



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

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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 O₃ 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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ABSTRACT

Lanthanum chromite is a ceramic electrical conductor being studied for possible use in high temperature solid electrolyte fuel cells. Electrical conductivity of $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$, $\text{LaMg}_{.02}\text{Al}_{.15}\text{Cr}_{.83}\text{O}_3$ and $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ 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 $\text{La}_{.90}\text{Mg}_{.10}\text{CrO}_3$ 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 optimization¹ 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 $1000^\circ C$. 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

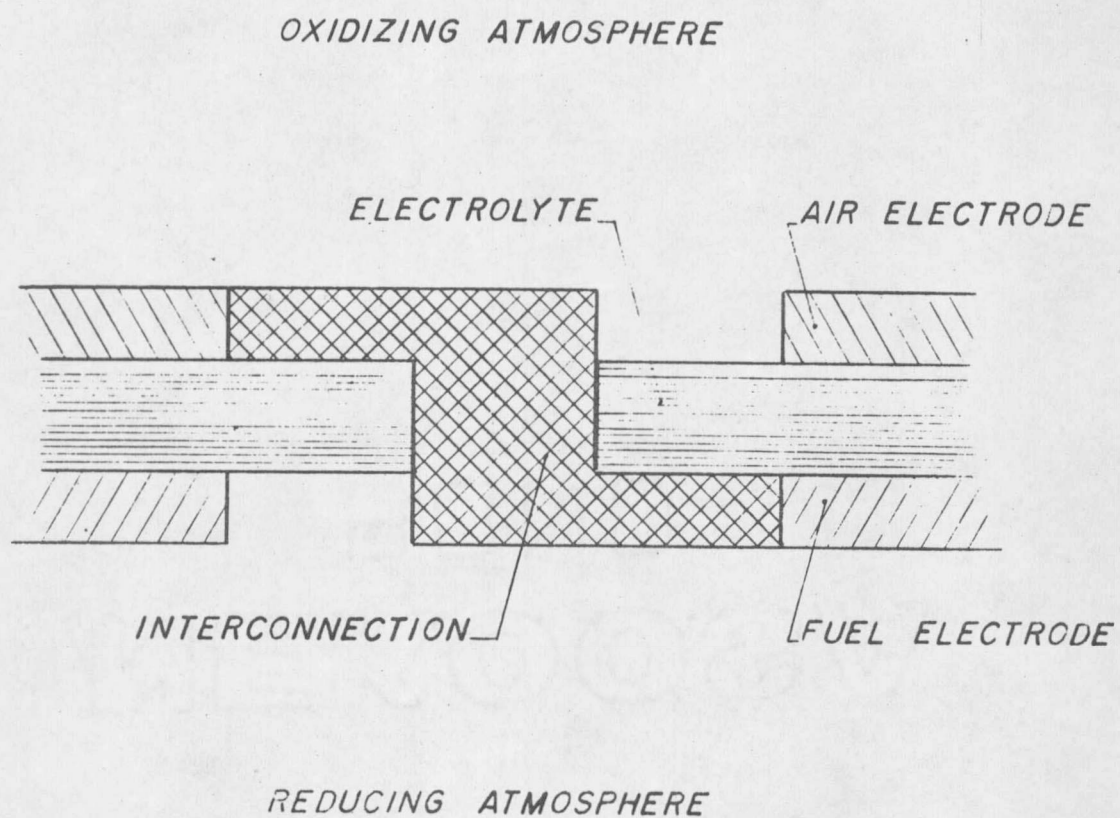


Figure 1. Fuel Cell Battery Interconnection.

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, ($\sigma \sim 10^6 \text{ (ohm-cm)}^{-1}$), and insulators having the lowest ($\sigma \sim 10^{-14}$ to $10^{-22} \text{ (ohm-cm)}^{-1}$).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, μ_e and μ_h , must also be considered. The electrical conductivity can then be written

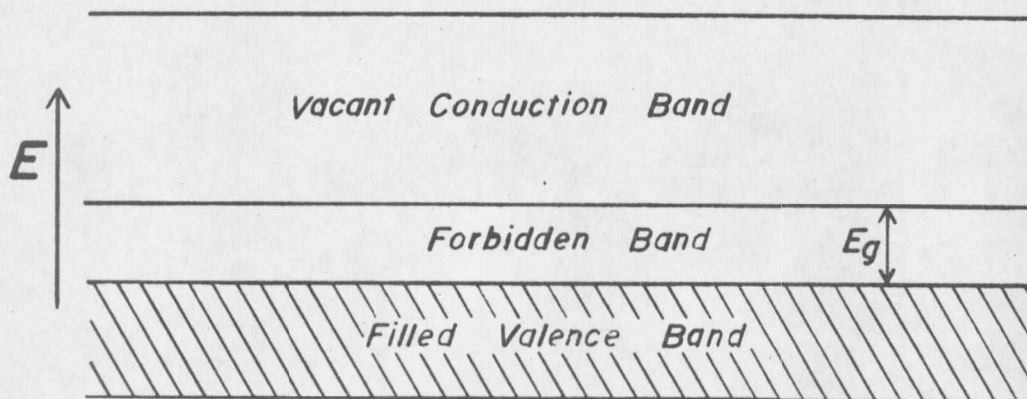


Figure 2. Simplified Band Structure of a Semiconductor at Absolute Zero Temperature.

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

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

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

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 :

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

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 :

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

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:

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

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:

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

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

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

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

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

the distribution functions can be approximated by

$$\begin{aligned} f_e &= \exp\{-(E-E_f)/kT\} & \text{for } E > E_c, \\ \text{and } f_h &= \exp\{-(E_f-E)/kT\} & \text{for } E < E_v. \end{aligned} \quad \text{Equation (9)}$$

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

$$\begin{aligned} n_e &= \frac{1}{2\pi^2} (2m_e/h^2)^{3/2} \int_{E_c}^{\infty} (E-E_c)^{1/2} \exp\{-(E-E_f)/kT\} dE \\ n_h &= \frac{1}{2\pi^2} (2m_h/h^2)^{3/2} \int_{-\infty}^{E_v} (E_v-E)^{1/2} \exp\{-(E_f-E)/kT\} dE. \end{aligned} \quad \text{Equation (10)}$$

Equations (10) can be integrated to give

$$\begin{aligned} n_e &= \frac{1}{4} (2m_e kT/\pi h^2)^{3/2} \exp\{-(E_c-E_f)/kT\} \\ \text{and } n_h &= \frac{1}{4} (2m_h kT/\pi h^2)^{3/2} \exp\{-(E_f-E_v)/kT\}. \end{aligned} \quad \text{Equation (11)}$$

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

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

The temperature dependence of the mobilities, μ_e and μ_h , must also be considered. For an intrinsic semiconductor at high temperatures ($T \gg$ room temperature), the charge carrier mobilities are affected primarily by lattice scattering. It has been shown theoretically⁵ and experimentally⁶ 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

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

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

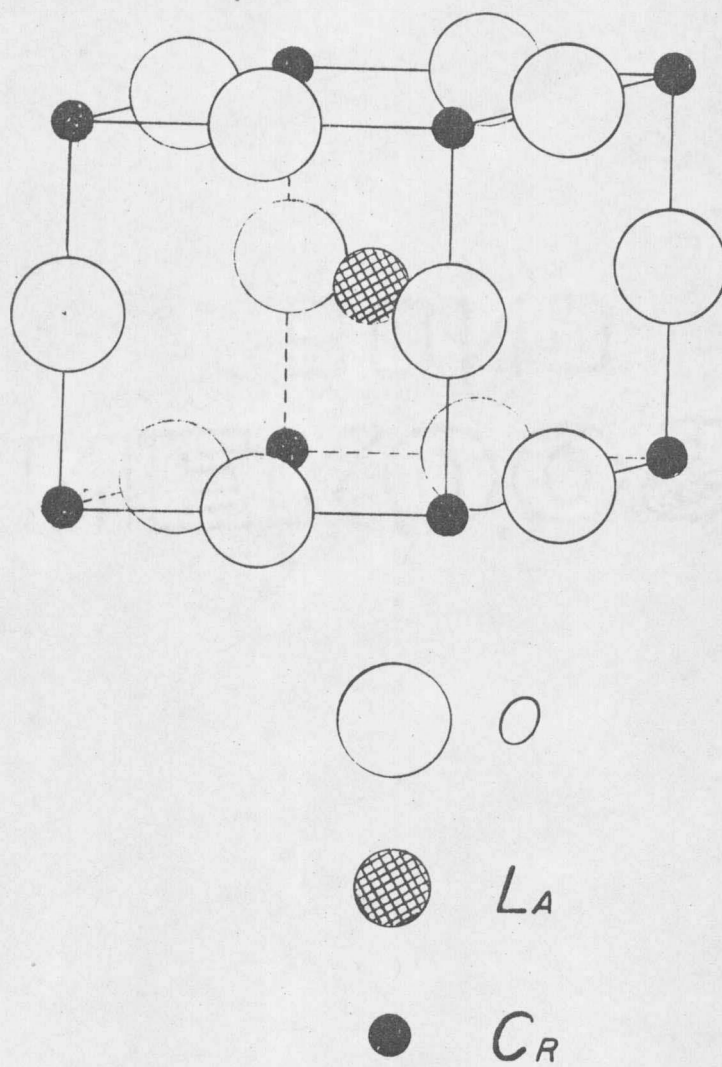


Figure 3. Lanthanum Chromite Crystal Structure.

