SOLID ELECTROLYTE FOR FUEL CELL

by

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Professor Millard:

This thesis, entitled, "Solid Electrolyte for Fuel
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I SUMMARY

A ceramic diaphragm suitable for fuel cell use was made as suggested in the literature as follows: a mixture of 75% sodium carbonate, 5% tungstic oxide, and 20% common soda glass were fired at 1200°C until bubbles (CO_2) ceased to come off. The molton mass was then cast into a rectangular shape by pouring into a mold. This diaphragm whose thickness was 3 mm. showed reasonably promising electrical properties in that its resistance decreased by a factor of 2600 from 520,000 ohms at 400°C to 200 ohms at 800°C. A cell was constructed containing this diaphragm which served to separate the electrodes. The electrodes consisted of mixtures of iron filings, Fe_2O_3, and Fe_3O_4. Hydrogen gas was passed through one electrode and air through the other. Open circuit voltage of this cell varied from 0.157 at 500°C to 0.40 at 700°C. Short circuit current varied from 0.008 to 0.24 amperes over thesame temperature range. With constant resistive load, current remained constant at 0.01 amperes while the voltage varied from 0.225 to 0.36 over the range 550°C to 650°C. Cell output was insensitive to gas flow rates except at very low flow rates. During operation of the cell, no polarization effects were observed. Due to equipment failure no efficiency determination could be made.

II INTRODUCTION

The normal present day method of generating electricity at power stations is inherently inefficient and quite wasteful of fuel since the use of the steam cycle results in a low thermodynamic efficiency. With the aid of superheaters and economizers the heat of combustion of the coal can be transferred to the steam with approximately 90 per cent. efficiency, and an efficiency of 70 per cent. can be obtained in the electrical generator, but the intermediate step of converting thermal energy into kinetic energy in the prime mover can never be much more than about 35 per cent. efficient even with a very high degree of superheat.[1] Consequently, the overall efficiency in the process of converting energy liberated in combustion to electricity seldom exceeds 25 per cent.

If all the energy from the complete combustion of carbon were available to do useful work, 1 lb. of coal could produce about 4.5 kwh.[2] However, in the production of electricity from fuel through the medium of steam, only about 1 kwh is actually obtained from 1 lb. of coal, and this represents an overall efficiency of about 22 per cent. A survey made in 1936 of the twenty-five most efficient power stations in Great Britain showed efficiencies ranging from 20.68 per cent. (1.44 lb/kwh) to 28.59 per cent.

(0.96 lb/kwh).[3] If electricity could be generated without using a prime mover, the loss of energy associated with this stage of the process could be avoided and a much higher overall efficiency would be possible.

The fuel cell represents an attempt to do this by generating electrical energy directly from the chemical energy contained in fuel.

Many such cells have been tried, beginning with the experiments of Humphrey Davy in 1801 to the more recent work of E. Baur in 1938, and O. K. Davtyan in 1946.

The number of fuel cells reported in the literature may be roughly divided into two classes--direct fuel cells, where coal or carbonaceous material is used as the attackable electrode, and indirect fuel cells, in which gaseous fuels such as carbon monoxide and hydrogen are used to saturate the negative electrode.[4]

The principal problem in constructing a fuel cell is to supply oxygen to the fuel in ionized condition and obtain electric power from the potential thus set up. Oxygen may be supplied in an ionized condition by using a reversible oxygen electrode, at which ionization takes place, as the cathode.

A Russian, O. K. Davtyan, has made use of electrodes consisting of Fe_2O_3 and granulated iron for the gas electrode and a mixture of Fe_2O_3 and Fe_3O_4 for the air electrode.[5]

Using this system with a solid electrolyte slab con-

sisting of a mixture of sodium carbonate, monazite, tungstic oxide, and soda glass and operating in the temperature range of 550-900 $^{\circ}$C, efficiencies up to 80 per cent. were reported. The efficiencies calculated were based on the free energy of the chemical reactions.

The purpose of this thesis was to construct a fuel cell similar to that reported by Davtyan and to investigate the electrical characteristics of the cell using an electrolyte consisting of 75 per cent. sodium carbonate, 5 per cent. tungstic oxide, and 20 per cent. common soda glass.

III PROCEDURE

The procedure for preparation of the solid electrolyte is given in the Appendix, sec. A.

