

**MEASUREMENT OF SURFACE EXCHANGE COEFFICIENTS
IN THIN FILMS USING ISOTOPE EXCHANGE DEPTH PROFILING**

by

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IN THIN FILMS USING ISOTOPE EXCHANGE DEPTH PROFILING**

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ABSTRACT

Optimizing the performance of mixed ionic electronic conductors (MIECs) will greatly increase the performance of solid oxide fuel cells, allowing them to produce more power and operate at lower temperatures. The performance of MIECs is governed largely by two material properties: the diffusion coefficient and the surface exchange coefficient. Doping most commonly optimizes these coefficients, however the optimal doping combination is often quite time consuming to determine. Traditional measurement methods are very capable of measuring the bulk diffusion coefficient but lack precision when measuring the surface exchange coefficient. A new technique is required to enable precision measurement of the surface exchange coefficient over a wide range of values. In this work, the technique of isotope exchange depth profiling (IEDP) of thin films is developed. IEDP of thin films is shown to be a powerful tool for the optimization of MIEC performance.

IEDP is a technique where an isotope enriched atmosphere is allowed to diffuse into a material for a given exchange time. Secondary ion mass spectrometry is used to measure the concentration of isotope as a function of depth giving a diffusion profile in the material. This diffusion profile is then fitted to the diffusion model to extract the surface exchange coefficient. Using this technique on thin films requires films to be produced that are less than 10 μm thick. The diffusion profiles are then fit

to the solution to diffusion in a plane wall instead of the traditional semi-infinite solution. This accounts for the finite diffusion distance that is not seen in IEDP of bulk materials.

First, numerical modeling of the technique is used to predict the range of experimental surface exchange coefficient values that can be measured using practical experimentation. The model uses the solution of the diffusion equation in a plane wall using the surface evaporation boundary condition. The modeling was done in Mathematica version 8. This model assumes 1-dimensional diffusion with a zero flux boundary condition at the substrate. It is shown that IEDP of thin films is able to accurately measure surface exchange coefficients from $5 \cdot 10^{-16}$ cm/sec to $5.5 \cdot 10^{-5}$ cm/sec.

Next, two model MIEC materials, LaCoO_3 and SrCoO_3 , were measured using this technique at 400 °C and 500 °C. Sputtering targets were made of these materials using traditional ceramic processing techniques. These films were deposited using magnetron sputtering to a thickness near 100 nm. These films were exchanged in a highly enriched atmosphere for times between one minute and one hour. Secondary ion mass spectrometry provided a diffusion profile in the material and this profile was fitted to the plane diffusion model. Surface exchange coefficients of LaCoO_3 were measured to be $2.274 \cdot 10^{-8}$ cm/sec and $1.061 \cdot 10^{-7}$ cm/sec at 400 °C and 500 °C respectively. Surface exchange coefficients of SrCoO_3 were measured to be $9.891 \cdot 10^{-10}$ cm/sec and $2.117 \cdot 10^{-9}$ cm/sec at 400 °C and 500 °C respectively.

Chapter 1

INTRODUCTION

1.1 Solid Oxide Fuel Cells

Many environmental and economic concerns are driving the “clean energy” movement. Much of this concern arises from the low efficiency of traditional energy conversion devices and the large amounts of greenhouse gases produced by converting fuel to electric power through combustion. New technologies that can convert chemical bonds into electrical energy with increased efficiency are in high demand. Technologies that can operate from a variety of fuels are even more desirable, in order to ease the transition from the complex hydrocarbon fuels that are currently used to future sustainable resources such as biofuels and clean sources such as hydrogen. Solid oxide fuel cells (SOFCs) are expected to form an important part of a sustainable energy landscape, as they can directly and with high efficiency convert a variety of fuels such as biofuels or hydrogen, into electrical power [1].

SOFCs operate at high temperature. These fuel cells are composed of three layers: anode, electrolyte and cathode, figure 1. SOFCs use a dense ceramic electrolyte that is an electron insulator and an oxygen ion conductor. By flowing oxygen-containing air across the cathode side of the electrolyte and a fuel across the anode side, a chemical

potential gradient is created. The ionic conduction of the electrolyte ‘converts’ this chemical potential gradient into an electrical potential gradient that drives the current through an external load.

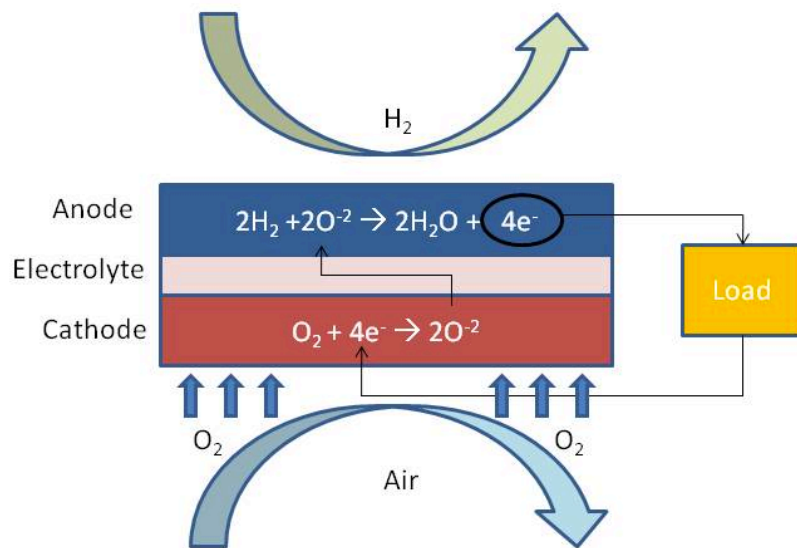
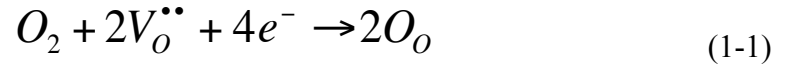


Figure 1: Diagram of the electrochemical reactions in a SOFC. The fuel shown is hydrogen, however various other fuels can be used.

These devices are limited to operating at high temperatures, typically exceeding 800 °C. High temperatures are needed for two main reasons. First, solid electrolytes exhibit thermally activated ion mobility and are not sufficiently conductive at lower temperatures. Second, the electrochemical half-cell reactions at the electrodes, particularly the cathode, are thermally activated and are also insufficiently reactive at lower temperatures. This greatly increases the time it takes to start-up and shut-down

as well as increases the cost of the SOFC by requiring exotic gas-sealing techniques, and non-traditional balance-of-plant components [2]. This limits the possible applications for SOFCs, in particular reducing the utility for the transportation industry, one of the largest potential markets for fuel cells. Decreasing the operating temperature will remove many of these limitations. Advancements have been made in finding new solid electrolytes with improved low-temperature ionic conductivity and new processing methods that provide thinner and thus lower-resistance solid electrolyte geometries [2] [3] [4] [5]. These improvements to the electrolyte have placed the burden of performance increasingly on the kinetics of the electrode reactions, in particular at the cathode [1] [6].

