Electrical conductivity and hydrogen diffusion properties of lanthanum chromite based ceramics
by Peter Scott Shifflett

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Physics
Montana State University


Abstract:
Lanthanum chromite is a ceramic electrical conductor being studied for possible use in high temperature solid electrolyte fuel cells. Electrical conductivity of La .90 Ca.10 Al .15 Cr .85 O 3' LaMg .02 Al .15 Cr 83 O3 and La Sr 84 Sr 16 AL .15 Cr 85.3 was measured at temperatures from 25 to 1200°C, in both air and Hydrogen atmospheres. The conductivity of the calcium and strontium doped samples was about 300 (ω-m) at 1000°C in air, but decreased by at least an order of magnitude when saturated with hydrogen. At room temperature the conductivity of the calcium doped sample decreased by more than four orders of magnitude when saturated with hydrogen. The magnesium doped sample showed similar behavior but with substantially lower overall conductivity. Hydrogen diffusion measurements in La .90 Mg .10 Cro3 yielded a diffusion constant of 190 cm2 /sec and a diffusion activation energy of 1.8 eV.

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Approved:

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# ABSTRACT

Lanthanum chromite is a ceramic electrical conductor being studied for possible use in high temperature solid electrolyte fuel cells. Electrical conductivity of $La_{.90}Ca_{.10}Al_{.15}Cr_{.85}O_3$, $LaMg_{.02}Al_{.15}Cr_{.83}O_3$ and $La_{.84}Sr_{.16}Al_{.15}Cr_{.85}O_3$ was measured at temperatures from 25 to 1200°C, in both air and hydrogen atmospheres. The conductivity of the calcium and strontium doped samples was about 300 $(\Omega\text{-m})^{-1}$ at 1000°C in air, but decreased by at least an order of magnitude when saturated with hydrogen. At room temperature the conductivity of the calcium doped sample decreased by more than four orders of magnitude when saturated with hydrogen. The magnesium doped sample showed similar behavior but with substantially lower overall conductivity. Hydrogen diffusion measurements in $La_{.90}Mg_{.10}CrO_3$ yielded a diffusion constant of 190 $cm^2$/sec and a diffusion activation energy of 1.8 eV.

# CHAPTER I

## INTRODUCTION

Much of the energy the world uses today is exhaustible and some of our primary energy sources may even become quite scarce within our lifetimes. This problem coupled with a growing awareness of, and concern for, environmental quality has, in recent years, led many private corporations, government and university researchers to work toward finding cleaner and more efficient ways of converting primary forms of energy into electricity. Direct energy conversion processes, in which primary energy sources are converted directly into electrical energy without the necessary use of mechanical elements, such as turbines or reciprocating machinery, are especially desirable.

One promising direct energy converter is the fuel cell. Unlike heat cycle conversion machines, the fuel cell is not limited by Carnot cycle efficiencies. It therefore has the potential to become by far the most efficient fuel to electrical energy converter. It is capable of excellent power to weight ratios. Most types would retain their excellent efficiencies as central power plant converters even when used for very small portable power converters. They operate with essentially no moving parts, are noiseless, and produce virtually no pollutants.

High temperature solid electrolyte fuel cells are especially interesting. They would be capable of electrochemically burning cheap and conventional carbonaceous fuels derived from coal. An overall system efficiency of 60% may be possible with optimization[1] and high power to weight ratios are likely. In addition, cost would be low since no expensive catalysts are required.

Although solid electrolyte fuel cell studies date to the late 1930's, the only extensively tested prototype battery was built by Westinghouse Corporation in the 1960's.[2] The design consists basically of a porous $ZrO_2$ tube which is coated with thin layers of fuel electrode, non-porous $ZrO_2$-based electrolyte, and air electrode respectively. On the air side of the Westinghouse fuel cell, oxygen accepts electrons from the air electrode to form $O^{2-}$ ions which are transportable through the solid electrolyte at operating temperatures of around 1000°C. On the fuel side of the cell, a carbonaceous fuel mixture in gaseous form is supplied to the interior of the support tube where it diffuses through the tube pores to the surrounding fuel electrode. Here the fuel gases react with oxygen ions supplied by the electrolyte, liberating electrons to the fuel electrode. The air electrode thus has a positive electric potential relative to the fuel electrode, and this potential can supply power to an external circuit. If in a practical power system, the fuel mixture consists of hydrogen and carbon monoxide, both derivable from coal, the resultant exhaust would be carbon dioxide and water vapor.

An actual fuel cell battery would consist of individual cells connected in series along the length of the support tube as shown in Figure 1. The connection between the air and fuel electrodes of adjacent cells must be made with a thin gas-tight electronic conductor. The interconnection material is submitted to particularly severe conditions. It must be chemically stable in both oxidizing and reducing atmospheres at 1000°C, while retaining a sufficiently low electronic resistivity for efficient operation. In addition, it must be compatible with the other materials in the fuel cell; cationic diffusivity should be low and coefficients of thermal expansion must match.

The most promising materials tested by Westinghouse Corporation for use in the interconnection layer are modified lanthanum chromite ceramics. The electrical conductivity of these materials depends upon the temperature and the atmosphere in which the measurements are made. Other investigators have examined the conductivity of modified lanthanum chromites in various oxygen partial pressures and atmospheres, but little information is available concerning their conductivity in reducing atmospheres.

It was the objective of this work to measure the electrical conductivity of several lanthanum chromite based ceramics, exposed to an environment approximating that which they would experience in an operating fuel cell battery. Diffusion of hydrogen through lanthanum chromite was also measured at high temperatures. These measurements

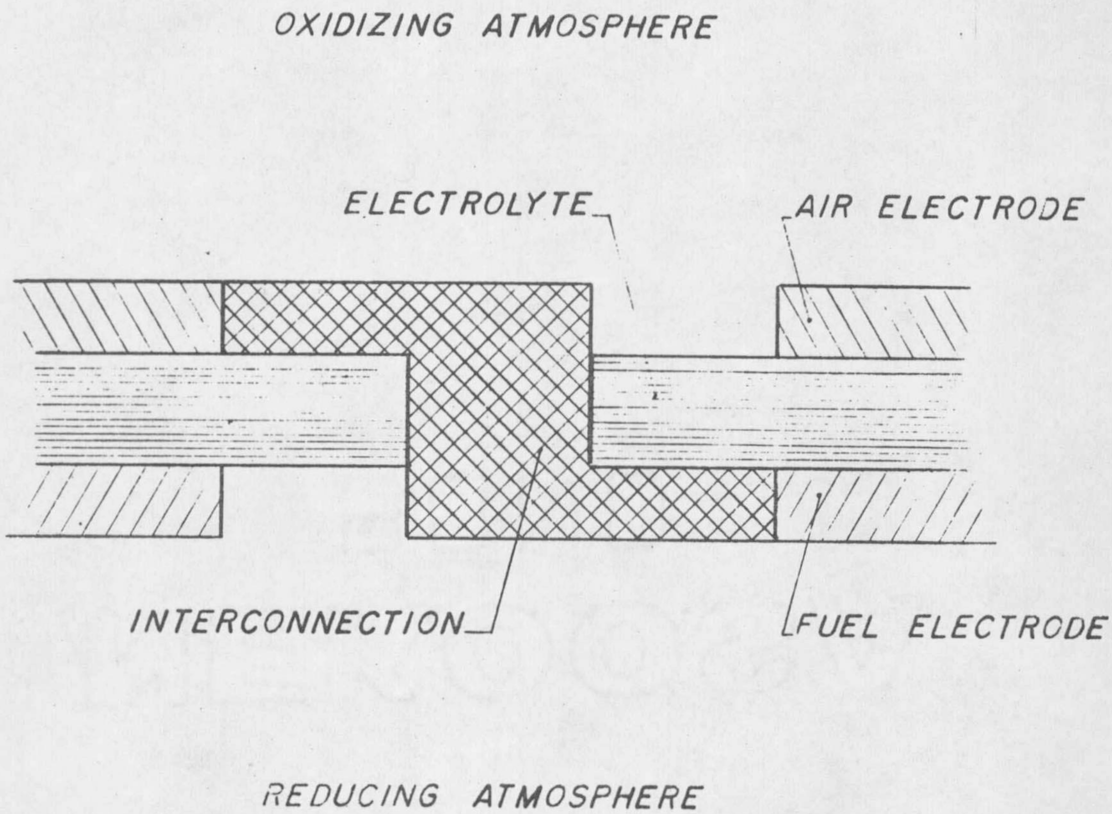


Figure 1. Fuel Cell Battery Interconection.

will aid in deciding what material would be most suitable for use in the interconnection layer.