The cell was assembled as indicated in Fig. 1. The porcelain cement used as gasketing material was dried according to instructions accompanying the cement. The cell was then tested for possible leaks in both the hydrogen side and the air side. This was done by soaking the whole apparatus in water and passing gas into the cell. Whenever leaks were discovered, the cell was taken apart and reassembled. When at last after a few trials the cell was assembled without air leaks, it was considered to be ready for operation.

The cell was then placed in an electric furnace and the temperature gradually raised. At 500°C the hydrogen supply was turned on. Temperature was measured with a thermocouple. At this temperature and at 500° intervals thereafter, readings were teken on an ammeter and voltmeter. The method of taking readings was as follows: At each temperature the open circuit voltage and short circuit current were recorded. Then the voltage and current readings with a constant load were recorded. These readings are tabulated in Table I.

The resistance of a sample electrolyte was separately determined at the temperatures ranging from 400°C to 800°C. The sample electrolyte measured 1/2 cm. on an edge and was
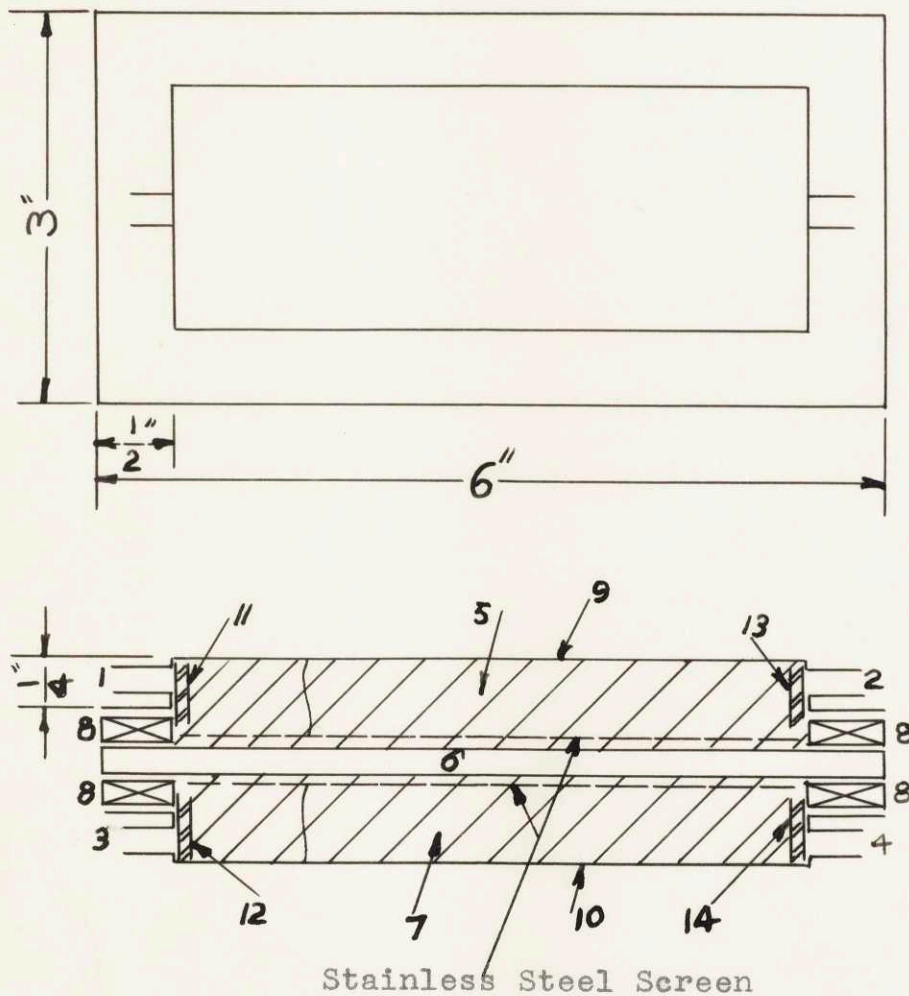
Stainless Steel Screen

FIGURE I

5/24/53   R P

FUEL CELL

TABLE I

Temperature °C	Open circuit voltage volts	Short circuit current	Load voltage volts	Load current amperes	Electrolyte resistance ohms
400					520,000
500	0.157	0.008			400,000
550	0.258	0.0106	0.225	0.01	230,000
600	0.350	0.08	0.308	0.01	150,000
650	0.40	0.22	0.36	0.01	33,000
700	0.40	0.24			3,500
750					590
800					200