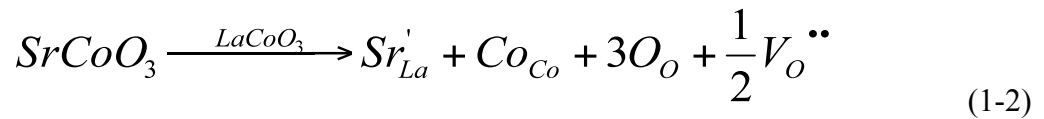
The electrochemical reaction at the cathode is the oxygen reduction reaction and can be described using Kröger-Vink notation as:



where $V_o^{\bullet\bullet}$ represents a vacancy with a +2 charge on a location normally occupied by an oxygen atom, e^- represents an electron, and O_o represents an oxygen ion at the normal oxygen site in the lattice. Gaseous, ionic and electronic species are involved in this reaction meaning the reaction can only take place where all three species are present. Early cathodes involved a porous mixture of electronic conductors and ionic conductors. The reaction could take place where the two materials meet in the presence of the gaseous species in the pores. This region is called the triple phase

boundary. This triple phase boundary represents a much smaller region than the total volume of the cathode. For this reason, a focus has been put into research of new cathode materials. Mixed ionic electronic conductors (MIECs) are materials that can conduct both ionic and electronic species. Using MIECs increases the triple phase boundary to the entire surface area of the cathode, thereby maximizing the area where the reaction can take place.

MIECs are a small class of materials, most of which are chemically similar and crystallize in the perovskite structure (ABO_3) [7]. A number of these materials have shown to support high SOFC cathode reaction rates, such as $La_xSr_{1-x}CoO_3$ [8][9], $Sm_xSr_{1-x}CoO_3$ [10], $La_xSr_{1-x}FeO_3$ [11], and $La_xSr_{1-x}Co_yFe_{1-y}O_3$ [12] [13]. The x and y variations in these materials' chemical formulae show that a wide range of compositions can be fabricated. Doping increases the number of oxygen vacancies in the material by substituting an atom of a higher oxidation state with one of a lower oxidation state, for instance doping La^{3+} with a Sr^{2+} . The charge imbalance is compensated, in part, by creation of oxygen vacancies. For example, in Kröger-Vink notation, doping of Sr on a La site in $La_xSr_{1-x}CoO_3$ is represented by:



The parameters that are most significant in predicting a MIEC's performance relate to how oxygen is transported through the material and exchanged at the material surface. This is shown, for example, by the Adler, Lane and Steele (ALS) model [14],

which derived the area-specific electrode polarization resistance, R_{chem} , of a porous MIEC cathode:

$$R_{chem} = \left(\frac{RT}{2F^2} \right) \sqrt{\frac{\tau}{(1 - \varepsilon) * a * C_0^2 * D * k_{surf}}} \quad (1-3)$$

In this model τ is the tortuosity of the pores, ε is the fractional porosity, a is surface area per unit volume, C_0 is the molar concentration of oxygen ions in the material, D is the bulk diffusion coefficient, k is the surface exchange coefficient, R is the gas constant, T is absolute temperature, and F is the Faraday constant. Many of these factors are either constants (nearly constant in the case of C_0) or depend on the processing and manufacturing of the cathode. The two remaining material dependant parameters, the bulk diffusion coefficient and the surface exchange coefficient, are material-dependent; however their exact dependence on composition is unknown. Since we are uninterested in manufacturing details, the bulk diffusion coefficient and the surface exchange coefficient are the critical parameters for determining performance.

1.2 Measurement Methods for the Bulk Diffusion Coefficient

Of the two critical material properties, the one that has been investigated the most is the bulk diffusion coefficient. There are a number of techniques for measuring bulk diffusion coefficient. The three most commonly used techniques are discussed below.

1.2.1 Electrical Conductivity Measurement (Electrical Driving Force)

Electrical measurements have been used to analyze the conductivity of a number of MIEC materials [15][16]. The premise of this measurement technique is to create a voltage gradient across the material of interest and to measure the current thus created. Using two electrodes or a four-probe technique (as shown in figure 2), the total conductivity of the tested sample is thus determined. Electrical methods cannot distinguish between ionic and electronic conductivity. This is not a problem if the material has a single mobile charge carrier like metals, which primarily conduct electrons, or solid electrolytes, which are predominantly ionic conductors. However MIECs can conduct both ions and electrons, and so special consideration must be taken to differentiate between the two conduction mechanisms.

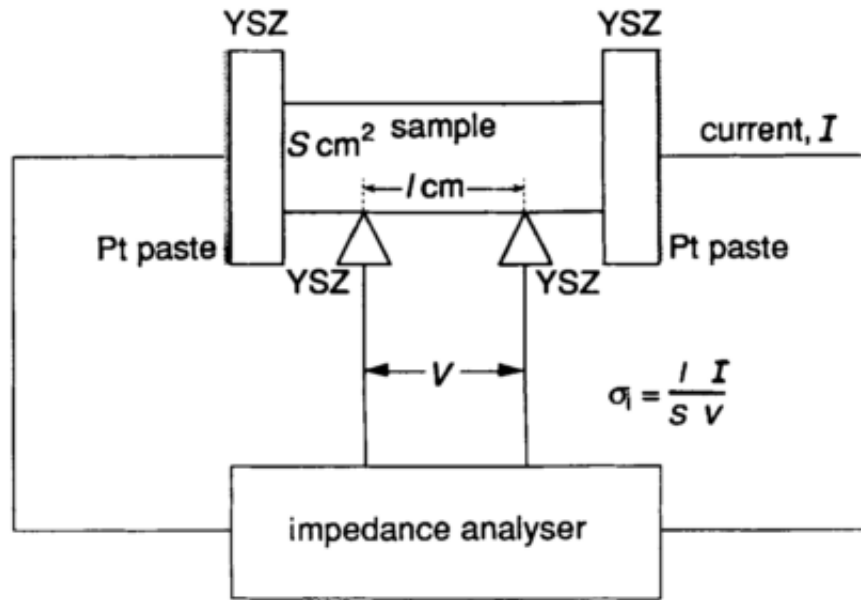


Figure 2: Schematic for a four-probe electrical conductivity experiment with electron-blocking electrodes. Figure reprinted from [17]

One way to decouple these different conduction mechanisms is to use blocking electrodes. In this technique, electrodes that permit transport of only one type of charge carrier (electronic or ionic), is used [18]. In the case of ion blocking electrodes, a metal or semi-conductor material that only permits electrons to pass is used. To measure the ionic conductivity, electron-blocking electrodes are used. These electrodes use an electrolyte material to create a barrier for electrons and permit only ions through. The example shown in figure 3 uses yttrium-stabilized zirconia (YSZ) electrodes to permit current only via oxygen ions. On top of the YSZ is a platinum electrode where the leads for the measurement are attached. Since the only charge

carriers to reach the platinum electrodes are oxide ions, the conductivity measured is the ionic conductivity. Blocking electrodes require a more extensive experiment set up than other methods described below. Complications can also arise between the blocking electrodes and the MIEC particularly if there is a thermal expansion mismatch or if reactions take place altering the chemistry at the interface. Electrical measurements are done at or near SOFC operational temperature so the experimental set up requires the sample to be in a high temperature furnace. Measurements at high temperature force the use of expensive refractory materials, such as platinum, in the wiring and electrodes. This expense can be prohibitive, especially if number of material samples is large.

