



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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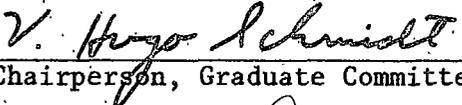
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ABSTRACT

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

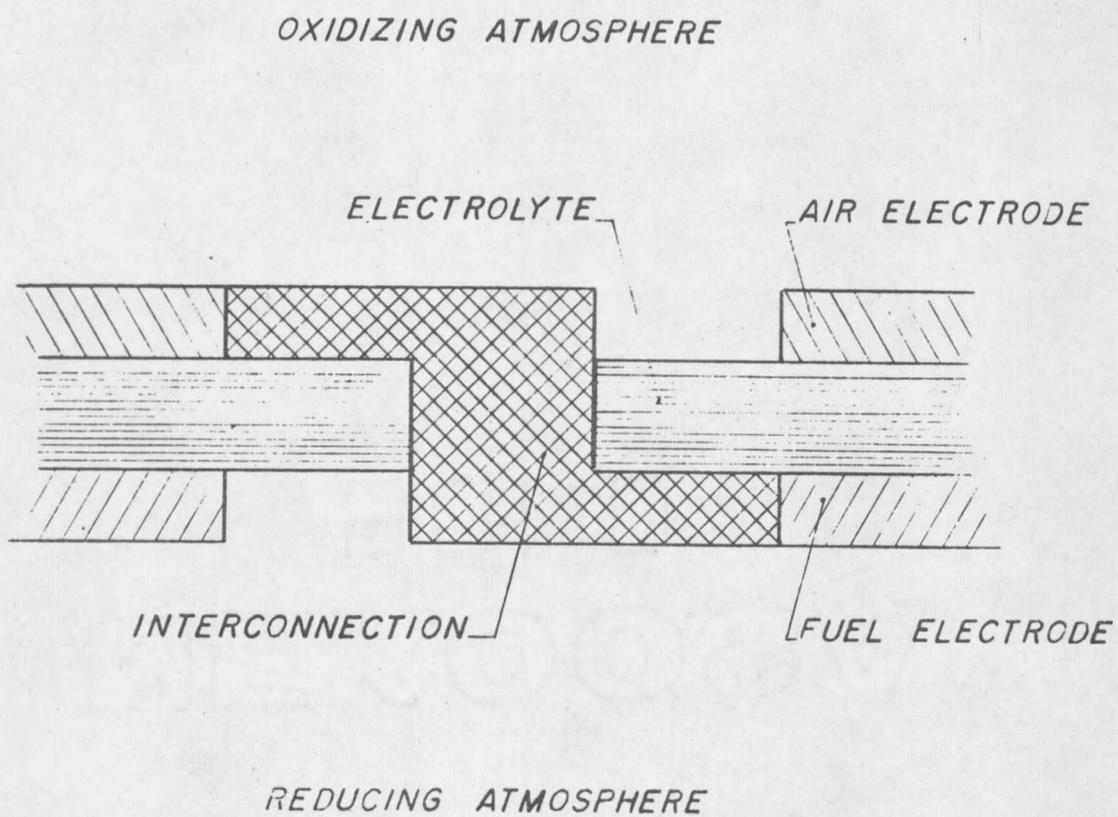


Figure 1. Fuel Cell Battery Interconnection.

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, ($\sigma \sim 10^6$ (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, μ_e and μ_h , must also be considered. The electrical conductivity can then be written

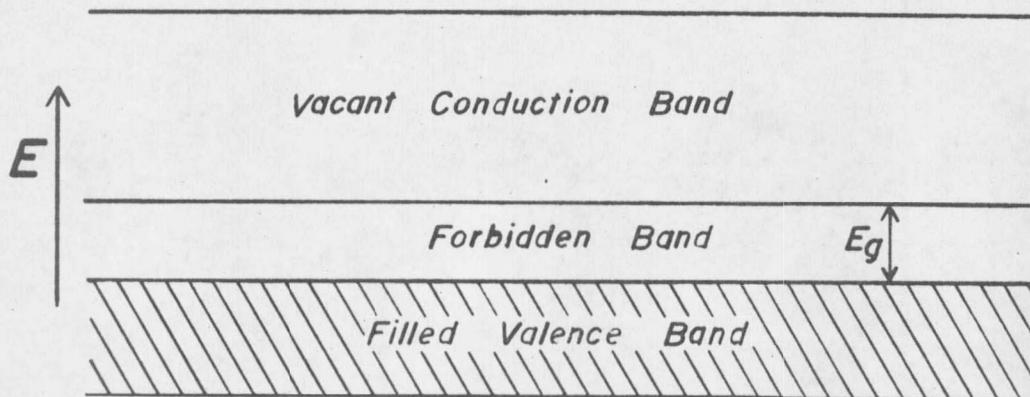


Figure 2. Simplified Band Structure of a Semiconductor at Absolute Zero Temperature.

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

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

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

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

$$f_e = \exp\{-(E-E_f)/kT\} \quad \text{for } E > E_c, \quad \text{Equation (9)}$$

and

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

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

$$n_e = \frac{1}{2\pi^2} (2m_e/h^2)^{3/2} \int_{E_c}^{\infty} (E-E_c)^{1/2} \exp\{-(E-E_f)/kT\} dE \quad \text{Equation (10)}$$

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

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

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

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:

