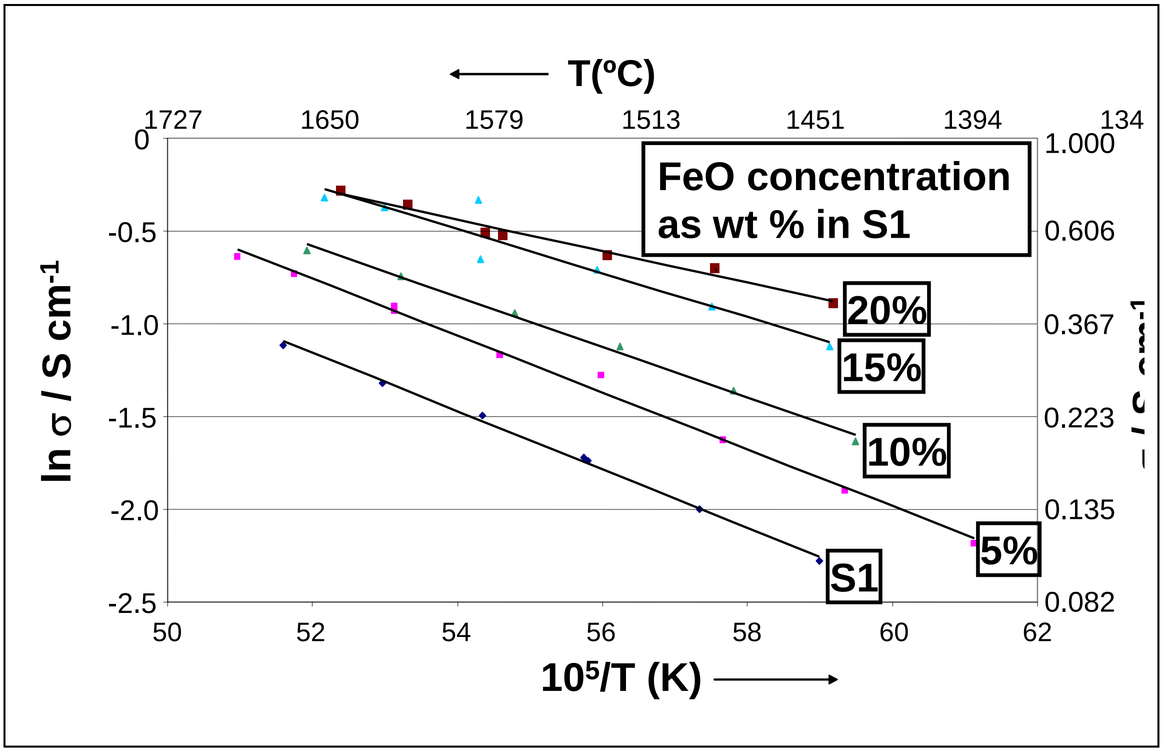

Figure 2. Variation of electrical conductivity with temperature and composition. Composition S1 is 24.59% CaO, 26.15% MgO, 49.26% $SiO_2$ on a molar basis. The concentration of FeO is given in weight per cent.