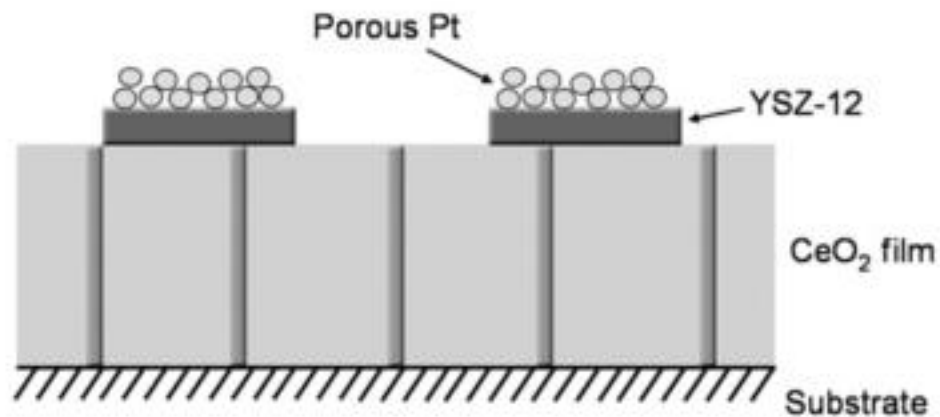


Figure 3: Schematic of electron-blocking electrodes on a thin film material. Figure reprinted from [18]

Conductivity is the product of charge, charge carrier density, and charge carrier

mobility, as seen in equation 1-4:

$$\sigma = qn\mu_q \quad (1-4)$$

where σ is conductivity, q is the electrical charge of the carrier, n is the density of charge carriers and μ_q is the mobility of the charge carriers. If the carrier density and charge are known, or can be assumed, conductivity can be used to determine mobility. The bulk diffusion coefficient can then be determined via the Einstein relationship, equation 1-5. In this relationship, the bulk diffusion coefficient is related to the mobility of the charged particles via the Boltzmann's constant, k_B , absolute temperature, T , and the electrical charge of the carrier.

$$D = \frac{\mu_q k_B T}{q} \quad (1-5)$$

It is important to note that this method uses an electrical driving force—a voltage gradient—to move the charge carriers. The nature of the driving force is the key difference between all of the methods that will be described.

1.2.2 Electronic Conductivity Relaxation (Chemical Driving Force)

The second method is electronic conductivity relaxation (ECR). In this method, the conductivity is measured as a function of time as a sample is equilibrated in one partial pressure of oxygen (pO_2) and then exposed to a step change in the pO_2 . This creates a gradient in the partial pressure of oxygen between one side of the sample and the other. The conductivity measurement is often done with a four-probe

technique where a constant current is applied and a voltage is measured. Blocking electrodes can be used but are not necessary. An example of the experimental setup is shown below in figure 4.

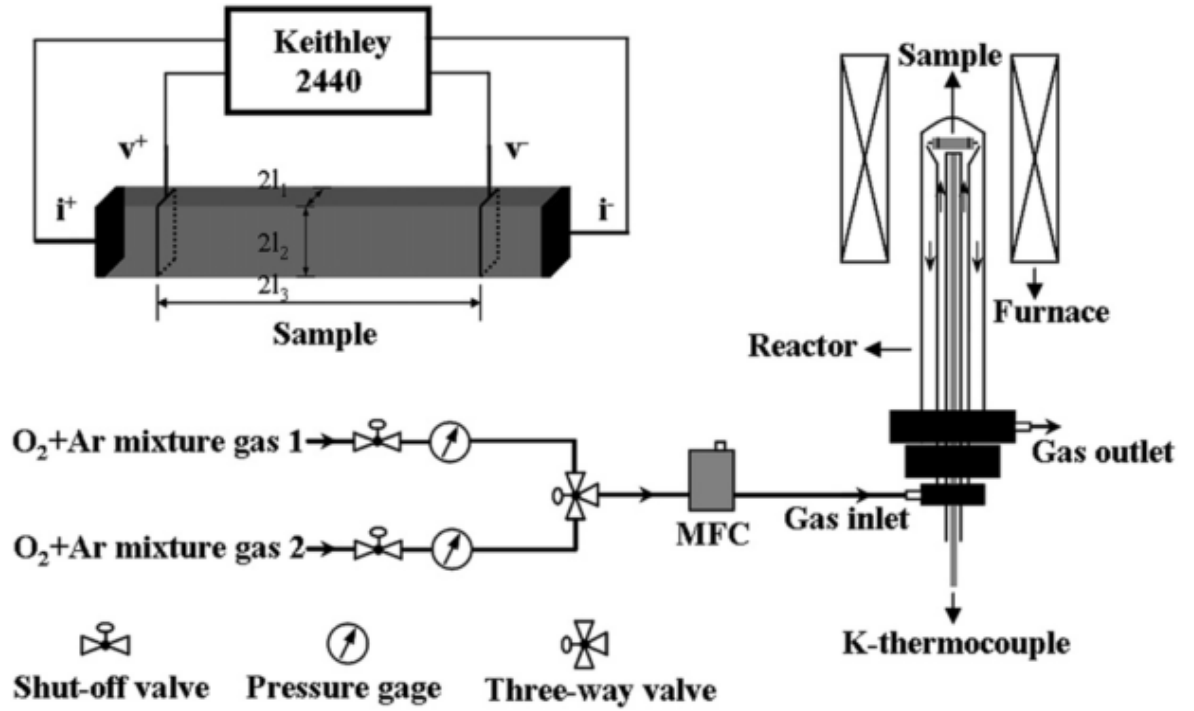


Figure 4: Experimental setup for electronic conductivity relaxation. Figure reprinted from [19]

Since this change in conductivity is driven by the change in pO_2 , the driving force is a chemical one. The voltage gradient used in measuring the conductivity is minimized such that it does not significantly contribute to ionic motion. This means the diffusivity values that are derived from this method are the chemical diffusion

coefficient, D_{chem} . This has a slightly different interpretation than the standard diffusion coefficient, D , however they can be related to one another as shown in Ref. [20].

Electronic conductivity relaxation has become a prominent way to investigate the diffusion properties of MIECs because “the electrical conductivity of these materials has high sensitivity to changes in oxygen concentration or oxygen partial pressure” [19]. The diffusion coefficient is determined from the time-dependent conductivity, the three dimensional version of this equation is shown below [21]:

$$\frac{\sigma_t - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \sum_{p=1}^{\infty} \frac{2L_x^2 \left(\frac{-\beta_m^2 D_{\text{chem}} t}{x^2} \right)}{\beta_m^2 (\beta_m^2 + L_1^2 + L_1)} * \frac{2L_y^2 \left(\frac{-\gamma_n^2 D_{\text{chem}} t}{y^2} \right)}{\gamma_n^2 (\gamma_n^2 + L_2^2 + L_2)} * \frac{2L_z^2 \left(\frac{-\delta_p^2 D_{\text{chem}} t}{z^2} \right)}{\delta_p^2 (\delta_p^2 + L_3^2 + L_3)} \quad (1-6)$$

$$L_x = x * k_{\text{chem}} / D_{\text{chem}}, L_y = y * k_{\text{chem}} / D_{\text{chem}}, L_z = z * k_{\text{chem}} / D_{\text{chem}} \quad (1-7)$$

$$\beta_m \tan \beta_m = L_x, \gamma_n \tan \gamma_n = L_y, \delta_p \tan \delta_p = L_z \quad (1-8)$$

Where the change in conductivity with respect to time is represented by $\frac{\sigma_t - \sigma_0}{\sigma_\infty - \sigma_0}$.