## CHAPTER II

## BACKGROUND

Solids can generally be classified into three distinct groups depending on their electrical conduction properties: metals, insulators and semiconductors. Experimental measurements of conductivity cover a wide range of values, with metals having the highest conductivity, ($\sigma \sim 10^6$ (ohm-cm)$^{-1}$), and insulators having the lowest ($\sigma \sim 10^{-14}$ to $10^{-22}$ (ohm-cm)$^{-1}$).[3] The conductivity of semiconductors, as the name would imply, lies somewhere between these two extremes depending upon the temperature and the presence of defects or impurities.

In very pure form, semiconductors exhibit what is known as intrinsic conductivity. Intrinsic conductivity denotes electrical conduction due to electrons and holes which are present because of a natural or "intrinsic" property of the material at a given temperature. Extrinsic conductivity, on the other hand, refers to electrical conductivity arising from charge carriers supplied by an impurity. Certain impurities, or dopants, can drastically affect the electrical properties of a semiconductor. For example, at room temperature, the conductivity of pure silicon is increased by a factor of $10^3$ when boron is added in the ratio of $1/10^5$ atoms.[3]

In order to present a clear picture of lanthanum chromite conductivity, this review will dwell initially on intrinsic semiconductors.

A discussion of the effects of the impurities on the conductivity of lanthanum chromite will follow. Also, a brief introduction to small-polaron hopping transport will be presented as an alternative conduction mechanism.

At absolute zero, intrinsic semiconductors would be indistinguishable from insulators. This situation can be characterized by a band structure like that shown in Figure 2.[3] The empty conduction band is separated from a filled valence band by a forbidden zone with energy gap $E_g$. For semiconductors, $E_g$ has values on the order of 1 eV.[4] Since the electrons in a completely filled band cannot carry current, at absolute zero any pure semiconductor will be nonconducting. However, as the temperature is increased, there is a non-zero probability that electrons will be excited from the valence band to the conduction band. Thus, with an increasing concentration of electrons in the conduction band, conductivity will increase with temperature. The positive holes left in the valence band also increase in concentration and aid in the increase of conductivity with temperature.

To calculate the conductivity of a semiconductor as a function of temperature, it is necessary to know the number, $n_e$, of electrons per unit volume in the conduction band and the number, $n_h$, of holes per unit volume in the valence band. The mobility (drift velocity/electric field) for both electrons and holes, $\mu_e$ and $\mu_h$, must also be considered. The electrical conductivity can then be written

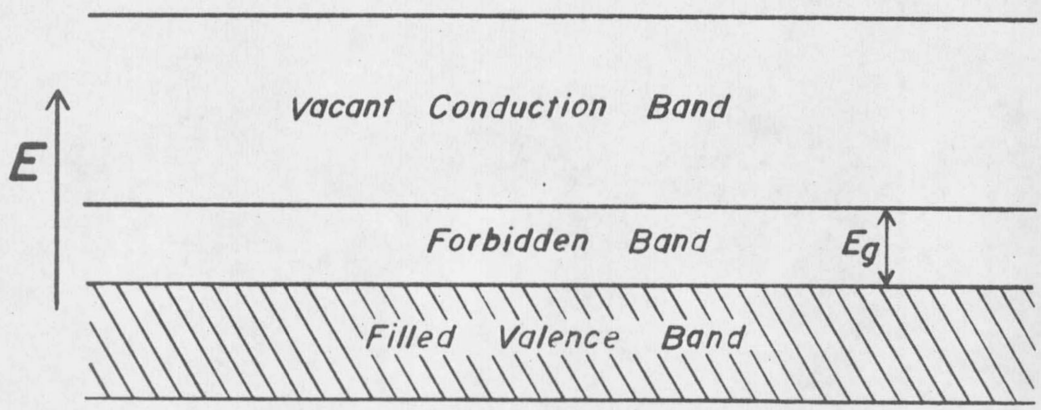


Figure 2. Simplified Band Structure of a Semiconductor at Absolute Zero Temperature.

$$\sigma = [e]\ (n_e\mu_e + n_h\mu_h), \qquad \text{Equation (1)}$$

where the mobilities are both taken to be greater than zero and e is the electric charge. Under intrinsic conditions, $n_e$ and $n_h$ are equal. Therefore, Equation (1) can be written

$$\sigma = [e]\ (\mu_e + \mu_h)(n_e n_h)^{1/2}. \qquad \text{Equation (2)}$$

Because the electrons in a solid must obey the Pauli exclusion principle, the probability that an electron state of energy E is occupied in the conduction band is given by the Fermi-Dirac distribution, $f_e$:

$$f_e = \frac{1}{1+\exp\{(E-E_f)/kT\}} \qquad \text{Equation (3)}$$

where $E_f$ is a function of the number of electrons in the system, N, and the temperature, T, and is known as the Fermi energy, and k is Boltzmann's constant. Similarly, the probability that a hole state of energy E is occupied in the valence band is given by $f_h$:

$$f_h = 1-f_e = 1-\frac{1}{1+\exp\{(E-E_f)/kT\}} = \frac{1}{1+\exp\{(E_f-E)/kT\}}. \qquad \text{Equation (4)}$$

Therefore, $f_e$ and $f_h$ are simply the distribution functions for electrons in the conduction band and holes in the valence band respectively.

The electron density in the conduction band may be written as an integral over the density of states in the conduction band, $g_c(E)$, weighted with the electron distribution function:

$$n_e = \int_{E_c}^{\infty} g_c(E) f_e dE \qquad \text{Equation (5)}$$

where $E_c$ is the energy at the bottom of the conduction band. Similarly, the hole density in the valence band is an integral over the density of states in the valence band, $g_v(E)$, weighted with the hole distribution function:

$$n_h = \int_{-\infty}^{E_v} g_v(E) f_e dE \qquad \text{Equation (6)}$$

where $E_v$ is the energy at the top of the valence band.