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.

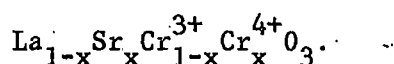
Wirtz⁹ has analyzed the conductivity of doped lanthanum chromite and other rare earth perovskites. In his analysis, it was assumed that for pure LaCrO_3 , the lanthanum cation acts as an electron donor which supplies its valence electrons to the bonds formed between the

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 σ , π 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 σ , π 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 σ , π and $P\pi$ bands. The 3 remaining chromium d-electrons fill the lower half of a higher energy collective electron band (π^* 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

$$\sigma \propto T^n \exp(-E/kT), \quad n \geq 0$$

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 $(\text{La},\text{Sr})\text{CrO}_3$ system can then be expressed by



The result will be one less electron in the uppermost occupied energy band (π^* 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 Cox¹¹ have reported a weight loss in a $\text{La}_{.75}\text{Sr}_{.25}\text{CrO}_3$ 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 $\text{La}_{.75}\text{Sr}_{.25}\text{CrO}_{2.89}$. A cell volume increase was also noted and was also explained by an oxygen deficiency. Westinghouse Corporation workers¹² saw a similar oxygen loss in $\text{LaMg}_{.02}\text{Al}_{.23}\text{Cr}_{.75}\text{O}_3$ 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 Aldred⁸ 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

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

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

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

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 Aldred⁸ 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. Meadowcroft¹⁰ 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 Morgan¹⁴ 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 $\text{La}_{.95}\text{Mg}_{.05}\text{CrO}_3$.

Based on the weight loss measurements made by Westinghouse Corporation workers¹² 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 diffusion¹⁶ and statistical mechanics¹⁷ 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

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

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

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

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:

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

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

$$D = D_0 \exp(-\varepsilon/kT), \quad \text{Equation (21)}$$

where ε is the diffusion activation energy, k is Boltzmann's constant, T is the temperature, and D_0 is a diffusion constant that is independent of temperature. Equations (20) and (21) can be combined to obtain

$$t = \frac{h^2}{6D_0} \exp(\varepsilon/kT) . \quad \text{Equation (22)}$$

Therefore, if $\ln t$ is plotted against $1/T$, a straight line should result with slope equal to ε/k . D_0 can also be determined from the Y-axis intercept.

CHAPTER III

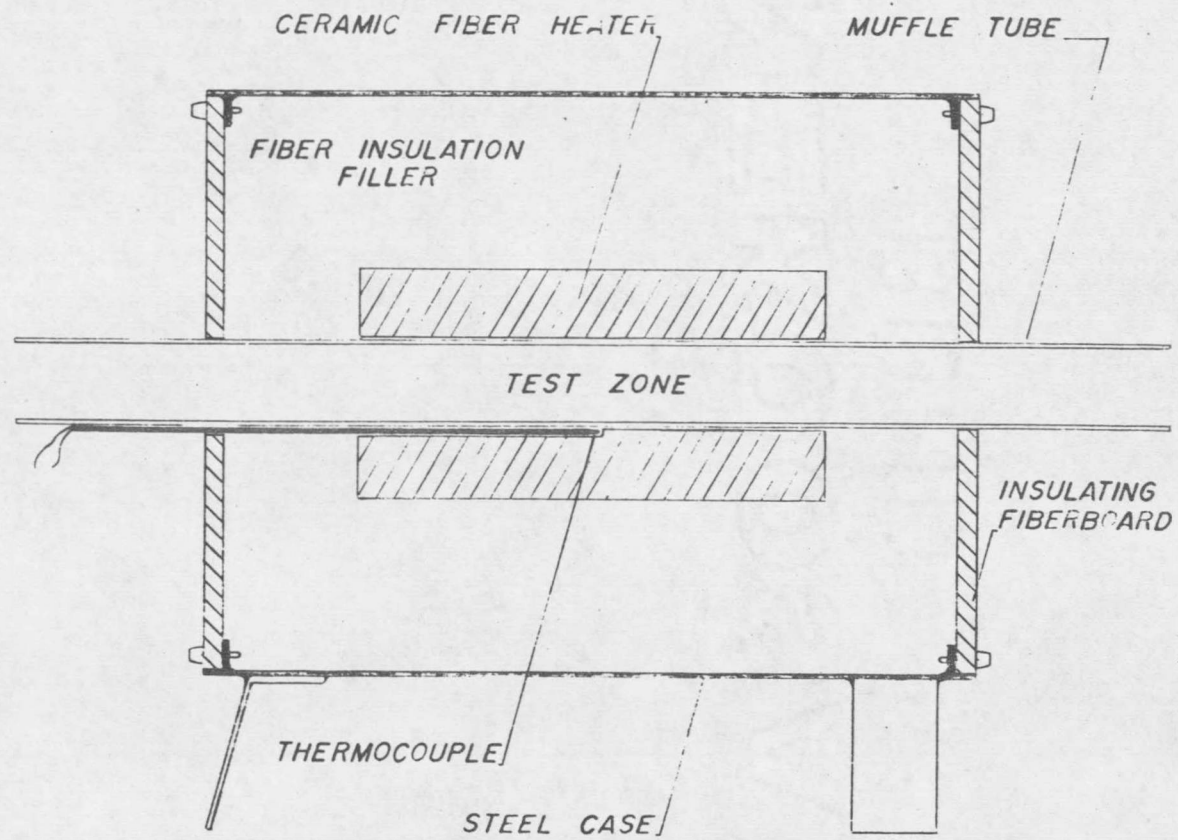
EXPERIMENTAL

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

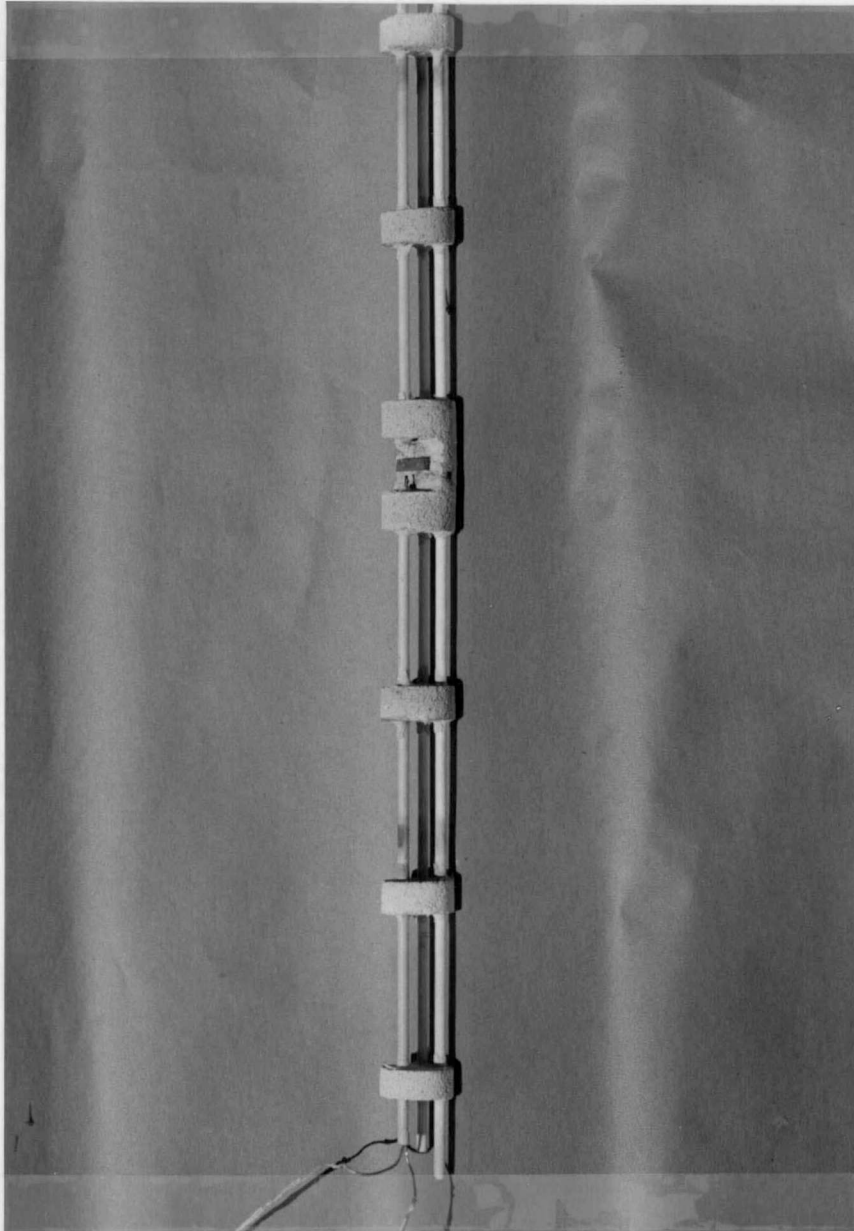


Figure 5. The Sample Holder.