3 mm. thick. The electrolyte was firmly clamped between steel plates and the values of resistance (DC resistance) were read directly from a vacuum tube ohmmeter. The resistance readings are tabulated in Table I.
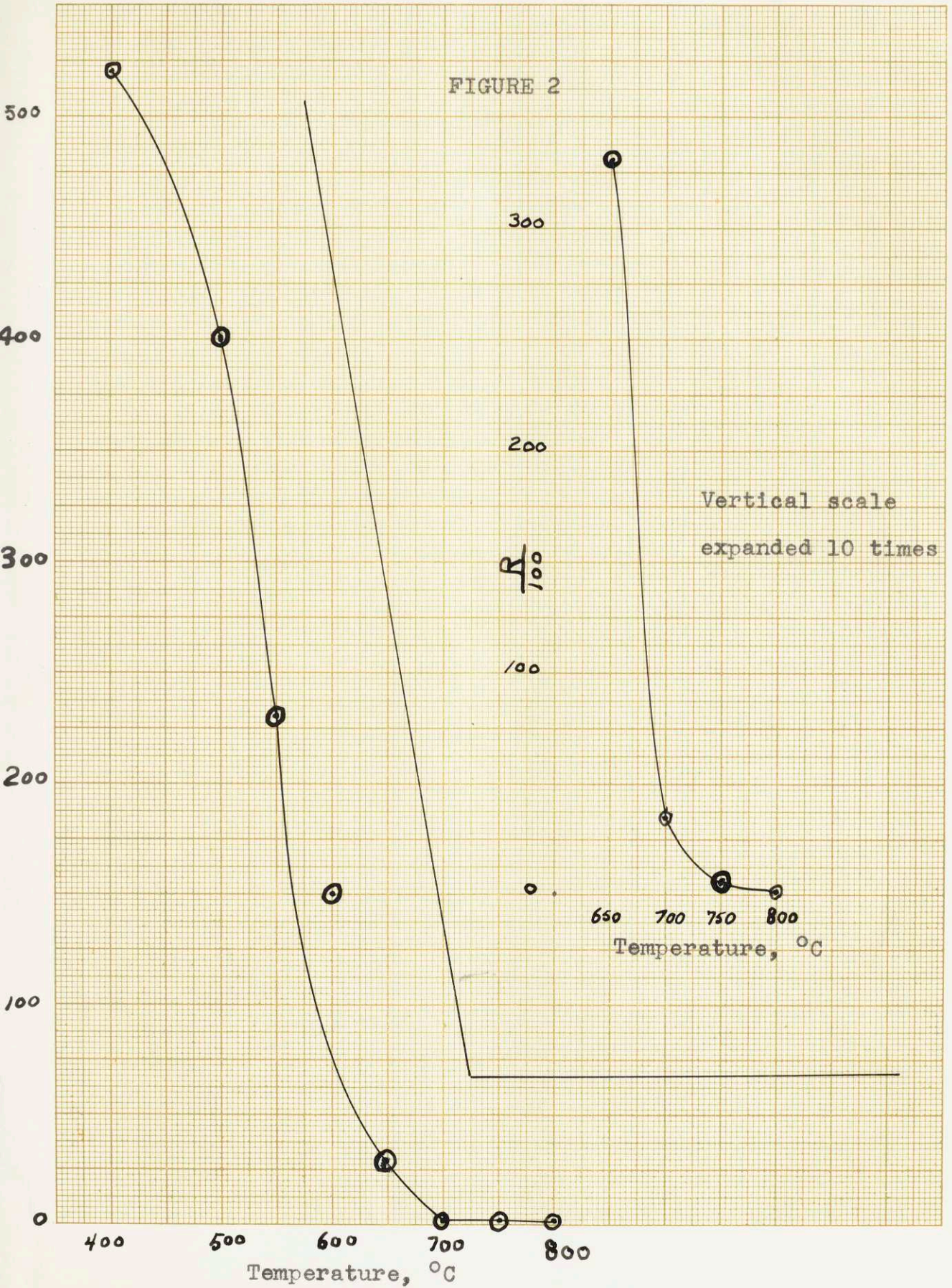
IV RESULTS

The first result of importance is that a ceramic plate was obtained intact despite the rather sketchy material contained in the literature. The details of preparation of the electrolyte slab or diaphragm are given in the Appendix, sec. A. The physical properties of the electrolyte were satisfactory. That is, it was impermeable to hydrogen and air up to a temperature of 650°C. The electrolyte, although brittle at room temperature, has a fairly high compressive strength.