If it is assumed that the electrons in the conduction band and the holes in the valence band are sufficiently dilute that they do not interact appreciably with each other, they can be treated as being free. In this case, the density of states for the conduction and valence bands can respectively be taken as

$$g_c(E) = \frac{1}{2\pi^2}(2m_e/h^2)^{3/2}\ (E-E_c)^{1/2}$$

and

$$g_v(E) = \frac{1}{2\pi^2}(2m_h/h^2)^{3/2}\ (E-E_v)^{1/2}\ , \qquad \text{Equation (7)}$$

where $m_e$ and $m_h$ are the effective masses of the electrons and holes.[3]

If a nondegenerate semiconductor is assumed, that is, if

$$E_c-E_f \gg kT \text{ and } E_f-E_v \gg kT, \qquad \text{Equation (8)}$$

the distribution functions can be approximated by

$$f_e = \exp\{-(E-E_f)/kT\} \quad \text{for } E>E_c \; ,$$

and

$$f_h = \exp\{-(E_f-E)/kT\} \quad \text{for } E<E_v \; . \qquad \text{Equation (9)}$$

Using these approximations [Equation (7) and Equation (9)], the density integrals [Equations (5) and (6)] can be written as

$$n_e = \frac{1}{2\pi^2}(2m_e/h^2)^{3/2} \int_{E_c}^{\infty}(E-E_c)^{1/2}\exp\{-(E-E_f)/kT\}\, dE$$

$$n_h = \frac{1}{2\pi^2}(2m_h/h^2)^{3/2} \int_{-\infty}^{E_v}(E-E_v)^{1/2}\exp\{-(E_f-E)/kT\}\, dE \; . \qquad \text{Equation (10)}$$

Equations (10) can be integrated to give

$$n_e = \frac{1}{4}(2m_e kT/\pi h^2)^{3/2}\exp\{-(E_c-E_f)/kT\}$$

and

$$n_h = \frac{1}{4}(2m_h kT/\pi h^2)^{3/2}\exp\{-(E_f-E_v)/kT\} \; . \qquad \text{Equation (11)}$$

Finally, using Equations (11) in Equation (2), the conductivity can be written as,

$$\sigma = \frac{1}{4}(\mu_e+\mu_h)(m_e m_h)^{3/4}(2kT/\pi h^2)^{3/2}\exp(-E_g/2kT). \qquad \text{Equation (12)}$$

The temperature dependence of the mobilities, $\mu_e$ and $\mu_h$, must also be considered. For an intrinsic semiconductor at high temperatures (T >~ room temperature), the charge carrier mobilities are affected primarily by lattice scattering. It has been shown theoretically[5] and experimentally[6] that the temperature dependence of the lattice scattering mobility typically obeys a simple power law:

$\mu \propto T^{-3/2}$. The power of T can, however, have values more positive than -3/2 depending on the lattice scattering mechanism. Therefore, the intrinsic conductivity of an ideal semiconductor can be written as

$$\sigma = AT^n \exp(-E_g/2kT), \quad n \geqq 0 \quad , \qquad \text{Equation (14)}$$

where A is a constant which depends upon the crystal properties.

It should be kept in mind that real semiconductors are rarely so ideal. At high temperatures, the semiconductor can become partly degenerate and the band gap can even be expected to decrease with increasing temperature.[7] However, if $\log\sigma$ is plotted against $1/T$, a straight line would be expected with slope equal to $-E_g/2k$. Deviations from straight line behavior can then be explained in terms of conditions not accounted for in the ideal intrinsic semiconductor theory.

Lanthanum chromite can be characterized as having an $ABO_3$ perovskite crystal structure with lanthanum ions occupying the body-center A sites, and chromium ions occupying the cube corner B sites as shown in Figure 3. The oxygen ions are situated between adjacent B sites on the twelve edges of the cube.[8] In order to predict theoretically the temperature dependence of the conductivity of lanthanum chromite, we must first have some idea as to the behavior of the outer atomic electrons as they exist in the crystal lattice.

The behavior of outer electrons in a crystal is often classified into two limiting cases depending upon the constituent atoms of the

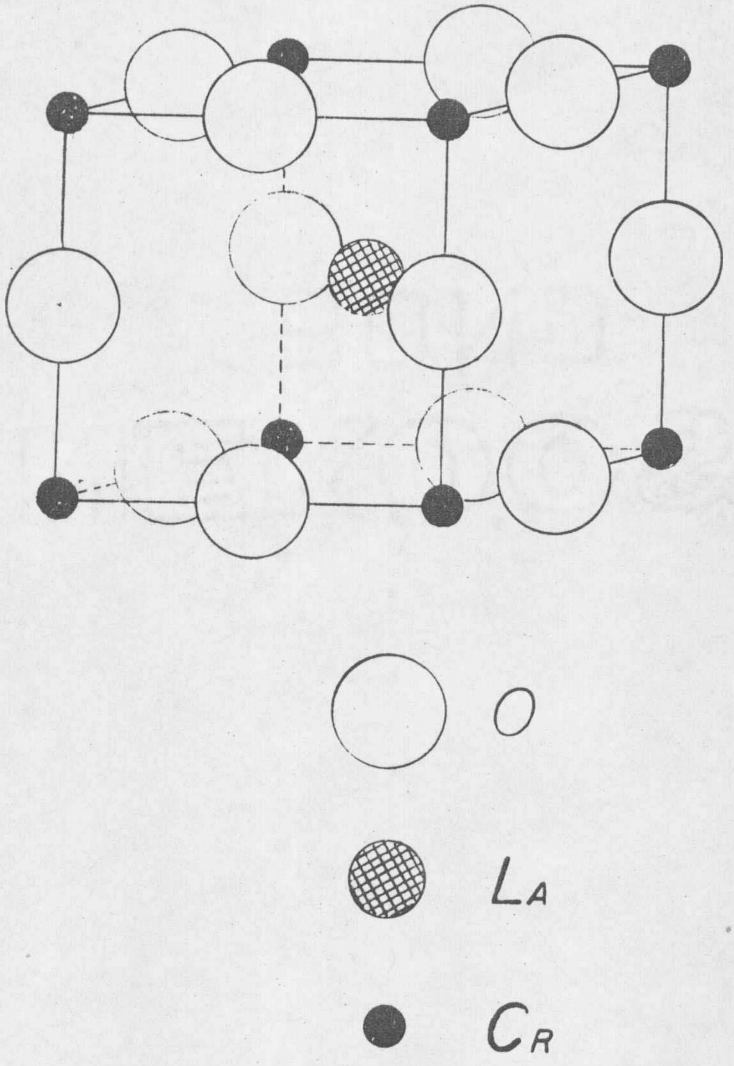


Figure 3. Lanthanum Chromite Crystal Structure.

lattice and the lattice structure itself. In the first case, the outer electrons are assumed to belong collectively to the crystal as a whole. In the second case they are assumed to be localized at specific atomic sites. Both cases can result in thermally activated conductivity using different charge transport mechanisms as pointed out by Karim and Aldred.[8]

Both the collective and localized electron models are based on the application of molecular orbital theory to determine the energy band structure of the crystal. If the composition and lattice structure of the crystal are known, the possible energy levels are found by postulating how the orbitals of the constituent atoms in a unit cell interact with each other. Once the band structure is known, the available electrons are used to fill the possible electronic states from the bottom up. If there are just enough electrons to completely fill a band and if there is an energy gap between the top of that band and the bottom of the next highest band, then an insulator or a semiconductor will result depending on the width of the gap. This is essentially what was done in the discussion of intrinsic semiconductors.