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

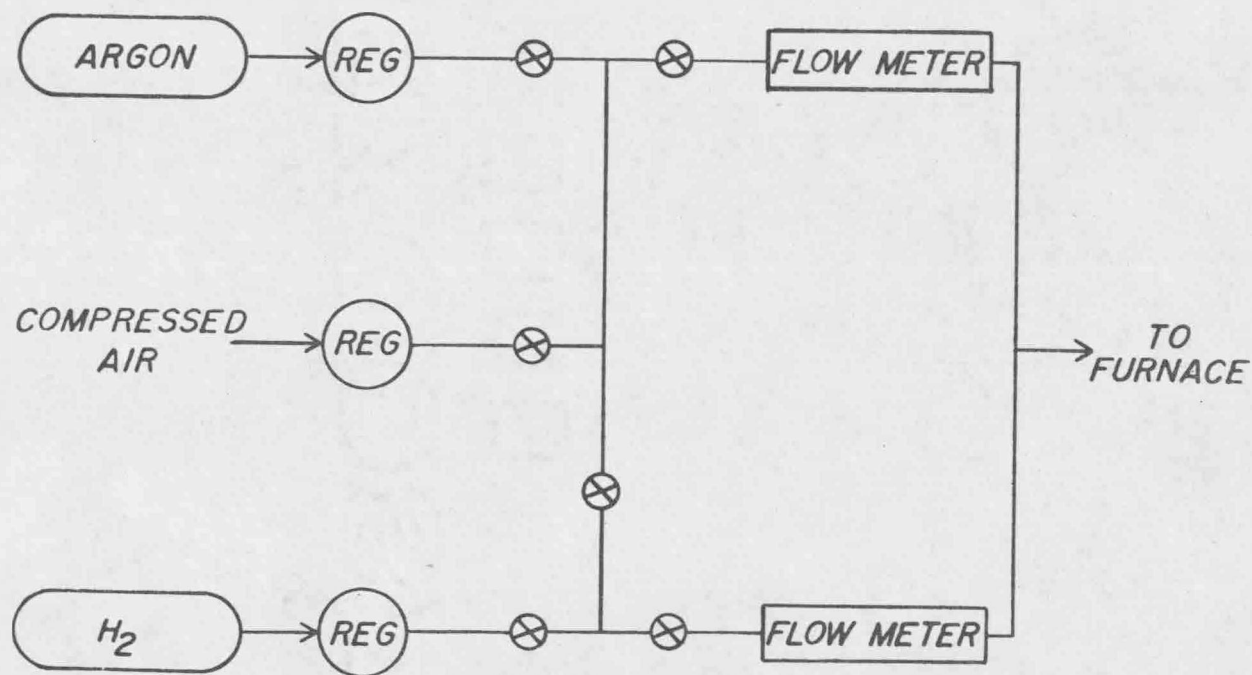


Figure 6. Schematic of Atmosphere Control System.

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. $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$
2. $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$
3. $\text{LaAl}_{.15}\text{Mg}_{.02}\text{Cr}_{.83}\text{O}_3$
4. $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$

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

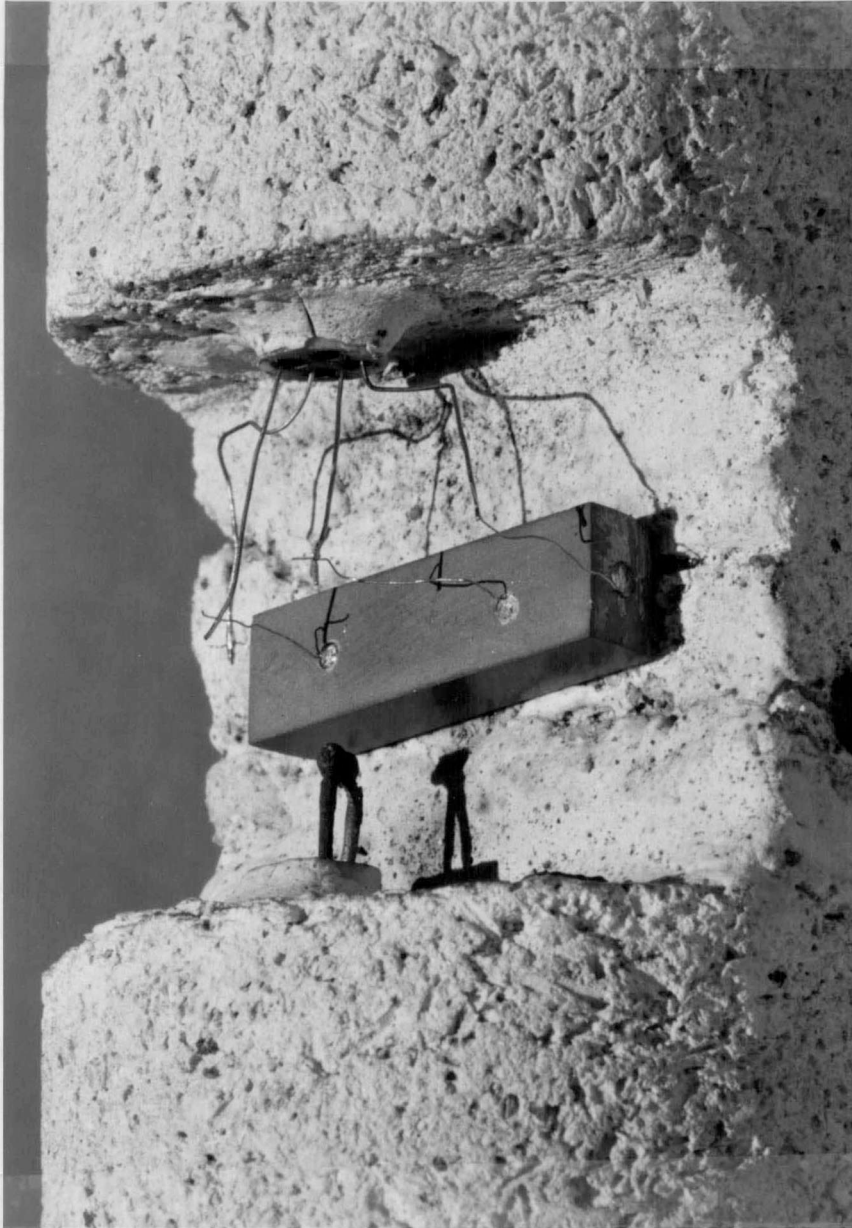


Figure 7. Sample Mounted in the Sample Holder.

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, σ , can then be calculated using

$$\sigma = L/RA,$$

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 as 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

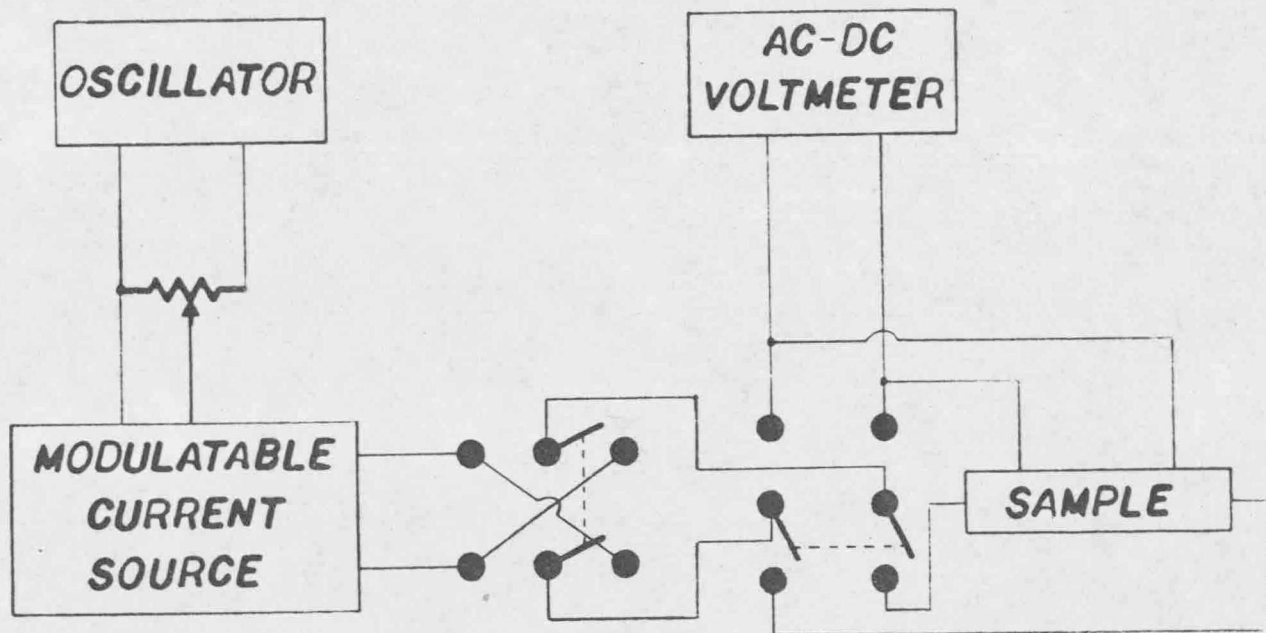


Figure 8. Schematic of Electrical Conductivity Experiment.