The diaphragm had the hoped for electrical properties in that resistance decreased with increasing temperature. The resistance variation with temperature for a sample of electrolyte was determined as described in the procedure. The data are tabulated in Table I and presented graphically in Fig. 2. The resistance varied by a factor of 2600 from 520,000 ohms at 400°C to 200 ohms at 800°C.

The fuel cell assembly operated satisfactorily and demonstrated that the diaphragm apparently acted as a solid electrolyte in that the cell operated as a fuel cell. The open circuit voltage varied from 0.157 at 500°C to 0.40 at 700°C. Short circuit current varied from 0.008 amperes at 500°C to 0.24 amperes at 700°C. With a constant resistive load on the cell, the current remained constant at 0.01 amperes while the voltage varied from 0.225 to 0.36 over the range 550°C to 650°C. The complete data

FIGURE 2

are tabulated in Table I.

The cell was operated continuously for a period of two and a half hours. During this time no polarization effects were observable, i.e., cell output remained constant at a given temperature.

V DISCUSSION OF RESULTS

It was pointed out that resistance decreases with increasing temperature for the electrolyte. The graph of this is given in Cartesian coördinates, Fig. 2. A plot of resistance vs. temperature on semi-log paper does not straighten the curve. Similarly, a plot of resistance vs. the reciprocal of temperature does not give a straight line. Therefore it is apparent that resistance in this case does not vary expotentially with temperature as expected. This conceivably could be a result of faulty measuring instrument for resistance.

As may be seen from Table I, the trend is for voltage to increase with temperature. At low temperatures the very high internal resistance of the cell may have had an adverse effect on the development of voltage. This high resistance certainly caused a considerable voltage drop across the cell so that the output voltage was less than what was actually developed. Unfortunately, the cell had to be turned off at a relatively low temperature due to failure of one of the brazed joints in the hydrogen side of the cell.

The cell output was rather insensitive to wide variations in the flow rate of both air and hydrogen. The gas flow could be varied over wide ranges and have a noticeable effect only at very low flow rates. At very low flow rates the voltage and current decreased considerably. Unfortunately, a pressure surge in the hydrogen line in-

capacitated the flow meter so that no quantitative flow
data were obtained.

No efficiency determinations were made because some
of the effluent water vapor from the cell condensed in the
copper tubing leading to the drying apparatus giving an
erroneous value for the quantity of water produced as a
function of time.

Rather fine powder was used for the electrodes. It
is entirely possible that larger particles would have done
just as well. The reason for choosing fine particles was
to present as much electrode surface as possible to the
electrolyte. The reactions between electrode and electro-
lyte (Appendix, sec. E) may very well take place only at
the interface of the two and for that reason a large con-
tact area is desirable.

VI RECOMMENDATIONS

It is recommended that in any future work on fuel cells that the following be investigated:

1. The low temperature melt ($850^{o}C$) of Na_2CO_3 and soda glass forms a hard, brittle, opaque mass on cooling. This mixture could possibly be used as a solid electrolyte.

2. Very thin electrodes. As was pointed out in the Discussion of Results, the electrode reactions may occur only at the interface of the electrodes and the electrolyte. Therefore the decreased internal resistance resulting from very thin electrodes would result in better cell performance.

3. Other mixtures of electrolyte. The electrolyte used in this cell was what may be considered a typical mixture. Other mixtures may well be better adapted to fuel cell operation.

4. Composition of electrodes. The electrodes used in this cell were similar in composition to those used in cells reported in the literature. Different ratios of the electrode components might work better. The means of supporting the electrodes might also be investigated. For instance, the electrode powders might be carried by some porous medium.

APPENDIX

VII APPENDIX

A. <u>Details</u> <u>of</u> <u>preparation</u> <u>of</u> <u>electrolyte</u>

The solid electrolyte used in the fuel cell consisted
of a mixture of 75% sodium carbonate, 5% tungstic oxide,
and 20% common soda glass. The components were first
thoroughly mixed. The mixture was fired in a clay crucible
(type I). During the firing the temperature was maintained
at 900°C until the major portion of the evolved carbon
dioxide came off. Firing was carried out in a ceramic
pot kiln and the temperature was measured with an optical
pyrometer. After the major portion of the CO_2 came off,
the temperature was progressively raised to 1200°C, and
held at this temperature until the evolution of gas (CO_2)
ceased. The electrolyte was fired in small portions to
prevent loss by foaming. Fresh mixture was added to the
fired portion until the whole quantity was fired. The
molton mass was then poured into a mold to produce the re-
quired shape (see sec. B, Appendix). After cooling, the
surfaces of the electrolyte were ground flat. The elec-
trolyte was then ready for assembly of the cell.