Wirtz[9] has analyzed the conductivity of doped lanthanum chromite and other rare earth perovskites. In his analysis, it was assumed that for pure $LaCrO_3$, the lanthanum cation acts as an electron donor which supplies its valence electrons to the bonds formed between the oxygen and chromium ions, but does not contribute to the formation of the energy levels directly. The oxygen and chromium orbitals interact in the lattice to produce a series of energy bands, the first three of which are labeled $\sigma$, $\pi$ and $P\pi$. The name of each band signifies the type of bonding that led to its formation. The number of allowed electronic states in the $\sigma$, $\pi$ and $P\pi$ bands are 12, 6 and 6 respectively, for a total of 24 allowed states. To fill these states, 3 electrons are supplied by the $La^{3+}$ cation, 6 are supplied by each of the three $O^{2-}$ ions, and 3 come from the $Cr^{3+}$ cation. Thus, there are 24 outer electrons per unit cell that are associated with the oxygen atoms; just enough to completely fill the $\sigma$, $\pi$ and $P\pi$ bands. The 3 remaining chromium d-electrons fill the lower half of a higher energy collective electron band ($\pi^*$ band). It is energetically favorable for this band to be split into upper and lower halves because of electron spin correlation. Based on this model, hole type semiconducting behavior is predicted for $LaCrO_3$ and an exponential temperature dependence is expected. A pre-exponential term may also be possible depending on the lattice scattering mechanism involved. Therefore, the conductivity/temperature equation appropriate for a collective electron model would be

$$\sigma \propto T^n \exp(-E/kT), \quad n \geq 0 . \qquad \text{Equation (15)}$$

The theory also predicts the effects of dopants and point defects on the conductivity. The result of these impurities is the introduction of new energy levels in the band gaps. Strontium and magnesium are the most common dopants used to increase the conductivity of $LaCrO_3$. It is generally believed, for example, that when a $Sr^{2+}$ ion is substituted for a $La^{3+}$ ion, a $Cr^{4+}$ ion will form to preserve charge neutrality (controlled valency doping).[10] The $(La,Sr)CrO_3$ system can then be expressed by

$$La_{1-x}Sr_{x}Cr^{3+}_{1-x}Cr^{4+}_{x}O_3.$$

The result will be one less electron in the uppermost occupied energy band ($\pi^*$ band), producing a charge carrying hole. Therefore, strontium doping in $LaCrO_3$ enhances conductivity by increasing the number of positive charge carriers. Missing $La^{3+}$ ions would lead to similar behavior, providing three holes for each lanthanum ion missing.

Charge compensation for missing or replaced cations could alternatively be accomplished by the formation of oxygen vacancies.[11] If this occurs, fewer $Cr^{4+}$ ions would be produced, resulting in a lower charge carrier concentration and a lower conductivity. Thus, the electrical properties of the material may depend on whether the atmosphere it is exposed to is oxidizing or reducing. Khattak and Cox[11] have reported a weight loss in a $La_{.75}Sr_{.25}CrO_3$ sample after it had been reduced in dry hydrogen at a temperature of 1200°C for 16 hours. They attributed the weight loss to an oxygen deficiency resulting in a composition change to $La_{.75}Sr_{.25}CrO_{2.89}$. A cell volume increase was also noted and was also explained by an oxygen deficiency. Westinghouse Corporation workers[12] saw a similar oxygen loss in $LaMg_{.02}Al_{.23}Cr_{.75}O_3$ at 1000°C using a hydrogen and water mixture for the reducing atmosphere.

As mentioned earlier, thermally activated conductivity can also occur with a localized electron model. In this model it is assumed that the number of charge carriers is essentially temperature independent, but that the mobility varies exponentially with temperature. The charge carrier localization is due to a strong interaction with the lattice, causing a local deformation in the crystal around the carrier. The charge carrier is then spatially localized, or trapped, by the potential well that results from its own presence. This self-trapped charge carrier, along with its corresponding lattice polarization, is known as a small polaron. The mobility temperature dependence is determined by thermally activated hopping of the small-polaron between atomic sites. Polaron theory can be quite difficult and does not belong in this review; it is discussed in great detail in an article by J. Appel.[13]

Karim and Aldred[8] have discussed small-polaron conductivity for the specific case of strontium doped lanthanum chromite. They agree that when a $Sr^{2+}$ ion is substituted for a $La^{3+}$ ion, charge neutrality requires a 3+ to a 4+ valency change in a chromium ion, just as in the collective electron model. However, they propose that the resulting hole in the d-electron band forms a small polaron with its surrounding distorted lattice. The small polaron can then be thermally induced to hop out of its potential well to an adjacent lattice site by creating an empty potential well nearby. According to Karim and Aldred, the temperature dependence of the mobility of these hopping holes is given by

$$\mu \propto T^{-1}\exp\{-W_H/kT\}, \qquad \text{Equation (16)}$$

where $W_H$ is a hopping energy.

If it is true that the number of charge carriers is constant with temperature, then $W_H$ can be interpreted as a conductivity activation energy and the conductivity will thus have the form

$$\sigma \propto T^{-1}\exp\{-E/kT\} \ . \qquad \text{Equation (17)}$$

Comparing Equations (15) and (17), we see that the only difference in conductivity between the collective and localized electron models is in the pre-exponential term, so far as the temperature is concerned.

Karim and Aldred[8] have also obtained evidence supporting a small-polaron conduction mechanism in strontium doped lanthanum chromite samples based on conductivity and Seebeck coefficient measurements. Their conductivity data produced straight lines when $\log \sigma T$ was plotted against $1/T$ as would be expected with small-polaron conduction, and an essentially temperature independent Seebeck coefficient indicated a constant charge carrier concentration in the doped samples. Meadowcroft[10] has also collected conductivity data of strontium doped lanthanum chromite which supports a localized electron model.

Since charge carrier concentration is largely determined by the impurities present, at low temperatures a large variation in conductivity would be expected, using either the collective electron model or the localized electron model, when a dopant is added. At high temperature though, the result of doping a lanthanum chromite sample may be different depending on which model the sample obeys. For the collective electron model, intrinsic conductivity is likely to dominate at high temperatures because of its strong exponential temperature dependence, and the conductivities of variously doped samples will tend to merge to roughly equal values. For the localized electron model however, since the number of carriers is assumed not to change with temperature, an increase in doping will result in a proportional increase in conductivity even at high temperatures. Both types of behavior are commonly seen in various semiconductors and can often be used as additional evidence in support of one or the other transport mechanisms.

There has been some controversy as to the lattice site that the magnesium dopant occupies. The fact that increasing the magnesium content helps to increase the conductivity suggests that the magnesium ions are substituting for lanthanum ions on the A sites, just as with strontium. However, x-ray powder diffraction studies done by Brodmann and Morgan[14] indicate that the magnesiums are instead occupying the B sites. Anderson et al.[15] also have evidence for B site occupation based on the temperature at which an orthorombic to rhombohedral phase transition occurs in $La_{.95}Mg_{.05}CrO_3$.

Based on the weight loss measurements made by Westinghouse Corporation workers[12] and by Khattak and Cox,[11] it appears that a high temperature reducing atmosphere acting on a lanthanum chromite sample results in oxygen diffusing out of the sample. This not only decreases conductivity, but could also lead to damage at the lanthanum chromite - air electrode interface if the interface has poor oxygen access to the external oxygen supply. The indium oxide air electrode would then effectively be reduced to an indium suboxide which would form a thin nonconducting layer and reduce cell performance.[12]

Besides oxygen diffusion out of the interconnection layer, hydrogen diffusion through the layer could also cause problems at the lanthanum chromite - air electrode interface, as well as affect the lanthanum chromite conductivity. We therefore undertook to determine the extent of hydrogen diffusion through a thin layer of lanthanum chromite.

The theory of diffusion is given in great detail in diffusion[16] and statistical mechanics[17] books and will not be repeated here. A result of the theory for simple Brownian motion diffusion through membranes is that the expected squared distance, $\langle x^2 \rangle$, that a diffusing gas particle penetrates into the membrane is given by

$$\langle x^2 \rangle = 6Dt \qquad \text{Equation (18)}$$

where t is the mean time of travel and D is the diffusion coefficient. Assumptions required for Equation (18) to hold true are that the diffusing gas does not react chemically with the membrane and that the diffusion constant isn't a function of the concentration of the gas in the membrane.