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 ϵ 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.

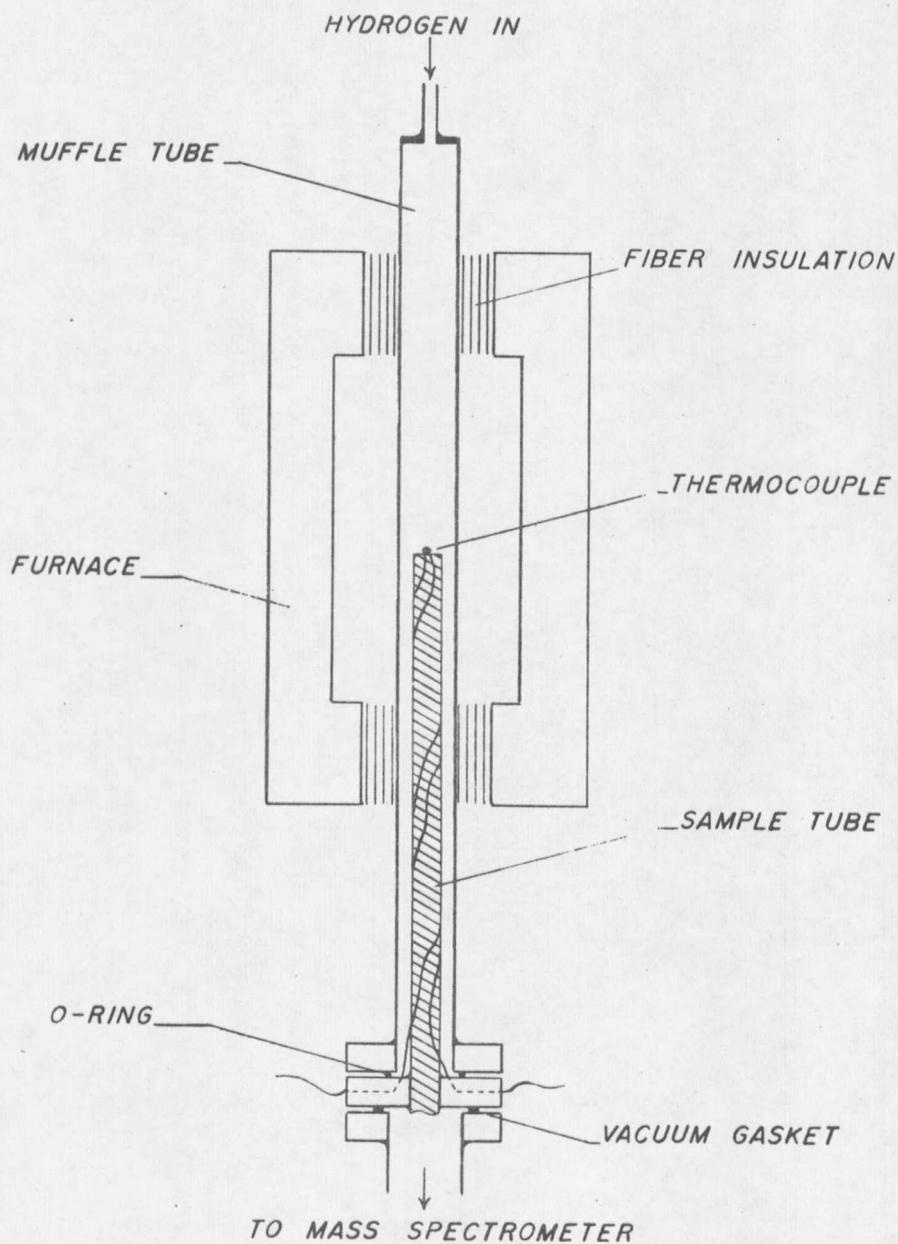


Figure 9. Schematic of Hydrogen Diffusion Apparatus.

2. Scavenge muffle tube with rotary pump.
3. Adjust temperature of assembly to desired value.
4. Adjust mass spectrometer to monitor the hydrogen peak and display on an X-Y recorder with a time base driving the X-axis.
5. Allow system to come to thermal equilibrium.
6. Apply hydrogen at a fixed pressure to the outside of the sample tube.
7. Watch for an increase in hydrogen line height on the X-Y recorder. Note the time lag from the moment of hydrogen application to the sensing of hydrogen in the mass spectrometer.
8. Scavenge hydrogen from the muffle tube with the rotary pump and observe the decay of the hydrogen peak with time.

The above procedure was followed in 50°C intervals from 100°C to 900°C. Diffusion was first observed at 500°C and it increased with each increase in temperature. There was a diffusion time lag associated with each temperature and it could be read directly from the X-Y recorder.

CHAPTER IV

DATA AND DISCUSSION

Conductivity data were first taken on all of the samples in air. The results of these measurements are plotted in Figure 10 showing $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$, $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ and $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$; and in Figure 11 showing $\text{LaMg}_{.02}\text{Al}_{.15}\text{Cr}_{.83}\text{O}_3$. These plots were all obtained with the four contact DC method. AC data were also taken on all of the samples, except for $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$, with the AC bridge.

Measurements taken with the AC bridge yielded results identical to the DC measurements at all temperatures above about 200°C. At temperatures below this, the AC conductivities were typically slightly lower than the DC readings, becoming as much as 2% lower at room temperature. This could possibly be due to some ionic contribution to the conductivity, noticeable only at lower temperatures. However, since roughly the same discrepancy was observed for all of the bridge frequencies (120 Hz, 1 kHz, 10 kHz), it is believed that the effect was caused by a calibration problem in the AC bridge that was accentuated at the high resistances that occurred in the samples at low temperatures. If it were due to ionic conductivity, the 10 kHz readings would be expected to yield much higher resistances than the 120 Hz readings. In any case, the discrepancy would not be noticeable on graph paper and it disappeared altogether above about 200°C.

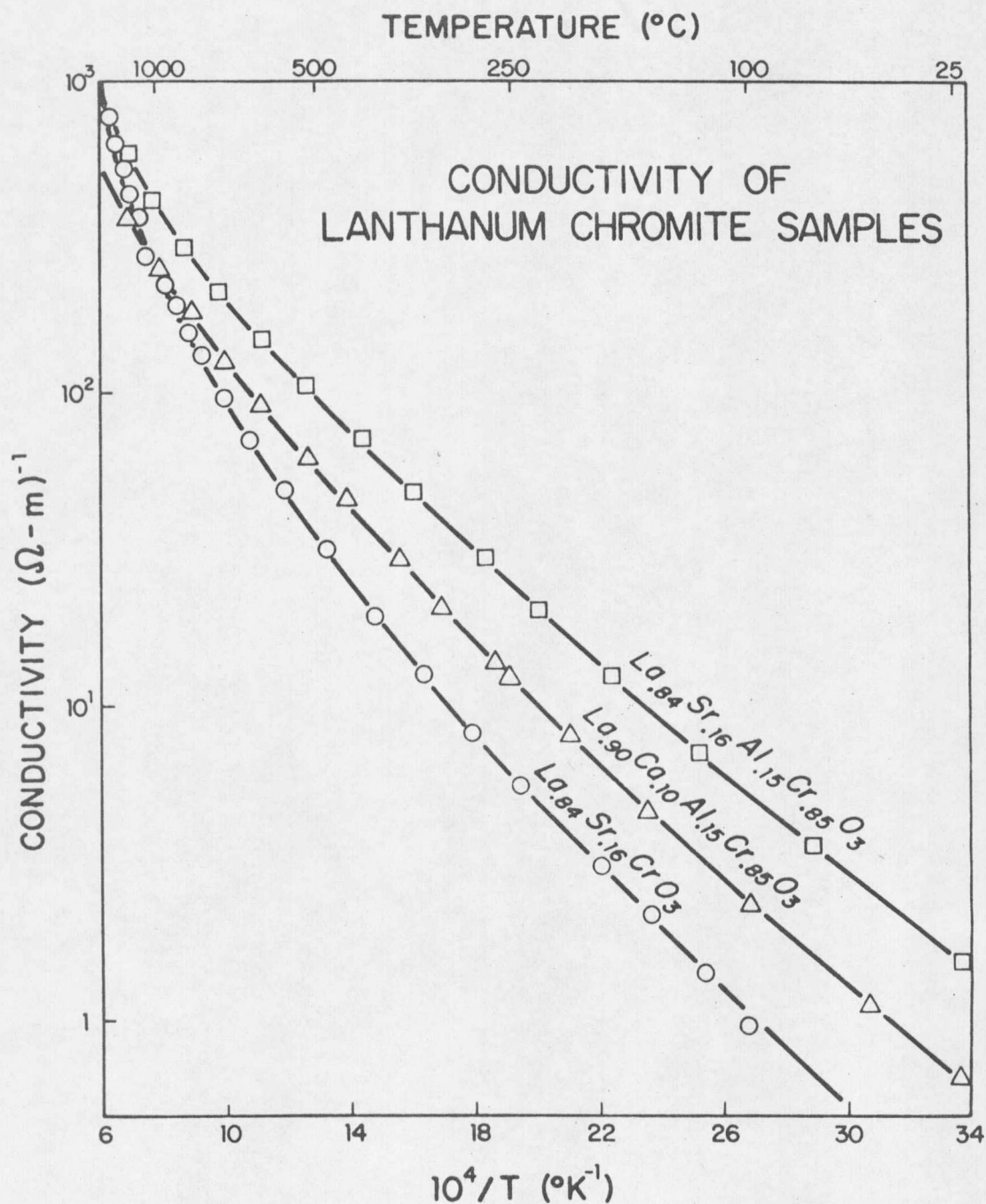


Figure 10. Electrical Conductivity of Lanthanum Chromite
Samples in Air Atmosphere.