D_{chem} and k_{chem} are the chemical diffusion coefficient and the chemical surface coefficient. The dimensions of the sample are x , y and z . t is time in seconds and β , γ , and δ are the non-zero roots of equation 1-8.

This technique involves very precise changes in the oxygen partial pressure and therefore requires mass flow controllers to be used in the system. The method also

requires electrodes to be attached to the sample so that high temperature conductivity measurements can be taken. This can increase the complexity of the experiment and sample preparation, making it more challenging to test a wide variety of materials and dopant concentrations.

1.2.3 Isotope Exchange (Zero Driving Force)

Isotope exchange is another commonly used technique for measuring oxygen transport parameters [22][23][24]. The technique requires placing the sample in an atmosphere of a stable tracer isotope; for oxygen ion-conducting materials the stable isotope used is most commonly oxygen-18 (^{18}O) figure 5. The natural isotopic abundance of oxygen is 99.76% ^{16}O , 0.21% ^{18}O , and 0.03 % ^{17}O [25], but can be commercially purchased at ^{18}O concentrations up to 97 atom%. The introduction of an atmosphere with a high concentration of the tracer isotope will cause the tracer isotope to diffuse into the material of interest, replacing the natural mixture of isotopes originally present in the sample. Before the isotope concentration in the atmosphere and the material have fully equilibrated, the sample is quenched. Quenching freezes the diffusion profile in place because the diffusion process is thermally activated. Secondary ion mass spectrometry (SIMS) is then used to measure the relative concentration of the tracer isotope to the total amount of the species (e.g., $^{18}\text{O} / (^{18}\text{O} + ^{16}\text{O})$) as a function of depth into the material.

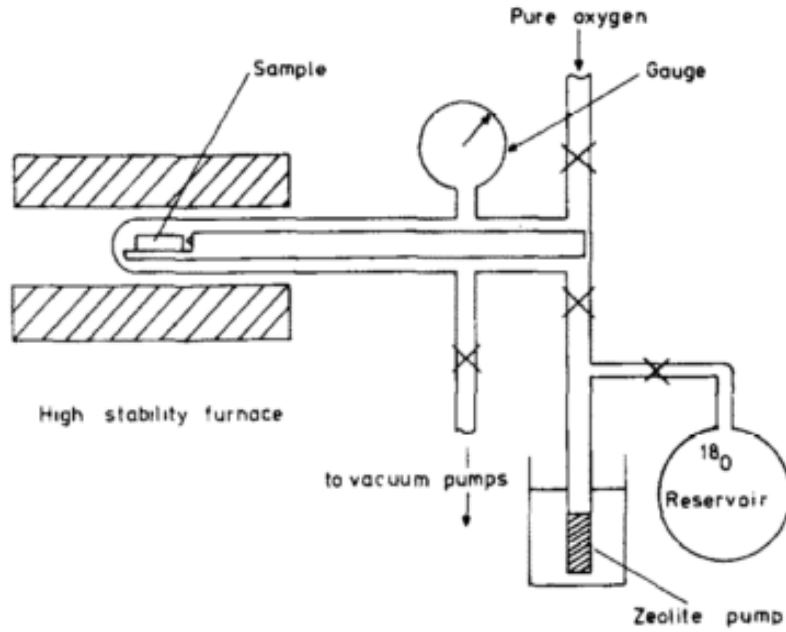


Figure 5: Isotope exchange experiment setup with the sample in a high temperature furnace. Figure reprinted from [26]

A standard way to understand the isotopic exchange process is that of semi-infinite diffusion with a first order surface exchange reaction. Crank provided a solution to the diffusion equation for a semi-infinite plane with a first order surface evaporation boundary condition, [27]. This solution can be used by analogy for these experiments, and is shown in equation 1-9

$$\frac{C - C_2}{C_0 - C_2} = \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) - e^{\frac{k}{D}x + \left(\frac{k}{D} \right)^2 Dt} \operatorname{erf} \left\{ \frac{x}{2\sqrt{Dt}} + \frac{k}{D} \sqrt{Dt} \right\} \quad (1-9)$$

In this equation, C is the concentration of the tracer at depth x and after an exchange time t , C_2 is the background (i.e., natural) concentration of the tracer in the material, and C_0 is the concentration of the tracer in the enriched atmosphere. By fitting the data of isotope concentration as a function of depth obtained from SIMS to this model, the diffusion coefficient and the surface exchange coefficient in theory can be derived. More details on this model, as well as experimental limitations on the ability to calculate these parameters with statistical significance are discussed in section 1.8.

There are two techniques for gathering the diffusion profile data using SIMS: depth profiling, shown in figure 6, and line scanning, shown in figure 7. Depth profiling involves analyzing the isotopic concentration at the top surface of the material, removing some of the surface within the SIMS machine (typically using a more powerful ion beam than the measurement beam), and then reanalyzing the isotopic concentration at the newly exposed surface. This process is then repeated as needed to build a depth-dependent concentration profile. This method can gather data on the diffusion profile for a relatively small depth into the material, limited by the tradeoff between depth resolution and the material removal rate within the SIMS machine. Typically, only short diffusion lengths can be measured. This technique is discussed in depth by Kilner and Steele [28]. They showed that diffusion coefficients can be measured between 10^{-11} and 10^{-19} cm^2/s and surface exchange coefficients can be measured from 10^{-7} cm/s and smaller.

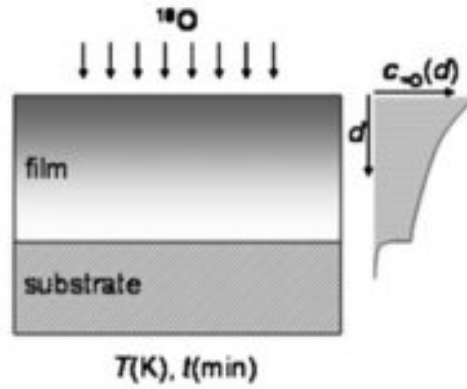


Figure 6: Schematic of depth profiling, reprinted from [22]

The second method, called line scanning, takes a section of the sample perpendicular to the isotope exchange surface. The SIMS analysis then analyses a number of spots on the perpendicular surface, proceeding away from the isotopic exchange surface. This method can analyze much larger diffusion distances, up to centimeters. The depth resolution of this technique necessarily suffers, limited by the SIMS analysis ion beam spot size, which is typically on the order of $1\text{ }\mu\text{m}$ [28]. This means to reach a reasonable number of scan points in the line, say 20, it would require the minimum depth penetration to be $20\text{ }\mu\text{m}$.