For sufficiently large t, the particle may be expected to travel clear through the membrane and exit the other side. The mean time required for this to occur is given by

$$t = h^2/6D\,, \qquad \text{Equation (19)}$$

where h is the membrane thickness. Therefore, if the membrane thickness is known and the mean time required for gas to diffuse through the membrane is measured, the diffusion coefficient can be determined:

$$D = h^2/6t \qquad \text{Equation (20)}$$

Of course, some particles will pass through the membrane in a much shorter time than t, while others will be slower. For a large number of particles however, the majority can be expected to pass through the distance h in a time near the mean time t.

Another result of diffusion theory is that the rate of diffusion depends exponentially upon the temperature and is often expressed as

$$D = D_o \exp(-\varepsilon/kT), \qquad \text{Equation (21)}$$

where $\varepsilon$ is the diffusion activation energy, k is Boltzmann's constant, T is the temperature, and $D_o$ is a diffusion constant that is independent of temperature. Equations (20) and (21) can be combined to obtain

$$t = \frac{h^2}{6D_o}\exp(\varepsilon/kT) . \qquad \text{Equation (22)}$$

Therefore, if lnt is plotted against 1/T, a straight line should result with slope equal to $\varepsilon/k$. $D_o$ can also be determined from the Y-axis intercept.

# CHAPTER III

## EXPERIMENTAL

The primary purpose of the experimental work was to obtain electrical conductivity measurements of lanthanum chromite based ceramics at temperatures up to 1150°C in both air and hydrogen atmospheres. To do this, a furnace was built that is capable of sustained temperatures of up to 1200°C.

The core of the furnace consists of a ceramic fiber heater manufactured by Watlow Company of St. Louis, Mo. The heater has cylindrical inside dimensions of 2x12 inches, and has a maximum power capability of 1240 watts. The core is surrounded by a fibrous ceramic insulation and is encased in a cylindrical steel shell, 20 inches long by 15 inches in diameter. The ends of the furnace are closed with 1/2 inch thick high temperature insulating fiberboard. A 1.75 inch inside diameter muffle tube made of mullite passes through the furnace from end to end and contains a removable sample holder. The entire furnace is mounted horizontally on a welded steel stand to provide easy access to the hot zone through either end of the muffle tube. A diagram of the furnace is shown in Figure 4.

A sample holder was designed and built to slide inside the muffle tube and minimize heat loss through the ends while allowing sufficient access to the sample for test leads and thermocouple wires. The

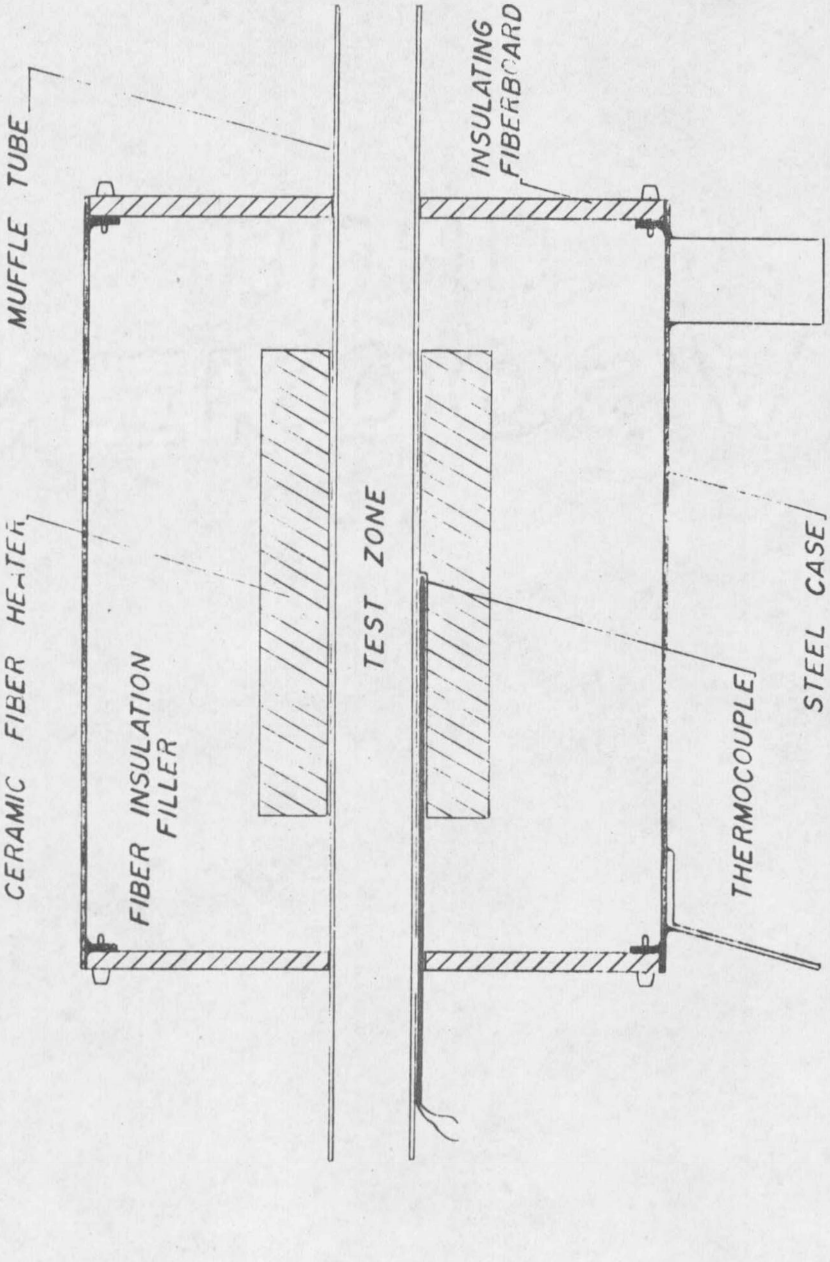


Figure 4. Schematic of Furnace.

holder also provides support for the sample and allows room for various sample shapes and sizes. The design is simple, consisting mostly of alumina rods and multiple hole tubes for support and wire access, and disk shaped firebrick wafers for structural rigidity and insulation. The center support block of the holder is carved out of firebrick and comprises the sample platform. A chromel-alumel thermocouple enters the left end of the sample holder through a two hole support tube, while the electrode wires enter through the other end. A photograph of the sample holder is shown in Figure 5.