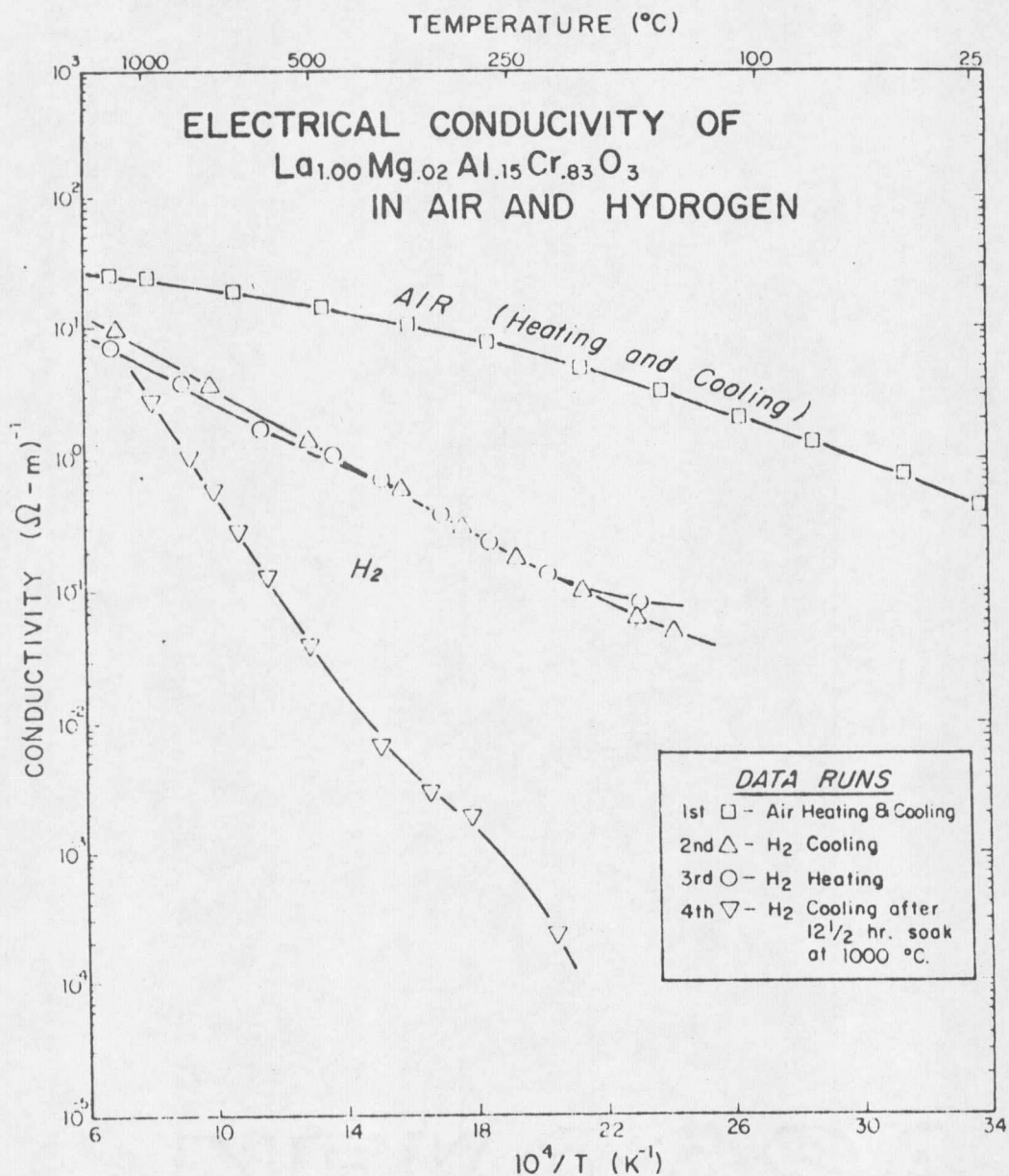


Figure 11. Electrical Conductivity of $\text{LaMg}_{.02}\text{Al}_{.15}\text{Cr}_{.83}\text{O}_3$ in Air and Hydrogen Atmospheres.

Therefore, the AC measurements have not been plotted. Detailed discussions of ionic conductivity in crystals appear in the literature.¹⁹

During routine measurements, capacitance and inductance were also occasionally checked with the AC bridge. These readings were always zero or extremely low for all temperatures and frequencies.

Other workers have taken similar measurements on these materials. $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$, in particular, has been studied by a number of experimenters with widely ranging results. For example, the following conductivity values have been reported at 1000°C: Brodmann and Morgan,¹⁴ $450 (\Omega\text{-m})^{-1}$; Karim and Aldrid⁸, $3000 (\Omega\text{-m})^{-1}$; Webb and Sayer,²⁰ $500 (\Omega\text{-m})^{-1}$. These widely varied values point out the tremendous effect differences in preparation can have on the conductivity. It is therefore not surprising to find that our value of about $250 (\Omega\text{-m})^{-1}$ at 1000°C differs from the above values. It is encouraging however, that our value differs only by about a factor of 2 from the Brodmann and Morgan value, since both of these samples were manufactured at General Refractories Company.

Conductivities of magnesium and aluminum doped lanthanum chromite samples have been given in a report by Anderson *et al.*¹⁵ in which it was assumed that the magnesium was replacing the lanthanum on the A site of the perovskite lattice. The formulations tested were $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{1-x}\text{Al}_x\text{O}_3$ with $x = 0.0, 0.25, 0.5, 0.75, 0.9$, and 1.0 . At 1000°C, both the $x = 0$ and $x = 0.25$ formulations yielded values of

about $500 (\Omega\text{-m})^{-1}$, as reported by Anderson, and it can be assumed that if a formulation with $x = 0.15$ had been tested, it would have produced similar results. Our magnesium and aluminum doped sample, with $x = 0.15$, had a conductivity of about $25 (\Omega\text{-m})^{-1}$ in air at 1000°C . Thus, our results are a factor of 20 below the inferred Anderson results at 1000°C . This difference might be explainable in terms of differences in sample manufacture. More important, though, is the fact that the samples reported by Anderson contained 2.5 times more magnesium than our sample. This could be taken as evidence that magnesium doping adds significantly to the conductivity of LaCrO_3 , although identical preparation methods would be needed to confirm this.

Brodmann and Morgan¹⁴ have made quantitative x-ray diffraction measurements on magnesium and strontium doped lanthanum chromites and found that the magnesium is replacing chromium rather than lanthanum. This was later confirmed by Anderson et al.¹⁵

The most significant feature of these data is the difference in curvature of the data plotted in Figure 11 as compared with the rest of the data plotted in Figure 10. The strontium and calcium doped samples all show different conductivities at low temperatures, but gradually approach equal values at 1000°C . This is the sort of behavior that is expected for semiconductors that obey a collective electron model in which the charge carrier concentration increases exponentially with temperature; the intrinsic conductivity overshadows

the extrinsic conductivity at high temperatures. The curvatures of the plots indicate a pre-exponential temperature term with a power greater than zero. This would also be expected with a collective electron model in which the carrier mobility increases as a simple power of the temperature. Therefore, it appears from our data that the calcium, strontium and strontium/aluminum doped samples obey a collective electron model and have conductivities of about $300 (\Omega\text{-m})^{-1}$ at 1000°C . In contrast is the magnesium/aluminum doped sample shown in Figure 11. Although this sample is roughly equal in conductivity with the others at room temperature, its conductivity at 1000°C is only about $25 (\Omega\text{-m})^{-1}$. Also, the curvature of the plot indicates an inverse temperature pre-exponential term. This is strong evidence in support of a localized electron (small-polaron) transport mechanism for this sample. To further illustrate the nature of the pre-exponential temperature terms indicated by these data, the calcium doped sample data is shown replotted in Figure 12 as σ/T versus $1/T$ and the magnesium doped sample data is shown in Figure 13 plotted as σT versus $1/T$.