B. <u>Casting</u> <u>the</u> <u>electrolyte</u>

At first a cast iron mold was used. The mold was
made by milling into the flat upper surface of the iron a
depression 6"x3"x3mm. Before pouring the electrolyte into
the mold, it was preheated to a temperature of 600°C and

lightly dusted with graphite dust. The molton mass was then poured into the mold and pressed flat with a graphite brick. Numerous failures occurred when using the cast iron mold. As a result of these failures, a mold of graphite was substituted. The graphite mold was similarly milled and preheated. With the graphite mold an electrolyte slab was successfully obtained.

During cooling of the electrolyte, extreme care was taken to reduce the temperature from 600°C to 300°C by 10C° intervals, and from 300°C to 100°C by 20C° intervals, and finally from 100°C to room temperature by allowing the slab to cool with the annealing furnace. Cooling was carried out in an electric furnace. Temperature was measured by means of a thermocouple.

C. <u>Steel</u> <u>containers</u> <u>for</u> <u>cell</u>

Two stainless steel containers were used in the cell assembly to serve as current conductors and to hold the cell components in place. These were cut to shape, bent and welded. Copper tubing, to carry the hydrogen and air to and from the cell, was brazed into position after drilling suitable holes.

Gasketing was accomplished by using a commercial porcelain cement (Sauereisen). This cement afforded a gas tight seal when properly applied and dried.

Asbestos packing was used at all gas inlets and outlets to prevent the powdered electrodes from being blown

out by the gas pressure. This method of keeping the contents in place was very effective.

D.   Electrodes

The negative (hydrogen) electrode consisted of a mixture of 75% Fe_2O_3 (standard CP), and 25% Fe in powder form. Similarly, the positive (air) electrode consisted of a mixture of 75% Fe_2O_3 and 25% Fe_3O_4 (USP) in powder form. In both electrodes, a stainless steel screen (200 mesh) was imbedded to serve as a current carrier and thereby reduce internal resistance. The screens were electrically connected to the steel shells of the cell.

E.   Details of operation

The operation of the cell is as follows:

Essentially, the cell consists of two gas electrodes—a gas electrode and an air electrode (Fig. 1, nos. 5 & 7, respectively). The solid electrolyte slab (6) rests between the electrodes. The steel shells (9&10) serve to hold the components in place and also serve as terminals from which the electric current is withdrawn. A porcelain cement gasket (8) seals the cell against gas leaks. Porous asbestos packing (11, 12, 13, 14) keep the contents of the cell in place during assembly and operation of the cell.

Fuel gas enters the cell through tube (1), makes contact with the entire surface of the electrode, and leaves through tube (2). After entering, a portion of the gas is

oxidezed by the electrode. Similarly, air enters by tube
(3) and makes contact with the air electrode, loses part
of its oxygen and leaves through tube (4). A potential
is set up through the oxidation of the fuel gas (reduction
of gas electrode) and oxidation of the air electrode.

At the air electrode the decomposition

$$Fe_2O_3 \quad = \quad (2FeO)^{++} + O^=$$
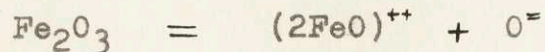
first takes place. $O^=$ is combined with the ion Na_2^{++} (in
electrolyte) into neutral Na_2O; Its withdrawl upsets the
dissociation equilibrium at the electrode, so that when the
oxygen from the air is added, the reaction

$$2e^- + (2FeO)^{++} + 1/2\ O_2 \quad = \quad Fe_2O_3.$$
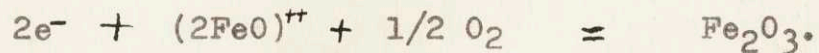
In the electrolyte the ion CO_3 wanders to the gas
electrode and oxidizes it according to the equation

$$CO_3^= + Fe \quad = \quad FeO + CO_2. + 2e^-$$

The neutral CO_2 meets by diffusion with the neutral Na_2O
and is again dissociated electrolytically into Na_2^{++} and
$CO_3^=$. The absorption of O by the gas electrode upsets the
dissociation equilibrium, which is restored again by the
final process

$$FeO + H_2 \quad = \quad H_2O + Fe$$

so that the circuit, if the electrodes are connected by
conductors, is closed.[6] Hydrogen was used in the cell.

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