Temperature control was accomplished with a Eurotherm temperature controller and a triac power unit. A chromel-alumel controlling thermocouple was inserted between the wall of the muffle tube and the heater core. With the thermocouple connected directly to the temperature controller, the temperature could be regulated to within 1°C. However, time required for stabilization, after increasing or decreasing the temperature, was quite long for low temperatures. Also, cycling the temperature over a wide temperature range required the constant attention of the experimenter since temperature changes had to be made in small increments. Therefore, a super-slow voltage ramp was designed and built, and connected in series with the thermocouple. Basically, the function of the voltage ramp is to trick the temperature controller into producing a temperature in accordance with the sum of the voltage ramp and thermocouple voltages. In this way, when

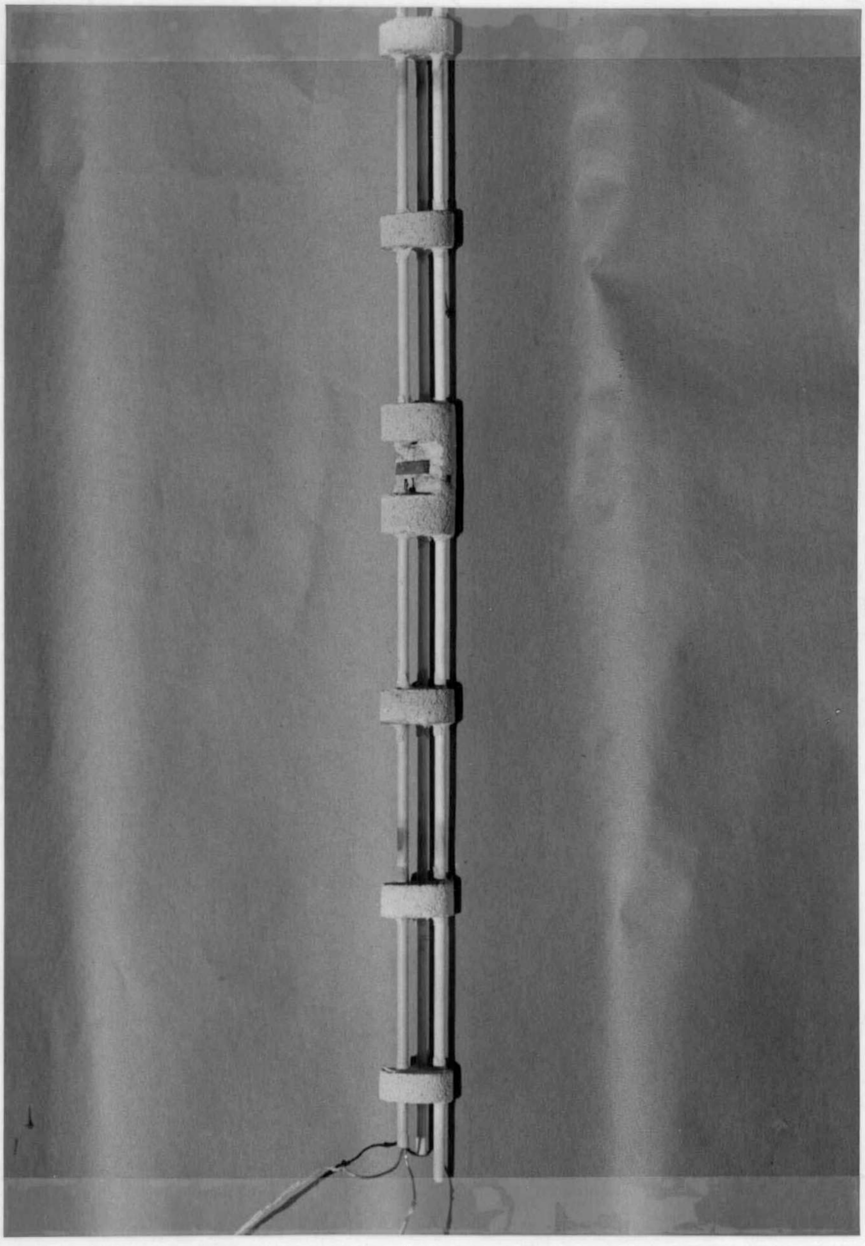

Figure 5. The Sample Holder.

the voltage ramp voltage is zero, the controller regulates according to its actual setting. But when the voltage ramp voltage increases, the controller will respond with a correspondingly lower temperature. Thus the temperature can be raised or lowered at a uniform rate.

The voltage ramp consists of a square wave oscillator driving a twelve bit binary counter which in turn drives a twelve bit digital to analog converter. By varying the oscillator frequency, the voltage output can be linearly ramped with a full scale period from several minutes up to several days. Additional logic allows the temperature to be ramped up to a specified point, where it will hold for a specified length of time before ramping back down to room temperature.

In a fuel cell, lanthanum chromite ceramics would be exposed to reducing atmospheres as well as to air. Therefore, in order to explore the electrical conductivity properties of these materials as they would be in actual operation, it was necessary to provide the furnace with the capability of maintaining the sample under reducing conditions. To do this a gas exchange system was used which allows the use of either air or hydrogen in the furnace, as well as argon which is typically used to purge the furnace and gas lines before an atmosphere change. A schematic of the system is shown in Figure 6.

The gas exchange system includes pressure regulators and flow meters controlling the three possible atmospheres. The furnace ends

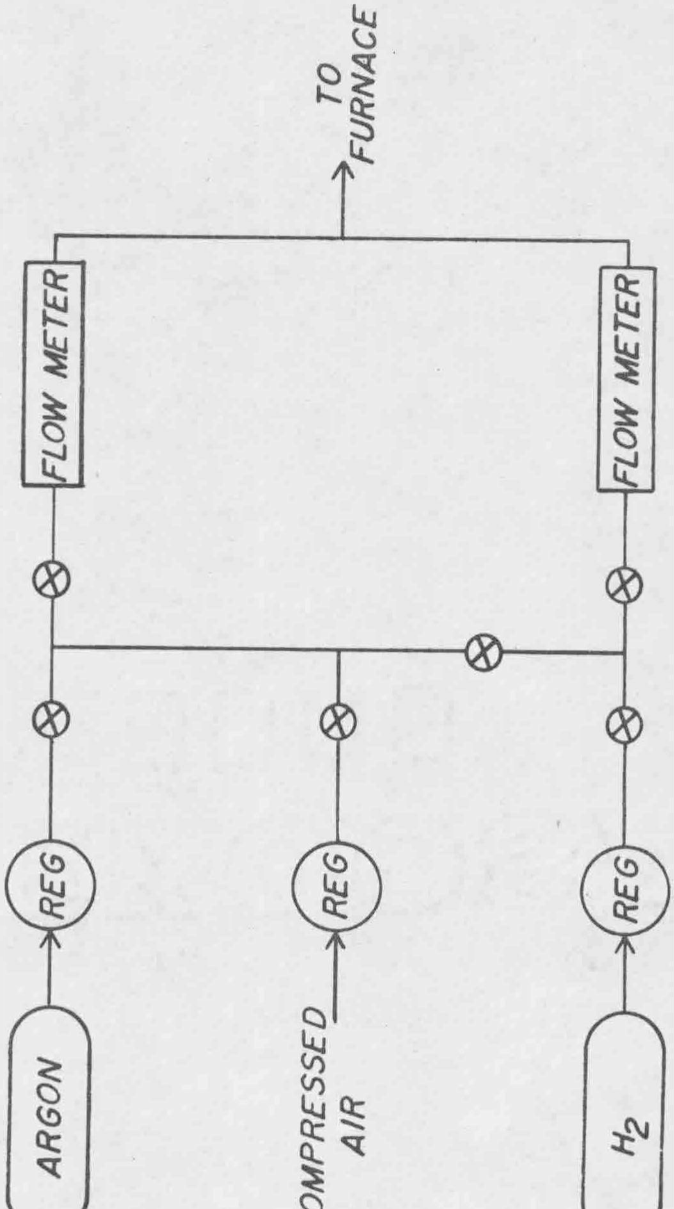


Figure 6. Schematic of Atmosphere Control System.

were sealed with end caps fabricated from clear plexiglas and sealed to the muffle tube with pliable silicone calk. The end caps were equipped with gas inlet and outlet tubes as well as feed-throughs for the thermocouple and test leads. All gaps around the leads were also sealed with silicone calk for gas tightness. The outlet tube was attached to a set of valves so the gas could be vented to the atmosphere directly or through a long hypodermic needle where, in the case of hydrogen, it could be safely disposed of by burning. Typical procedure of operation when switching from an air atmosphere to a hydrogen atmosphere, especially at high temperatures, was to first purge the system with argon at a high flow rate to thoroughly scavenge the furnace interior and sample holder of air. After several minutes of purging, the argon could be turned off and the hydrogen applied at the desired flow rate which was typically about 150 scc/min.