If the magnesium/aluminum doped sample does indeed conduct by small-polaron hopping, we have no ready explanation for why the other samples do not also. Although it was the only sample tested that had no lanthanum substitution, this lack would not be expected to result in much more than a reduction in the number of hole charge carriers

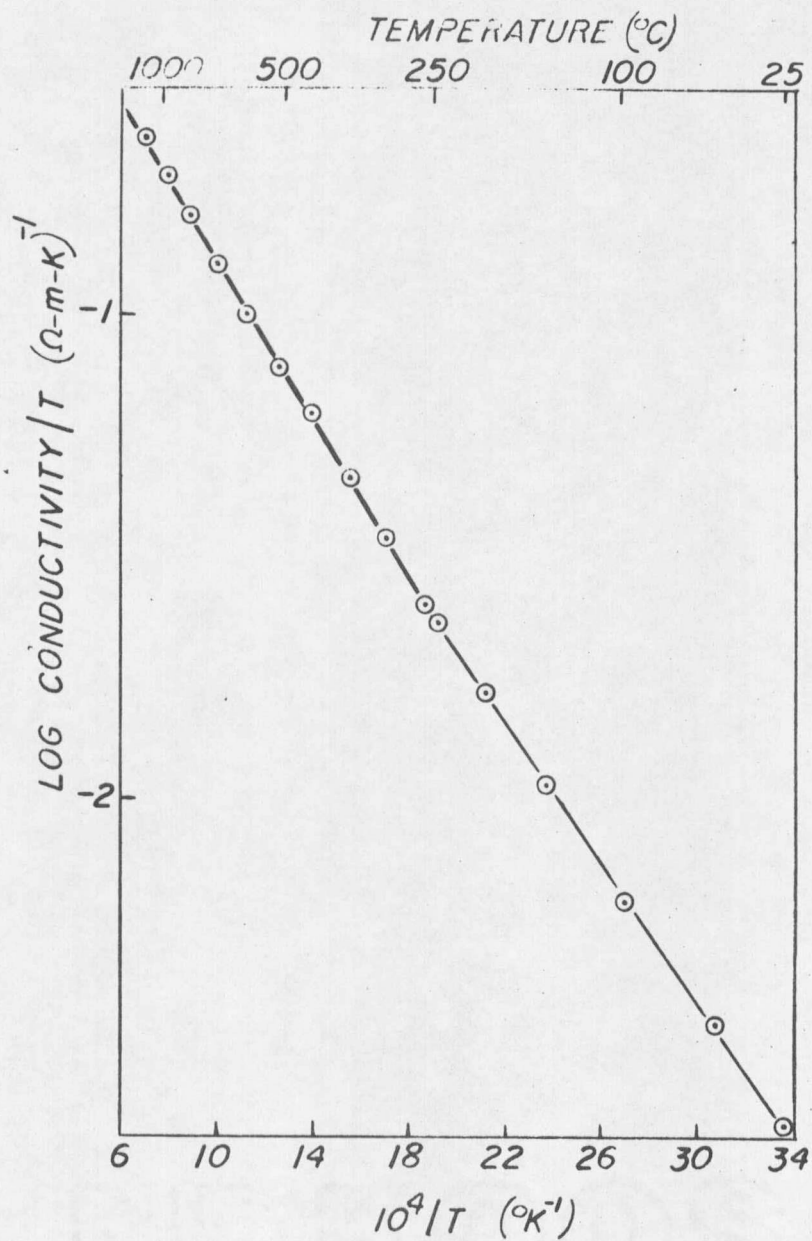


Figure 12. Electrical Conductivity Divided By Temperature
of $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ in Air Atmosphere.

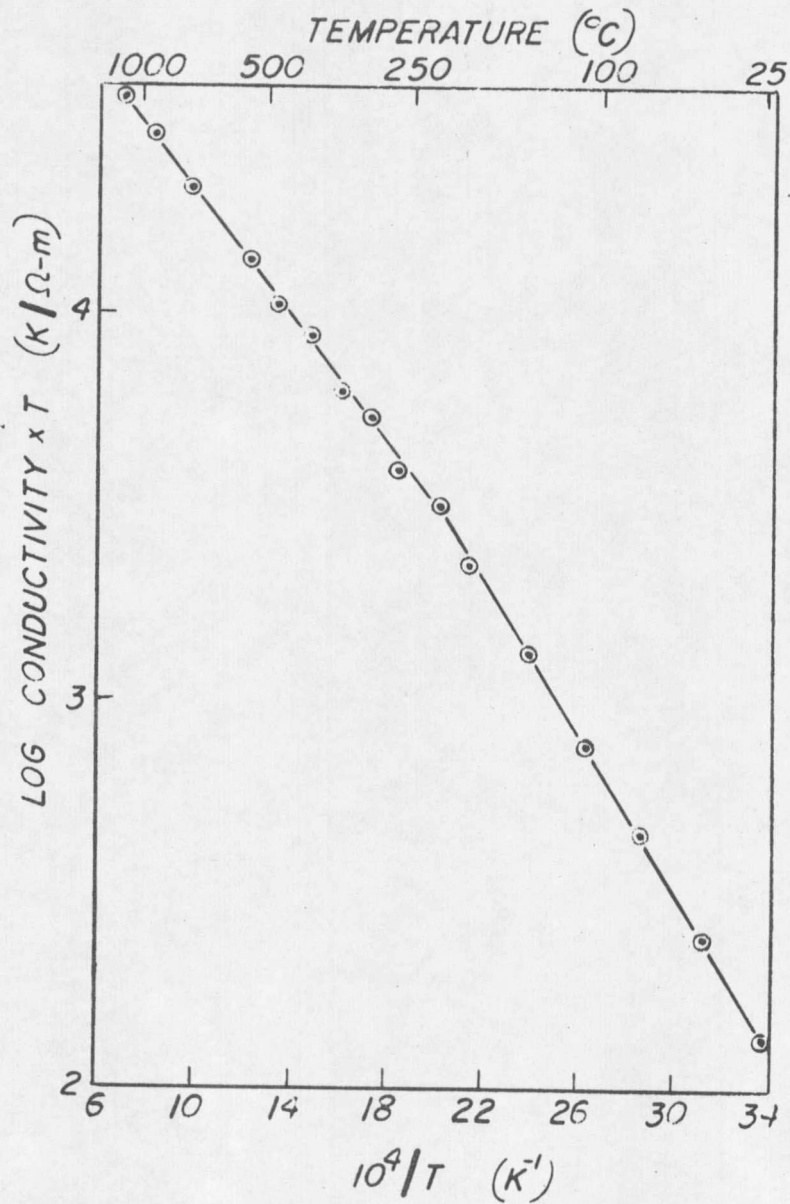


Figure 13. Electrical Conductivity Times Temperature of

$\text{LaMg}_{0.02}\text{Al}_{0.15}\text{Cr}_{0.83}\text{O}_3$ in Air Atmosphere.

since the lanthanum ions are essentially just electron donors. The small amount of magnesium present in the sample may have a more direct bearing on the band structure and, therefore, on the conduction mechanism. Since chromium orbitals are largely responsible for the nature of the band structure, a magnesium ion occupying a chromium site might be expected, at least locally, to alter the degree of d-electron localization. If magnesium doping causes d-electron localization, then any holes present could conduct by small-polaron hopping. Although this scheme seems somewhat reasonable, it would be hard to believe that only a 2% chromium substitution could result in the localization of all of the d-band electrons as would be the case in our sample.

The first lanthanum chromite sample tests in hydrogen were done at room temperature. The testing methods used were the standard four contact method and the two contact method. As mentioned before, one of the advantages of the four contact method is that only the sample resistance is measured and not the contact resistances. With the four contact method, no change in resistance was noted with the application of hydrogen. However, a very large change in resistance, between one and two orders of magnitude, was noted when the two contact method was used in hydrogen at room temperature. The change was very rapid and could be completely reversed when the hydrogen was displaced by air.

The fact that the increase in resistance with hydrogen was only detectable using the two contact method indicated that the effect was only occurring at the electrode-sample interfaces. In order to observe the contact resistance effect more closely, an ohmmeter was attached to a lanthanum chromite sample with a copper alligator clip on one end and a piece of platinum wire on the other. The platinum wire was mechanically held in place so that it was contacting the surface of the sample at a single point. Next, a very small diameter hypodermic needle was rigged to a flexible hose and attached to the hydrogen gas system. With the hydrogen gas flow rate set very low, the needle was used to supply a localized concentration of hydrogen to any point on the sample. When the needle was brought near the platinum contact point there was, as expected, a sharp increase in resistance as measured on the ohmmeter. When the hydrogen jet probe was removed from the platinum contact area, the resistance returned immediately to normal. This procedure was repeated with gold, silver, chrome, steel, aluminum, and copper wires as the contact, but it was found that only the platinum wire produced the contact resistance effect.

It seems likely that the platinum is acting as a catalyst for a reaction between oxygen ions in the lanthanum chromite, and hydrogen. This would create oxygen vacancies in the lattice and reduce the conductivity. Of course this catalytic reaction occurs only at the

platinum-lanthanum chromite interface and the bulk conductivity remains unchanged. It is important to keep this effect in mind when deciding what materials to use for the electrode contacts. When platinum contacts are used for conductivity measurements on lanthanum chromite, large resistance errors should be expected in the presence of hydrogen if the two contact method is used.

The high temperature data obtained in a hydrogen atmosphere will now be presented. The results depend greatly upon the thermal and atmospheric history of the samples, so the measurement procedure is described for each sample individually. Some significant features of the data are also noted for each sample. A discussion of the implications of the data will follow.