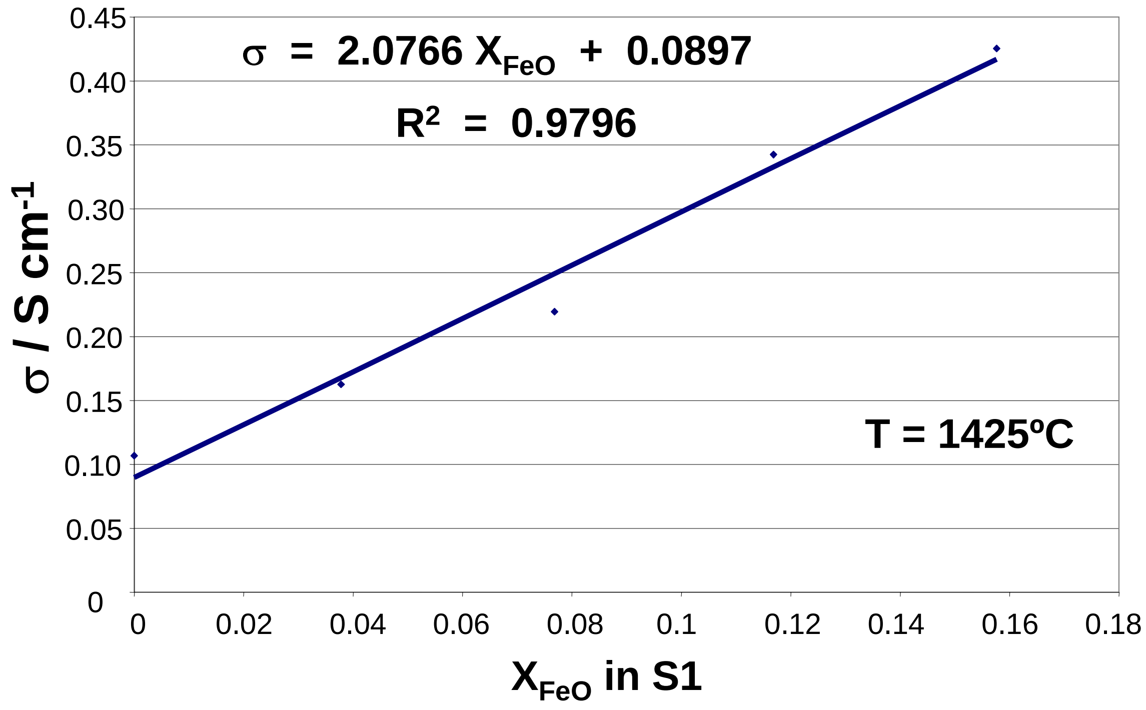

Figure 3. Isothermal variation of electrical conductivity with concentration of FeO. T =1425ºC.

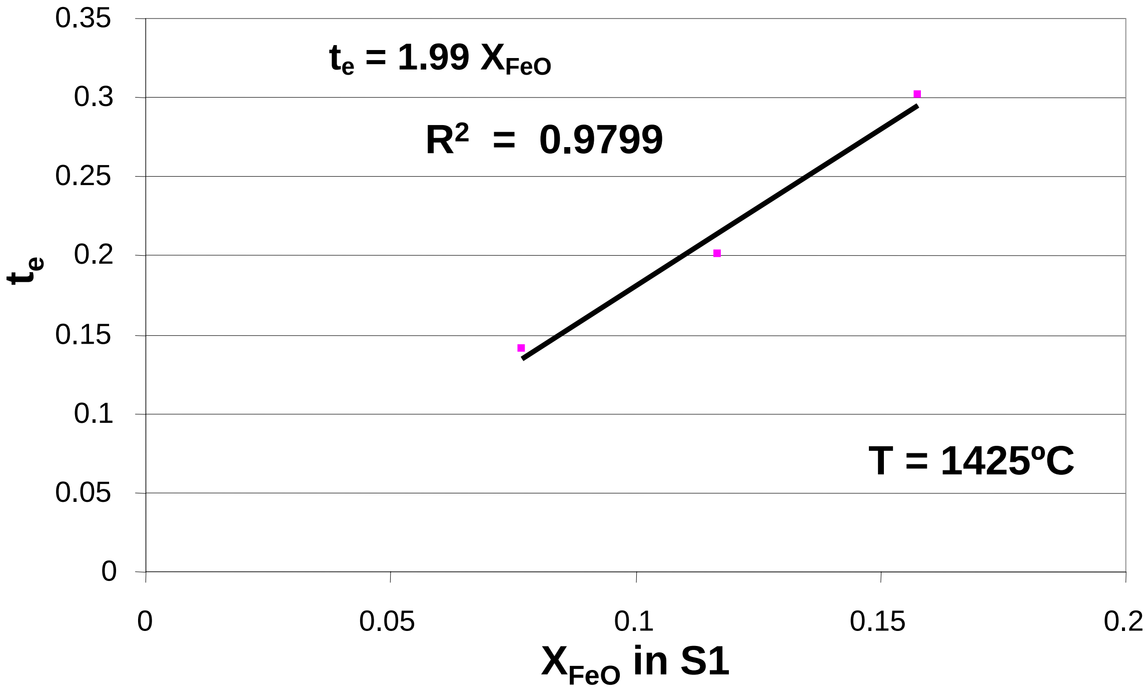

Figure 4. Isothermal variation of electronic transference number, $t_e$, with concentration of FeO. T = 1425ºC.