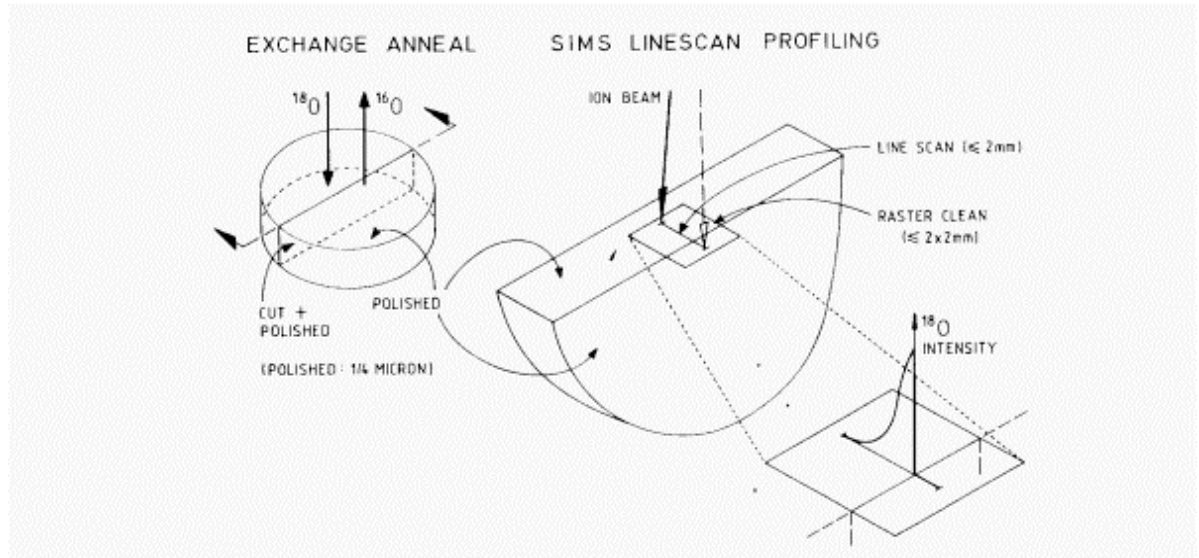


Figure 7: Schematic of the line scanning technique for SIMS analysis. Reprinted from [28]

Unlike the previous two measurement methods, the driving force in isotope exchange is neither electrical nor chemical. Rather it is the exchange of ^{18}O with ^{16}O . This is different from the chemical driving force because while the exchange atmosphere is isotope rich, it contains the same partial pressure of oxygen as the sample. The sample is equilibrated in a given partial pressure of oxygen (with a natural isotopic abundance) prior to the isotope exchange process. The diffusion of the isotope can be referred to as a “zero” driving force method.

This method has a few experimental advantages over the previous two methods because it does not require electrodes to be fabricated on the material. This method also does not involve data acquisition at high temperatures. On the other hand, the

method requires the use of a SIMS machine, which is rather specialized and expensive. This method is very accurate and reliable for determining the bulk diffusion coefficient because of the over determination that the large number of data points from SIMS analysis gives in the fitting of the diffusion model.

1.3 Measurement Methods for the Surface Exchange Coefficient

Electronic conductivity relaxation and isotope exchange depth profiling theoretically can measure both bulk diffusion and surface exchange coefficient. In each technique the data gathered is fitted to a model of the diffusion equation that incorporates both bulk diffusion and surface exchange coefficients. However, typical fabrication techniques used to create dense samples for ECR and IEDP yield samples with thicknesses on the order of hundreds of microns to tens of millimeters. IEDP often allows the isotope to diffuse to lengths greater than 100 μm . ECR requires the larger end on that spectrum because of the necessity to attach 4 probes to the sample. With these sample thicknesses the measurement methods above generally work well for deriving the bulk diffusion coefficient, they often lack statistical robustness when measuring the surface exchange coefficient. This is primarily due to the difficulty of isolating the effect of the surface exchange coefficient [29].

Isolating the effect of the surface exchange coefficient means creating a system where the surface exchange coefficient governs the shape of the diffusion profile. This can be done to such an extent where the bulk diffusion coefficient has no influence on the diffusion profile and is therefore undeterminable. A system that isolates the effect

of the surface exchange coefficient is known as a surface exchange limited system. The nomenclature is the same for the bulk diffusion coefficient being isolated in a bulk diffusion limited system, also sometimes shortened to a diffusion limited system. A surface exchange limited system offers the greatest accuracy for measuring the surface exchange coefficient because the solution to the diffusion equation can be to a good approximation simplified to a function of the one coefficient instead of two. In diffusion limited systems, the surface exchange coefficient cannot be measured accurately because it has little impact in the diffusion profile. Therefore, to measure the surface exchange coefficient most accurately, the system should be surface exchange limited.

The existence of limited systems has been discussed in the literature with respect to measurability of surface exchange coefficients in isotope exchange depth profiling experiment [29],[30]. Limited systems are based on the surface exchange coefficient and the bulk diffusion coefficient as well as the thickness of the material. The ratio of surface exchange coefficient to bulk diffusion coefficient describe a characteristic length, $L_c = D^*/k$. If this characteristic length is much smaller than the thickness of the sample, $L_c \ll L$, then the system is diffusion limited. The opposite holds true for surface exchange limited systems requiring a characteristic length much larger than the thickness of the sample, $L_c \gg L$. In the region where the characteristic length is approximately equal to the thickness of the material, both the surface exchange and bulk diffusion coefficients influence the shape of the diffusion profile and therefore can both be measured given the appropriate test parameters. Many

groups have determined characteristic lengths of specific materials based on measured surface exchange and bulk diffusion coefficients. Steele determined a characteristic length for a wide variety of doped oxides to be between 1 μm and 100 μm [30]. A characteristic length for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$ was found to be 3.3 nm at 700 $^{\circ}\text{C}$ by De Souza and Kilner [31]. LSCF, a promising MIEC, has a characteristic length of 125 μm calculated from k and D values at 800 $^{\circ}\text{C}$ given by Charter and Steele [28]. Most importantly for this work, the characteristic length of single crystal LaCoO_3 was found to be 700 – 4000 nm [32].

The fabrication techniques typically used to make the dense samples for the measurements described above produce materials that are sufficiently thick so as to diminish the impact of surface exchange on the measurement. For the MIEC materials of interest, the range of reasonable characteristic lengths L_C were significantly less than the thickness L of dense samples fabricated by traditional techniques. This difference in the characteristic length and the thickness of the sample $L_C \ll L$ creates a bulk diffusion limited system. Measurements like these offer a high sensitivity to the bulk diffusion coefficient but low sensitivity to the surface exchange coefficient. A goal of this thesis is to determine a measurement technique with high sensitivity to the surface exchange coefficient without regard to the sensitivity to the bulk diffusion coefficient. It will be shown that this can be done with isotope exchange experiments on thin films by, in effect, reducing the distance the isotope can diffuse to below the characteristic length of the material.