The first sample tested in hydrogen at high temperatures was $\text{LaMg}_{.02}\text{Al}_{.15}\text{Cr}_{.83}\text{O}_3$. The sample was surrounded by pure hydrogen and its temperature slowly raised without taking data. When the temperature reached 1140°C , conductivity readings were immediately started and taken as the sample cooled in controlled increments to 142°C . Readings were taken while heating, this time to a temperature of 1179°C . The data obtained from these heating and cooling runs are shown plotted in Figure 11 along with the previously obtained air data. The data indicated a marked decrease of the conductivity of the sample when exposed to hydrogen and we wondered whether the conductivity would continue to decrease for longer exposure times.

Therefore, the sample was held at high temperature (960°C) for 12.5 hours before cooling. The data taken during the final cooling cycle are also shown in Figure 11.

It is apparent from the curves in Figure 11 that a time-dependent decrease in conductivity took place in the sample when surrounded by hydrogen at high temperature. The activation energies of the sample before hydrogen exposure, during exposure, and after 12.5 hours exposure are 0.076 eV, 0.26 eV, and 0.76 eV respectively. These values were obtained from the data curves between 500°C and 1150°C.

Figure 14 shows the hydrogen data for the $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ and $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ samples. The air data of these samples are also displayed for convenience.

The $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ sample was raised to 1139°C in hydrogen while data were being taken. It was left at this temperature for 2.5 hours before taking cooling data. The heating portion of the run explicitly shows the manner in which the hydrogen data deviates from the air data. At temperatures below about 160°C, the air and hydrogen data are identical. Above 160°C however, the conductivity plots show an increasing divergence until, at 1000°C, the hydrogen data have decreased by more than an order of magnitude. The readings were all taken at approximately 30 minute intervals.

The cooling data for this sample show the dramatic decrease in conductivity after prolonged exposure to hydrogen at high temperature.

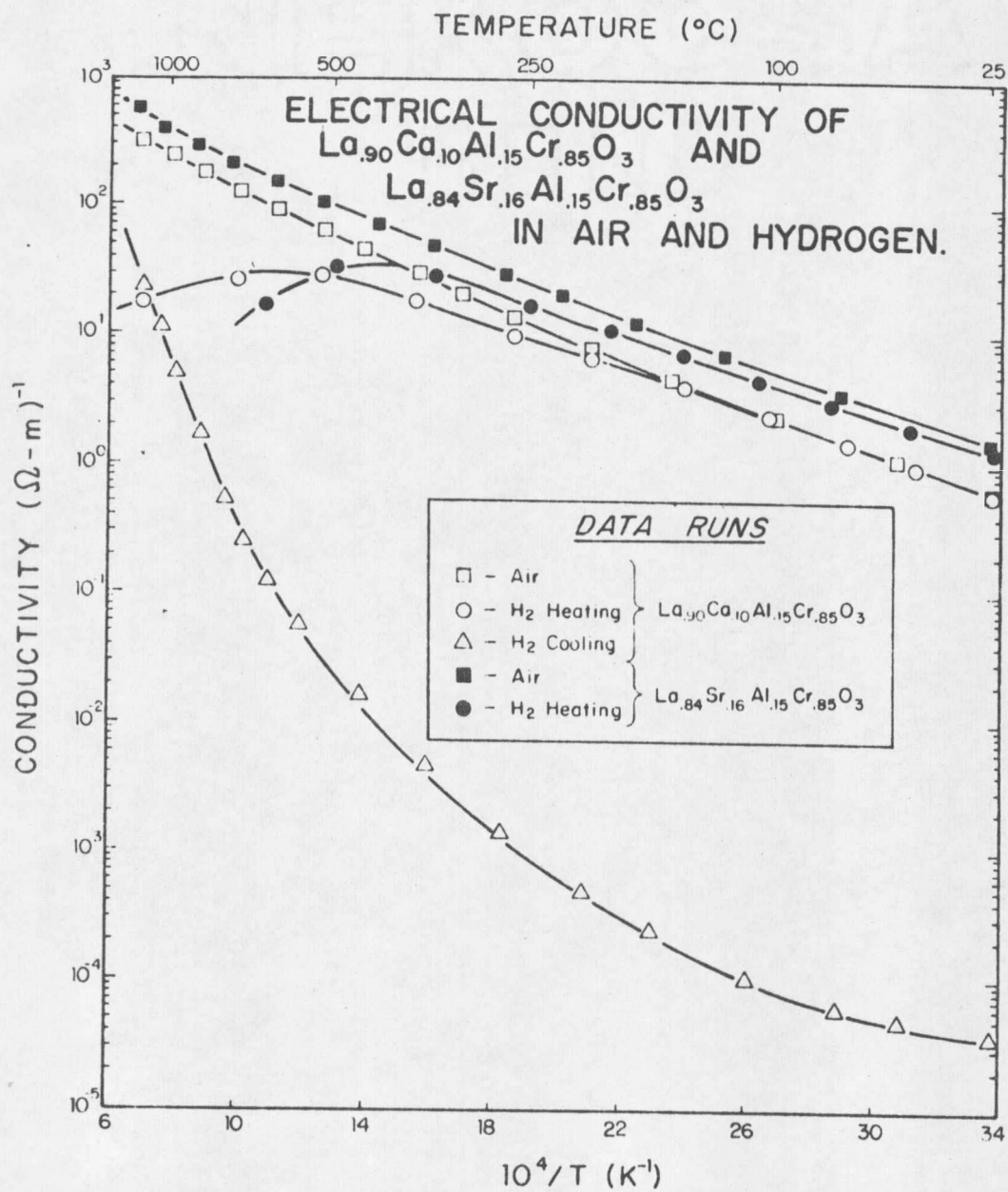


Figure 14. Electrical Conductivity of $\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ and $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ in Air and Hydrogen Atmospheres.

At room temperature the conductivity is more than four orders of magnitude lower after the hydrogen treatment. The conductivity remained low even after the hydrogen was replaced with air. However, after the sample was subsequently cooked in air at 1100°C for about 12 hours, its room temperature conductivity approached its original value. The activation energies for this sample are 0.25 eV in air atmosphere and 1.3 eV after 2.5 hours exposure to hydrogen. Again, these values are derived from the portion of the curves between 500°C and 1150°C.

The $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ sample data were taken by surrounding the sample with hydrogen and taking readings at approximately 30 minute intervals while increasing the temperature. Again, the data show the deviation from the air data of the same sample as the temperature is increased. It is not known why the hydrogen data differed from the air data even at the beginning of the run, but it is suspected that while changing from platinum to steel electrode wires, the contacts were altered in such a way that the electrical path was effectively increased.

Unfortunately, the $\text{La}_{.84}\text{Sr}_{.16}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ sample broke at approximately 700°C, making it impossible to take cooling data after high temperature hydrogen exposure. To see if this was a fluke due to a sample flaw or due to an interaction of the hydrogen with the sample, three other samples were prepared with similar dimensions, but without drilling electrode holes. They were placed, on separate occasions, in

the furnace and provided with a hydrogen atmosphere. For each sample, the temperature was increased at a rate of about 100°C per hour to a temperature of 1050°C. All three samples broke, although it is not known at what temperature breakage occurred. Since the sample had no breakage problems in air, it can be inferred that the hydrogen is in some way causing large structural changes in the ceramic.

The most significant feature of the lanthanum chromite conductivity measurements is the huge drop in conductivity after exposure to hydrogen at high temperature. Similar conductivity decreases have been noted in the literature by workers testing various lanthanum chromite formulations in various partial oxygen pressures. Westinghouse Corporation workers¹², for example, have compared the conductivity of a $\text{La}_{.95}\text{Mg}_{.05}\text{Al}_{.75}\text{Cr}_{.25}\text{O}_3$ sample before and after being exposed to a hydrogen-water atmosphere ($\text{PO}_2 = 5 \times 10^{-16}$ atm.) for 2 hours at 1000°C.

After this treatment, they found a 3×10^4 factor decrease in conductivity at 300°C. This compares reasonably well with our findings in $\text{LaMg}_{.02}\text{Al}_{.15}\text{Cr}_{.83}\text{O}_3$ of a conductivity decrease by a factor of 4×10^3 at 300°C, considering that the samples are not identical in constituent quantities. Westinghouse workers also noted a gradual return to air atmosphere type data after cooking in air at 1000°C. This also compares well with our room temperature observations of

$\text{La}_{.90}\text{Ca}_{.10}\text{Al}_{.15}\text{Cr}_{.85}\text{O}_3$ after being cooked at 1100°C in air.