The following bulk lanthanum chromite samples were supplied by General Refractories Company:

1. $La_{.84}Sr_{.16}Al_{.15}Cr_{.85}O_3$
2. $La_{.90}Ca_{.10}Al_{.15}Cr_{.85}O_3$
3. $LaAl_{.15}Mg_{.02}Cr_{.83}O_3$
4. $La_{.84}Sr_{.16}CrO_3$

A detailed description of their manufacture appears in an article by Brodmann and Morgan.[14] Bulk samples identical in composition to 1, 2, and 3 shown above, were also obtained from A-T Research Company. The preparation method for these samples is also described elsewhere.[18]

Samples were prepared for conductivity measurements by first cutting to approximate dimensions of 4x5x25 mm. The bulk samples were mounted on a modified milling bench and cut to size with a 4 inch diameter, 0.015 inch thick precision diamond saw. It is highly desirable to produce a uniform cross section along the length of the sample to insure that the conductivity calculations are accurate. After cutting, four holes were drilled for the current and voltage electrodes with a 1 mm diameter diamond drill. Drilling must be done with the sample immersed in water for lubrication and cooling. The electrode current holes were drilled in the ends of the sample and the voltage holes were drilled into the 5 mm wide face with a separation of about 13 mm. All holes were drilled to a depth of approximately 2 mm.

After the holes were drilled, 0.005 inch diameter platinum electrode wires were attached and held in place with platinum sponge packed tightly in the holes and around the wires. The sample was then mounted in the sample holder and the electrode wires were spot-welded to 0.010 inch diameter lead-in wires which were also made of platinum. A mounted sample is shown in Figure 7.

When measurements were being taken in a hydrogen atmosphere, it was found that the platinum electrode wires were being corroded in the

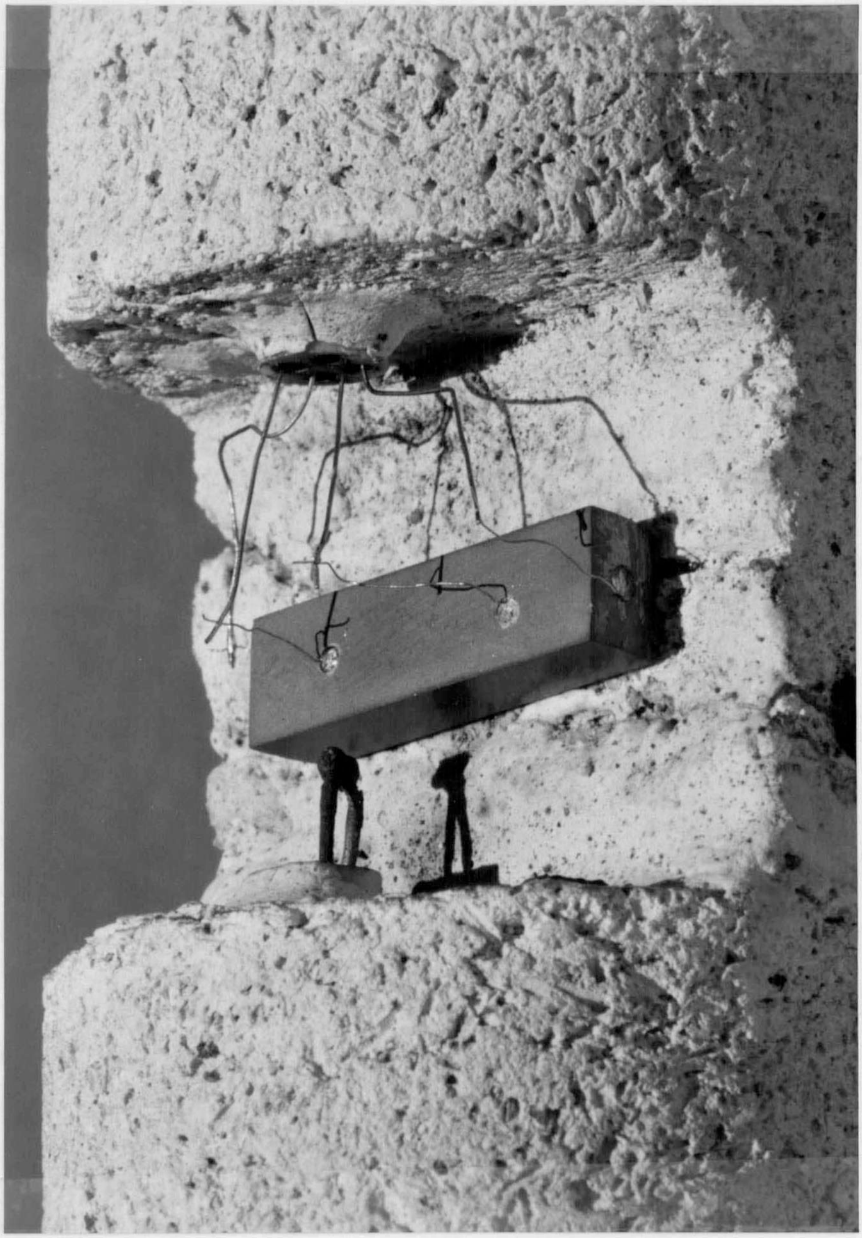

Figure 7. Sample Mounted in the Sample Holder.

presence of hydrogen at high temperature, resulting in breakage and considerable loss of time. Therefore, for all runs which required the sample to be exposed to hydrogen at elevated temperatures, steel lead-in wires and 0.003 inch diameter steel electrode wires were used in place of the platinum. The steel worked well in hydrogen, but of course could not be used in air at high temperatures.

The main difficulty encountered during sample preparation was that some of the bulk samples possessed a number of internal fracture lines. These samples broke along the fracture lines during the cutting process or while drilling the electrode holes. Samples supplied by General Refractories Company weren't too bad in this respect and it was possible to cut the samples from areas of the bulk pieces that had no fractures.

Conductivity measurements were taken utilizing the constant current method. This method uses a current source to supply a constant regulated current through the sample. Within the limitations of the equipment, the current, I, will remain the same regardless of the sample resistance. A separate high input impedance voltmeter is then used to measure the voltage drop V between any two points on the surface of the sample. If the voltage contacts are collinear with the current contacts, the resistance R of the sample between the voltage contacts is given by Ohm's law:

$$R = V/I \, .$$

Conductivity, $\sigma$, can then be calculated using

$$\sigma = L/RA \quad ,$$

where A and L are respectively the cross-sectional area of the sample and the distance between the voltage contacts. The technique can also be used with only two contacts by simply using the same two contacts for both current and voltage connections. The advantage of the four contact method over the two contact method is that it effectively eliminates any errors due to poor connection or anomalous behavior, such a polarization effects, at the electrode-sample interface. Also, a more uniform current distribution can be expected between the voltage contacts with the four contact method.

Measurements in air were taken using the four contact method only. Air measurements were also taken with an AC bridge (Hewlett-Packard 4262A). The AC bridge also uses a four contact method, but it does not utilize the constant current technique. When taking measurements in a hydrogen atmosphere, both the four contact and two contact methods were used. This was done because it was suspected that the hydrogen was having a large effect on the contact-sample interface resistance. This interface resistance could be observed by subtracting the four contact resistance from the two contact resistance.