A few alternate techniques have been reported to enable measurement of the

surface exchange coefficient. The most promising for measuring surface exchange coefficients in the range reasonable for MIEC cathode materials is in situ isothermal isotope exchange (IIE). Wachsman's group has developed IIE which involves exchanging a stable isotope with a porous powder sample [33][34]. The powder is controlled to have an average particle size on the order of hundreds of nm. This is measured by laser light scattering and the average particle size is dependant on what is commercially available for each material. Samples are normalized by surface area of the sample. The powder samples are loaded into a quartz continuous flow reactor tube and heated to the desired temperature for the exchange. The isotope exchange, taking place once the sample has equilibrated to the background atmosphere, involves continuously flowing of highly purified stable isotope, typically ^{18}O . Because the sample is porous, the isotope rich atmosphere can reach all of the powder particles at once. The flow rate of the isotope is kept high enough to ensure that the atmosphere near the surface of the particles does not deplete as the isotope diffuses into the material. The exchange of isotope is monitored in situ by a quadrupole mass spectrometer. The results from the exchange are the concentration of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ as a function of time. This raw data is converted to give the fraction of oxygen within the material that is ^{18}O as a function of time. This data is fit to Crank's solution to the diffusion equation for a spherical geometry with the surface evaporation boundary condition equations 1-10 through 1-12.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp(-\beta_n^2 Dt / a^2)}{\beta_n^2 (\beta_n^2 + L(L - L))} \quad (1-10)$$

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (1-11)$$

$$L = a \frac{k}{D} = \frac{a}{L_c} \quad (1-12)$$

These equations are similar to the plane diffusion equation discussed later, however these equations are expressed in terms of the total amount of isotope in the sample. In these equations, M_t is the total amount of isotope in the material. M_∞ is the total amount of isotope in the material as time goes to infinity. β_n is defined as the n th root of equation 1-11 and L is the dimensionless parameter of the depth of the sample, a , over the characteristic length, L_c . By fitting these equations to the data the surface exchange coefficient and the diffusion coefficient can be determined.

The theory behind the technique is to reduce the sample thickness to approximately equal to or smaller than the characteristic length. This limits the diffusion length of the isotope to a very short distance. This small sample thickness creates either a co-limited or surface exchange limited system. These limited systems provide the greatest opportunity to accurately measure the surface exchange coefficient. It is noted that the bulk diffusion coefficient in a surface exchange limited

system can not be accurately determined due to the experiment being insensitive to it. However, this is not seen as a disadvantage to the model because there are many traditional techniques that can be used to accurately determine the bulk diffusion coefficient. This technique is a powerful one as it is one of the only which can measure surface exchange coefficients in a surface exchange limited system however there are some drawbacks to the technique.

Wachsman's technique is limited to powder samples and involves experimental difficulties in that it requires powder particles of specific diameter. Unless the experimenter has access to methods of making particles with good composition and size control this limits the available materials and particle sizes to be tested to what is commercially available. This limitation in selection can be a drawback if the goal of the experiment is to optimize dopant concentration to maximize the diffusion properties of the material. IIE is also an expensive method. Continuous flow of highly enriched isotope such as ^{18}O is very expensive especially at the high purity required. IIE is also an in situ technique that can require specialized equipment. In situ techniques are difficult to set up when the experimental temperatures are over 500 °C. An ex situ technique would allow more standardized equipment which may be more readily available or could be done at an external laboratory.

The goal of this thesis is to develop a technique that will allow rapid determination of the influence of dopant concentration on the surface exchange coefficient. The technique must be able to easily test a wide range of materials with

varying dopant concentration. The sample fabrication technique must offer good compositional control across a wide range of materials and good thickness control of the material at very small thickness ranges, hundreds of microns and smaller.

1.4 Sputtered MIEC Thin Films

There are many fabrication techniques that can be used to create MIEC films. A summary of many available techniques was given by Gauckler et.al. [5]. The thin film fabrication technique used in this work is magnetron sputtering. This technique allows for thin films to be precisely deposited with composition that roughly matches the source material. Magnetron sputtering has been used for MIECs research, specifically for characterizing materials for performance at reduced temperatures [35], [36], [37]. As stated above, this is done by measuring the materials performance parameters denoted in the ALS model. The primary method of increasing the diffusion and surface exchange coefficients is by doping. Sputtering can accurately deposit a variety of materials simultaneously by co-sputtering, giving a range of doping combinations. Sputtering is also an advantageous technique for this work because it deposits dense films with very good thickness control.

Many potential MIEC cathode materials have been tested over the past 20 years. The majority of these materials have been perovskite type oxides as they show good oxide conductivity. One particular material that has shown interesting properties is strontium doped lanthanum cobaltite, LSC. In the context of the work presented in this thesis, this material could be fabricated by co-sputtering lanthanum cobaltite and

strontium cobaltite. Many individual doping compositions have been studied and some studies look at multiple doping combinations however there is still no model for doping percentage on the performance of the cathode material. In this work, analysis of the performance of lanthanum cobaltite and strontium cobaltite will be performed individually to understand the performance of the base materials. Future investigations based on this work can look into doping composition.

1.5 Summary of Literature Review

The oxygen reduction reaction in a solid oxide fuel cell requires a cathode material with high performance for both electrical and ionic conduction. Traditional cathodes made up of a mixture of an electrical conductor and an ionic conductor can only proceed with the reaction in the region where the gaseous, ionic, and electronic species are in proximity with each other, known as the triple phase boundary. MIEC are a promising cathode material because of their dual conductivity allowing the oxygen reduction reaction to take place over the entire surface area of the cathode.

The performance of a particular cathode material is based on the bulk diffusion coefficient and the surface exchange coefficient as well as geometrical parameters. The bulk diffusion coefficient has been found for a number of material compositions over a range of temperatures. This is done through a number of different techniques such as electrical conduction measurements, electronic conductivity relaxation, and isotope exchange depth profiling. Each of these techniques is based on a different driving force: electrical, chemical, and “zero” driving force respectively. These

methods have been used to relate temperature and pressures effect on the bulk diffusion coefficient and to optimize material compositions for the bulk diffusion coefficient. While bulk diffusion is well understood, surface exchange remains less studied. This is due to the difficulty of developing a technique that can accurately measure the surface exchange coefficient. The techniques used to measure the bulk diffusion coefficient tend to do so in a bulk diffusion limited system, which provides high accuracy for the bulk diffusion coefficient and low accuracy for the surface exchange coefficient. To accurately measure the surface exchange coefficient, it must be measured in a surface exchange limited or co-limited system. This limited system, described by the characteristic length, is achieved by having a very short distance for diffusion.

Currently one of the best techniques for measuring surface exchange coefficients is in situ isothermal isotope exchange done by Wachsman's group. This technique uses powder particles to decrease the diffusion length to the radius of the average particle size. This technique can accurately measure the surface exchange coefficient, but suffers from the need for particles with a tight size distribution as well as expensive in situ techniques. An ideal experimental setup would include a method of fabricating samples to a custom thickness and good compositional control that could be analyzed ex situ to maintain a reasonable cost.

In this work, a test method is developed that combines the technique of isotope exchange depth profiling with thin film fabrications to enable robust determination of the surface exchange coefficient. Isotope exchange depth profiling provides the

advantages of a “zero” driving force system. This provides a very easy experimental setup, requiring just a thin film of the material of interest on a substrate. No electrodes are needed and measurements at high temperature are not required. Using thin films reduces the distance the isotope can diffuse and thereby any gradient of isotope concentration in the film. This reduces the influence of the diffusion coefficient on the system and makes the isotopic concentration more highly dependent on the surface exchange coefficient. With this method, robust measurement of the surface exchange coefficient can be achieved. Depth profiling SIMS analysis will be used as opposed to line scanning because depth-profiling offers the depth resolution required for use with thin films.