Faber et al.²¹ have observed a decrease in conductivity of LaCrO_3 by a factor of 10^2 at 300°C when equilibrated with a partial oxygen pressure of 10^{-4} atmosphere. They also recorded an isothermal (1400°C) decreasing of conductivity with decreasing oxygen partial pressure. It is not known, however, what gas was used to provide the oxygen partial pressures. It is suspected that a reducing atmosphere would produce different results as compared to an inert atmosphere even though the oxygen partial pressure may be the same. This suspicion is based on the large reaction affinity of hydrogen with oxygen ions in the sample. The chemical stability of lanthanum chromite and other perovskites in a reducing atmosphere has been discussed in an article by T. Nakamura et al.²²

As mentioned earlier, diffusion was measured by observing the time lag from the moment of hydrogen application to the sensing of hydrogen in the mass spectrometer. Figure 15 shows a semilogarithmic plot of the time lag versus inverse temperature. The error bars indicate only the uncertainties in the time lag values read from the X-Y recorder. Other factors could easily have caused additional errors. For example, it was not known to what extent the hydrogen would react chemically with the sample. If the apparent initial diffusion rate was limited at high temperatures because of hydrogen reacting chemically with the lanthanum chromite, some temperature dependence would be expected in addition to the exponential behavior predicted from

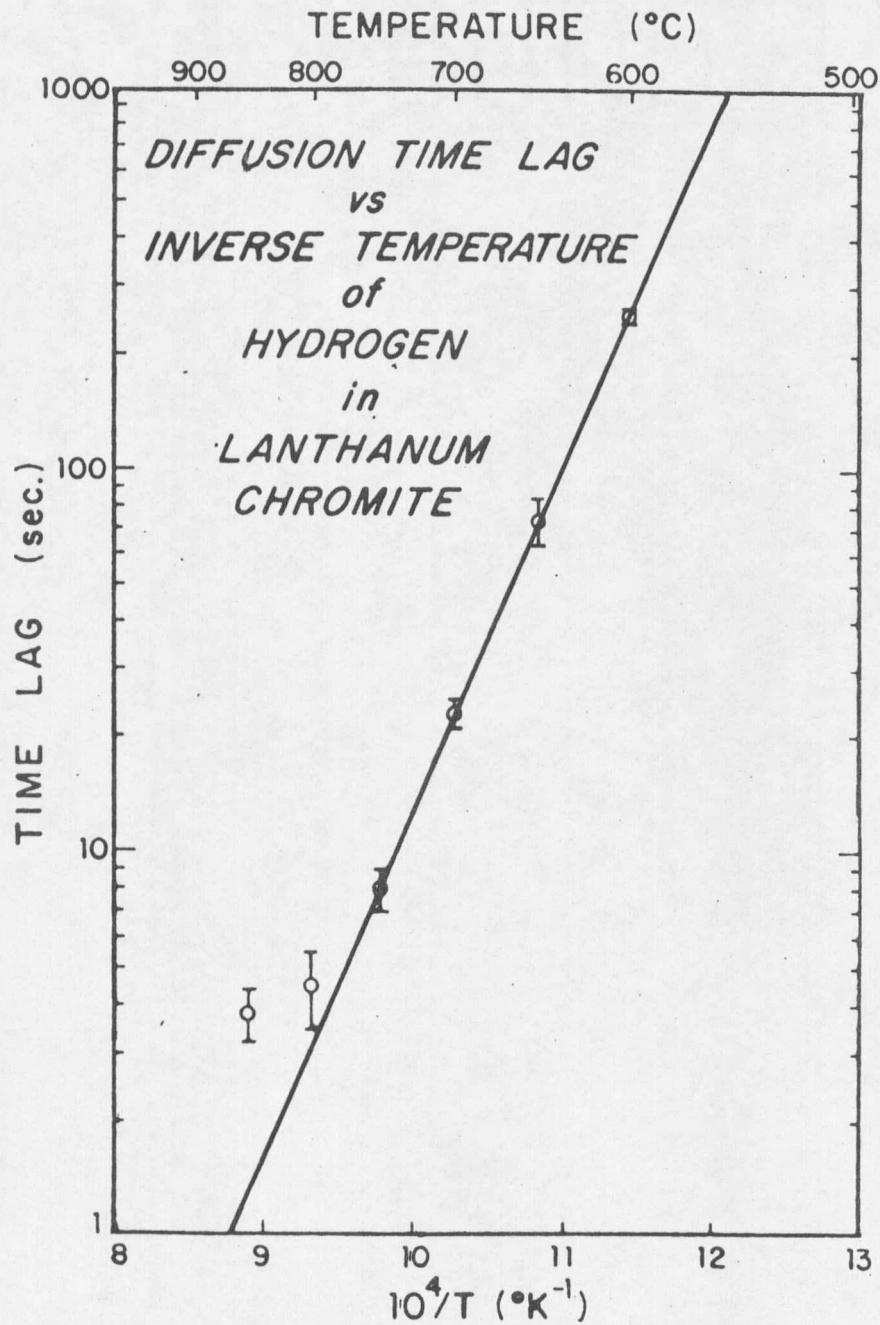


Figure 15. Hydrogen Diffusion Time Lag in Lanthanum Chromite.

simple diffusion theory. Indeed, the data plotted in Figure 15 appear to indicate some non-logarithmic behavior at temperatures above 800°C. The solid black line drawn between the points ignores the troublesome high temperature behavior and based on its slope and position, the following activation energy and diffusion constant were determined:

$$\varepsilon = 1.8 \text{ eV}; D_0 = 190 \text{ cm}^2/\text{sec.}$$

There is also the possibility that a portion of the hydrogen detected was due to leakage around grain boundaries in the sample film. However, since the data on the whole are quite linear, it seems likely that the observations were primarily due to Brownian diffusion through the lanthanum chromite crystals, at least at lower temperatures. The non-exponential high temperature behavior might also have resulted from the time required for the diffusion through the porous zirconia substrate tube and even through the vacuum system to the detector.

CHAPTER V

SUMMARY AND CONCLUSIONS

The purpose of this work was to examine the electrical conductivity and the hydrogen diffusivity of several lanthanum chromite based ceramics. These materials are of interest because they are highly refractory and are good electronic conductors at high temperatures. Specifically, they may be of use in high temperature solid electrolyte fuel cell batteries as an interconnection between adjacent cells.

Examination of the literature showed that lanthanum chromite and its doped derivatives are electronic semiconductors with an ABO_3 perovskite crystal structure. Although they are not intrinsic semiconductors, a review of intrinsic semiconductor theory was presented to provide an idea of what sort of conductivity temperature dependence could be expected.

Two fundamentally different conduction mechanisms have been proposed in the literature that attempt to explain experimental conductivity results. One is based on a collective electron model in which the temperature dependence of the charge carrier concentration determines the conductivity, while the other assumes a localized electron model in which the conductivity temperature dependence is a result of thermally activated small-polaron hopping. Both models assume that the predominant charge carriers are holes and that the number of holes

can be increased by substituting Sr^{2+} ions for La^{3+} ions. This is a controlled valency doping technique and results in the formation of holes because a Cr^{3+} ion is then forced to become a Cr^{4+} ion to preserve charge neutrality.

The experimental work involved building a multiple atmosphere furnace, sample holder and temperature control equipment, and using this apparatus to measure electrical conductivities of lanthanum chromite samples in both air and hydrogen atmospheres at temperatures between ambient and 1150°C . High temperature diffusion apparatus was also built and used to measure hydrogen diffusion through a thin film sample of lanthanum chromite. The diffusion equipment design was based on a permeation method in which diffusion is determined by observing the mean time required for atmospheric pressure hydrogen to diffuse through the sample and into a high vacuum system where it is detected with a mass spectrometer.

The study of theoretical conduction mechanisms showed that the conductivity would have a temperature dependence of the form

$$\sigma \propto T^n \exp(-E/kT) ,$$

where $n \geq 0$ for a collective electron model semiconductor or $n = -1$ for a localized electron small-polaron semiconductor. All of our lanthanum chromite samples showed exponential temperature behavior as expected. The strontium and calcium doped samples appeared to have a pre-exponential term with $n > 0$ and therefore supported the collective

electron model, while the magnesium doped sample appeared to support small-polaron hopping conductivity. At 1000°C the conductivity of the magnesium doped sample was $25 (\Omega\text{-m})^{-1}$ while the other samples all had conductivities of about $300 (\Omega\text{-m})^{-1}$. Other workers have made similar measurements on similar materials and obtained widely differing results. This points out the importance sample preparation method has on the conductivity.

Conductivity measurements taken in a hydrogen atmosphere showed a dramatic decrease in conductivity as compared to the air data for the same sample. This sort of behavior has been observed by other workers and has been explained by the diffusion of oxygen out of the sample. The oxygen deficiency would provide an alternate means of charge compensation; fewer holes would be present and the conductivity would decrease. It may also be possible that hydrogen diffusion into the sample also affects the conductivity.

Based on our diffusion measurements, we obtained a diffusion constant of $190 \text{ cm}^2/\text{sec}$ and a diffusion activation energy of 1.8 eV. The data also indicated a possible change in diffusivity at high temperatures, but more experiments will be required to confirm this.

The equipment and techniques used for the conductivity measurements worked quite well and gave reproducible results. A change to steel electrode wires is necessary when using a hydrogen atmosphere to avoid platinum wire corrosion. Care should be taken when changing the

wires to avoid enlarging the electrode contact hole. Also, an important phenomenon to keep in mind when using platinum contacts in a hydrogen atmosphere is the catalytic contact resistance effect. This effect can lead to large conductivity errors if the two contact method is used.

The diffusion experiment went well once the sample-vacuum system sealing problem was solved. The sealing joint must be kept cool to avoid differing expansion coefficient problems.

Lanthanum chromites have applications where refractory electronic conductors are needed. High temperatures solid electrolyte fuel cells have such a need and it is our hope that the findings presented here will aid in determining which lanthanum chromite ceramic would be most appropriate as the interconnection material.

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