The AC bridge was not used for the hydrogen measurements. Instead, a frequency generator was used to modulate the current source and an AC digital voltmeter was used at the voltage contacts. The amplitude of the modulated current was adjusted with a potentiometer to give an r.m.s. AC output current equal to that of the DC current. DC and AC readings could then be easily compared. This AC method worked well if the frequency was kept below 1000 Hz; the current source did not regulate well when modulated at higher frequencies. A schematic of the electrical system used for the hydrogen measurements is shown in Figure 8.

Data were taken while both heating and cooling. This was done so that any conductivity changes caused by the recent thermal history of the sample could be noted. It was especially important to take both heating and cooling curves during the hydrogen experiments since we were interested in observing any changes in conductivity the hydrogen might cause in the sample at high temperatures.

All DC measurements were taken with both forward and reverse polarity and the values averaged. This was to minimize any polarization effects that might occur in the sample if a continuous unidirectional current were used.

After AC, DC, four contact, and two contact measurements were made and recorded at a given temperature, the conductivity was derived and plotted against $10^4/T$ on semilog paper. The temperature was then increased or decreased by an interval which was determined by referring to the semilog plot. The temperature intervals were chosen to give evenly spaced data points on the curve or to provide more points in

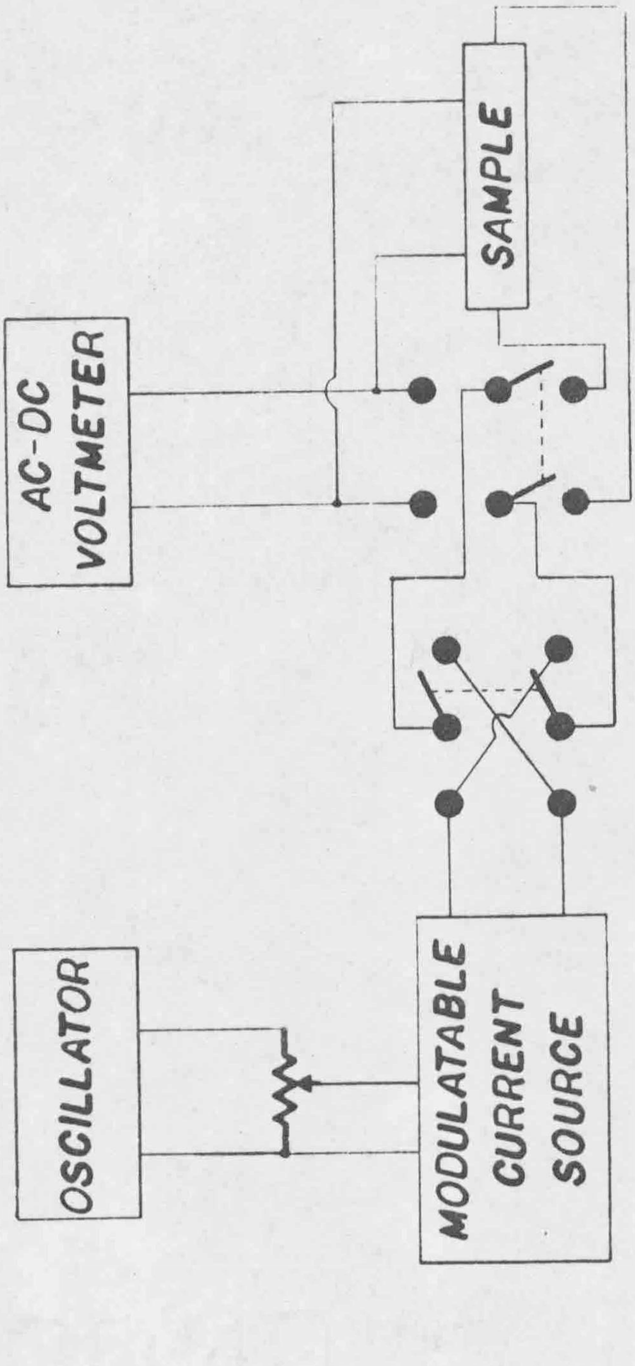


Figure 8. Schematic of Electrical Conductivity Experiment.

the more interesting areas of the curve. Between conductivity measurements at different temperatures, the sample was allowed at least a half hour to come to thermal equilibrium.

One important consideration when using a constant current source is the power being delivered to the sample by the test current: $P=I^2R$. If, for example, the sample resistance increases significantly during an experiment, the current must be reduced in order to keep the power within reasonable limits. If this is not done, the sample temperature will rise and the increase probably won't be detected by the thermocouple. This will result in an erroneous conductivity measurement. For the lanthanum chromite samples, the power was limited to about 10 milliwatts.

The approach taken to investigate the diffusion of hydrogen in lanthanum chromite was based on a permeation method using a Balzers Quadrupole Mass Spectrometer QMG 101 as the hydrogen sensing device. This method makes use of the sample as a barrier separating a constant pressure hydrogen supply from a high vacuum system. The mass spectrometer was situated in line with the vacuum system so that any hydrogen that diffused through the sample could be detected. By observing the time required for hydrogen to diffuse through at various temperatures, the diffusion constant $D_0$ and the diffusion activation energy $\varepsilon$ were calculated.

The vacuum system consisted essentially of a mechanical fore pump, an oil diffusion pump and an ion pump, connected to the mass spectrometer. The lanthanum chromite sample was mounted in a manifold between the mass spectrometer and a supply of hydrogen held at approximately atmospheric pressure. The sample manifold was surrounded by an oven made of ceramic fiber heaters with the temperature regulated by a chromel-alumel thermocouple, a temperature controller and a digital voltage ramp. An additional rotary pump was connected to the hydrogen supply with a valve to provide for hydrogen scavenging from the pressure side of the sample.

By far the most difficult problem with this sort of set-up is the matter of keeping a good vacuum seal on the sample even at high temperatures. A number of trials were made using thinly sliced bulk samples of lanthanum chromite with various types of seals. The fragility of the thin samples, the thermal expansion coefficient differences and the high temperature requirement caused considerable problems. In all cases, the seal either leaked initially or developed a flaw as the temperature was increased. Another consideration with this method is that the diffusion through the sealing material must be small compared to the diffusion through the sample.

The sealing problem was solved when A. Isenberg of Westinghouse Corporation donated a magnesium doped lanthanum chromite sample. The sample was in the form of a thin film coated on the outside of a 1/2 inch diameter porous zirconia tube. The layer was 30 - 40 microns thick and covered the full length of the 20 cm long tube including one closed end. The open end of the sample tube was epoxied to a stainless steel flange and mounted on the high vacuum system. Thus, the inside of the sample tube was exposed to high vacuum, while the outside of the tube was at atmospheric pressure. Tests showed that the thin lanthanum chromite layer had no leaks. Next, a muffle tube was built of thin wall stainless steel tubing and was fitted around the entire sample tube. Hydrogen admitted to the inside of this muffle tube would then completely surround the sample tube and diffusion measurements could be made. Finally, a thermocouple was attached to the end of the sample tube and the furnace was rigged to the outside of the muffle tube. The furnace was positioned so that the closed end of the sample tube could be heated to high temperatures, while the end epoxied to the vacuum system could be kept relatively cool, thereby insuring a good vacuum seal. A good vacuum was attained ($10^{-8}$ torr) with this set-up, and temperatures as high as 900°C were reached without damage to the lanthanum chromite sample tube or its surrounding stainless steel muffle tube. A diagram of the sample tube with its associated hardware is shown in Figure 9.

The following procedure was used for hydrogen diffusion measurements:

1. Apply high vacuum to inside of sample tube.