The ability of thin film isotope exchange depth profiling to measure surface exchange coefficient with high accuracy makes the technique valuable. An additional advantage over the other techniques described above is that it can be easily incorporated into combinatorial analysis. Combinatorial methods comprise a set of techniques for rapidly creating and analyzing libraries of materials. In this case, a film deposition technique can be used that provides a range of MIEC compositions (e.g., dopant concentration) on a single substrate [38]. Unlike standard physical vapor deposition methods, where the substrate is rotated to create a film of even thickness, combinatorial deposition techniques use a fixed substrate with the target aimed off-center, such that the deposition rate is positionally non-uniform. By depositing from more than one target at a time, with each target aimed at a different spot on the substrate, a gradient of composition can be created in the growing film. An example of

this is given in figure 8. In this example, three targets are used to create a film whose composition varies in two dimensions: the amount of a-site deficiency varies along one dimension, and the La/Sr ratio varies in an orthogonal direction. This compositional spread is created using targets of LaCoO_3 , SrCoO_3 and $(\text{La}_{0.5}\text{Sr}_{0.5})_{0.75}\text{CoO}_3$ [39]. The thin film isotope exchange method described in this work can be done on the entire substrate, with an array of SIMS depth-profile analyses performed across the substrate. The beam size used in SIMS can be very small (on the order of $10\text{ }\mu\text{m}$ or smaller [40]) relative to the size of the substrate (3 inches in diameter or larger), so many locations (and thus compositions) can be analyzed using a single sample. This has many advantages, the most prominent being that a large amount of data can be obtained quickly across a wide range of compositions in a specific material. This technique is also desirable because it reduces both the required amount of expensive ^{18}O isotopically enriched gas and SIMS operational time.

Combinatorial analysis of materials for surface exchange coefficients is a technique that can be a tool to optimize the oxygen ion transport of MIECs and, perhaps more importantly, offer insight into how composition impacts these properties [41]. While combinatorial analysis offers great promise for thin film isotope exchange depth profiling to be a very powerful technique, this thesis focuses on the validation of isotope exchange to measure surface exchange coefficients in thin films through mathematical analysis and experiments on two MIEC materials. Combinatorial analysis is not done in this work.

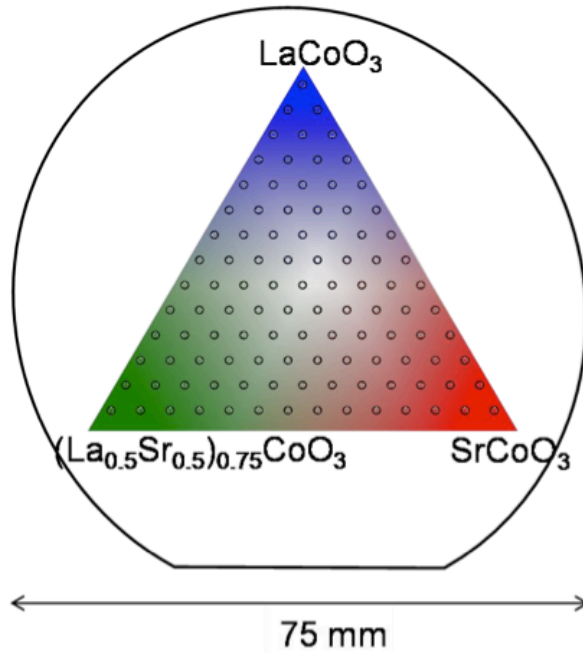


Figure 8: Example of a relevant material composition gradient on a 75 mm substrate created using combinatorial deposition techniques. Figure reprinted from [39]

1.6 Modeling

Before combinatorial analysis can be done, evaluation of the capabilities of thin film isotope exchange depth profiling to measure the diffusion and surface exchange coefficients was done. To do this, routines were written in Mathematica (Version 8, Wolfram) for both diffusion in a semi-infinite media with surface evaporation and diffusion in a plane sheet with surface evaporation models based on Crank's solutions [27]. For the remainder of this thesis these models will be referred to as the "semi-infinite" and "plane" diffusion models. Traditional isotope exchange

depth profiling (IEDP) experiments have focused on bulk samples whose diffusion profile data was fitted to the semi-infinite diffusion model, figures 6 and 7. The capabilities of bulk samples to measure surface exchange coefficients by fitting to the semi-infinite diffusion model was done in reference [28]. It was shown that there is a reasonably large window where surface exchange coefficients can be measured but all involved significantly slower bulk diffusion coefficients than is of interest for MIEC materials that are of interest for SOFC cathodes. This makes traditional IEDP using bulk samples to be an unusable technique for measuring surface exchange coefficients of MIECs. However, thin films have a very small distance for the isotope to diffuse so the semi-infinite diffusion model is limited. The plane diffusion model is more suited to modeling thin films due to symmetry: a zero flux boundary condition at the substrate-film interface can be mathematically treated as identical to a mirror plane of flux symmetry.

1.7 Processing and Experimental Limitations

There are many experimental limitations that must be taken into account when considering diffusion into thin films. These limitations define the experimentally measureable values of surface exchange coefficient and bulk diffusion coefficient. In this section, reasonable limitations are estimated so that approximations can be made of the range of surface exchange coefficient and bulk diffusion coefficient values that can be measured using the techniques described and developed in this thesis.

To start, a range of possible film thicknesses are defined. The minimal thickness is limited by the amount of secondary ion mass spectrometry (SIMS) data needed for a robust fit. Following the work of Kilner and Steele [26], a robust fit is defined as 25 data points of the diffusion profile verses depth. While secondary ion mass spectrometry machines vary in the amount of depth required to achieve this amount of data, primarily due to the strength of the ion beam used to sputter away material, approximately 4 angstroms of depth for each data point is deemed reasonable. This gives a minimum thickness of 10 nm. This is different from the result in [26] whose ion beam required ~30 angstroms of depth for each data point yielding a minimum thickness ~80 nm. A maximum thickness limitation is determined by the fabrication method. Sputtering was the deposition method of choice in this work, due to its accurate deposition thicknesses, good preservation of stoichiometry from target to film, and high film purity. This deposition method had very slow deposition rates (roughly 5 – 10 nm/hr). Thick films would take a very long time to deposit. The maximum film thickness generally achievable in a reasonable experimental timeframe was estimated to be 10 μm . Such a film thickness is a reasonable upper bound to what is achievable with most thin film deposition routes. Thick film deposition methods may be capable of producing thicker films, at the expense of possibly introducing porosity.

To allow the isotope to diffuse into the material, a specified time is set for each exchange experiment. This time, called the exchange time, has an upper and lower limit based on the experimental setup. The lower limit was set at 60 seconds. This was

found to be the shortest amount of time that was achievable using the experimental procedure described in Chapter 1. More complicated experimental procedures may provide the ability for slightly faster exchange times, but are unlikely to be much faster given finite sample quench rates and finite gas flow rates for the introduction and/or removal of isotopically enriched gasses. The upper limit on exchange time was set at 3 months. This was deemed, somewhat arbitrarily, as the maximum reasonable exchange time for an experimental timeframe.

Isotope concentration is another source of limitation in these experiments. The relevant concentration used in this work is the ratio of oxygen isotope ^{18}O to total oxygen (i.e., $^{18}\text{O} + ^{16}\text{O}$). A reasonable signal to noise ratio was estimated to require a minimum measured concentration within the sample of twice the background concentration. Background concentration of ^{18}O in un-enriched environments is 0.22%; therefore the minimum concentration estimated to be measurably increased from background was 0.44%. The maximum concentration possible is 100%, though as the material becomes “saturated” at such a high concentration, it becomes difficult to differentiate surface exchange or diffusion coefficients from being, effectively, infinite. For this reason, the maximum concentration estimated to be measurably decreased below a saturation limit was 90%.

These limitations offer a reasonable basis for diffusion equation models to be examined. The focus of this thesis is determining experimental methods by which oxygen surface exchange coefficient values can be measured for relevant oxide

material compositions. Using these experimental limits, model solutions to the diffusion equation provide a range of k values that can be measured.

1.8 Semi-infinite Diffusion

The solution to the diffusion equation in a semi-infinite medium, figure 9, with a first order surface exchange reaction boundary condition was solved by Crank [27]. The boundary condition is also known as the surface evaporation condition and is given as:

$$-D \frac{\partial C}{\partial x} = k(C_o - C_s) \quad x = 0 \quad (1-13)$$

where C_o is the concentration of the tracer in the atmosphere, D is the bulk diffusion coefficient, C_s is the concentration of isotope at surface of the material and k is the surface exchange coefficient. This boundary condition shows that the flux at the surface of the material depends on surface exchange coefficient and the concentration difference between the atmosphere and the surface of the material.

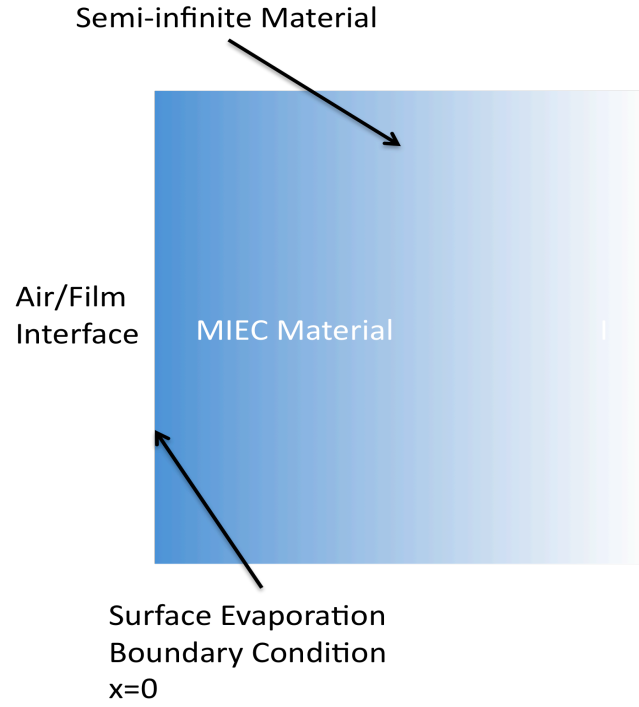


Figure 9: Schematic showing semi-infinite diffusion model. The surface evaporation boundary condition is at the air/film interface. The film is infinite in the positive x direction.

The diffusion equation solution is

$$\frac{C - C_2}{C_0 - C_2} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) - e^{\frac{k}{D}x + \left(\frac{k}{D}\right)^2 Dt} \operatorname{erf}\left\{\frac{x}{2\sqrt{Dt}} + \frac{k}{D}\sqrt{Dt}\right\} \quad (1-14)$$

where C is the concentration at distance x from the interface and time t since the isotopic exchange began. C_2 is the background concentration of the tracer in the material (0.0022, the same background concentration of ^{18}O in the atmosphere).

To understand the range of possible k values that could be measured with the semi-infinite diffusion model, an understanding of how the surface exchange coefficient and bulk diffusion coefficient impact the diffusion profile is required. Plots of equation 1-14 for various values of k and D were made with the Mathematica program given in Appendix B. These plots simulate a semi-infinite material that had been exchanged for 60 seconds. Variation in the shape of the diffusion profile caused by the surface exchange coefficient is shown in figure 10. As k goes to zero, the concentration level at the surface reduces to background levels. Adjusting the k value does not affect the total “penetration depth” of the isotope, meaning that all of the diffusion profiles reach near background isotope concentrations at about the same depth. Larger k values lead to increased surface concentration until saturation at the surface makes the diffusion profile indistinguishable from a diffusion profile with infinite surface exchange. Note that a surface exchange coefficient indistinguishable from infinite has no influence on the shape of the diffusion profile. The system is entirely “diffusion-limited” and can be well-estimated using a simpler solution to the diffusion equation, given by Crank as:

$$\frac{C - C_2}{C_0 - C_2} = \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (1-15)$$

Diffusion-limited systems are discussed in greater detail in Chapter 3. The goal of this work was to measure surface exchange coefficients and therefore surface saturation conditions are to be avoided. Allowing for noise in the data, especially at the surface

where contamination, interface roughness, and other effects can affect SIMS data, the maximum normalized surface concentration at which an estimate for k can be made was estimated to be 0.9.

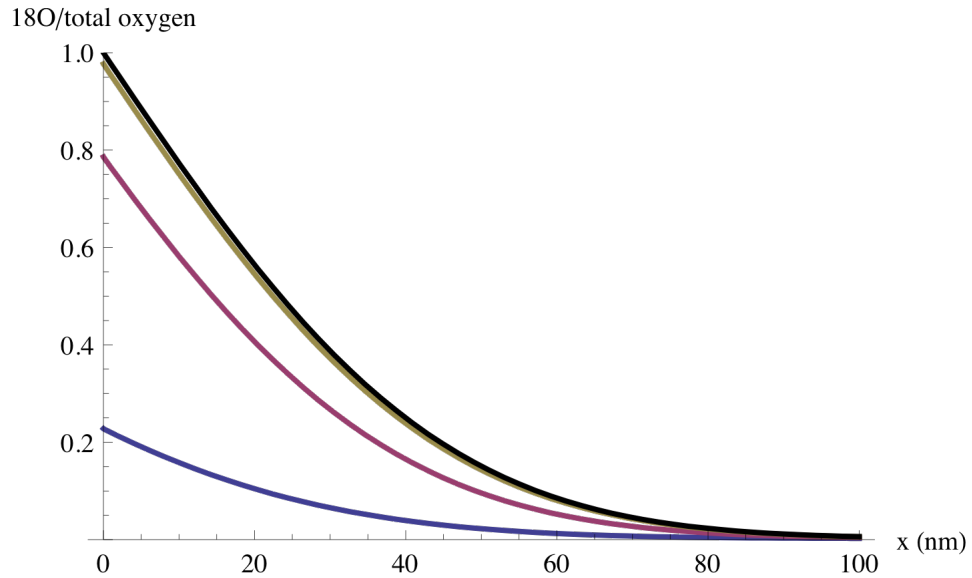


Figure 10: Semi-infinite diffusion profiles where $k = 10^{-6}$ cm/sec (yellow), $k = 10^{-7}$ cm/sec (red), and $k = 10^{-8}$ cm/sec (blue). Also shown is $k = \infty$ (black). In all cases, $D = 10^{-13}$ cm²/sec and the exchange time is 60 seconds. Position $x=0$ nm represents the air/film interface. Larger k values lead to greater isotope concentration at every distance, x , however all diffusion profiles reduce to nearly background concentrations at similar penetration depths.

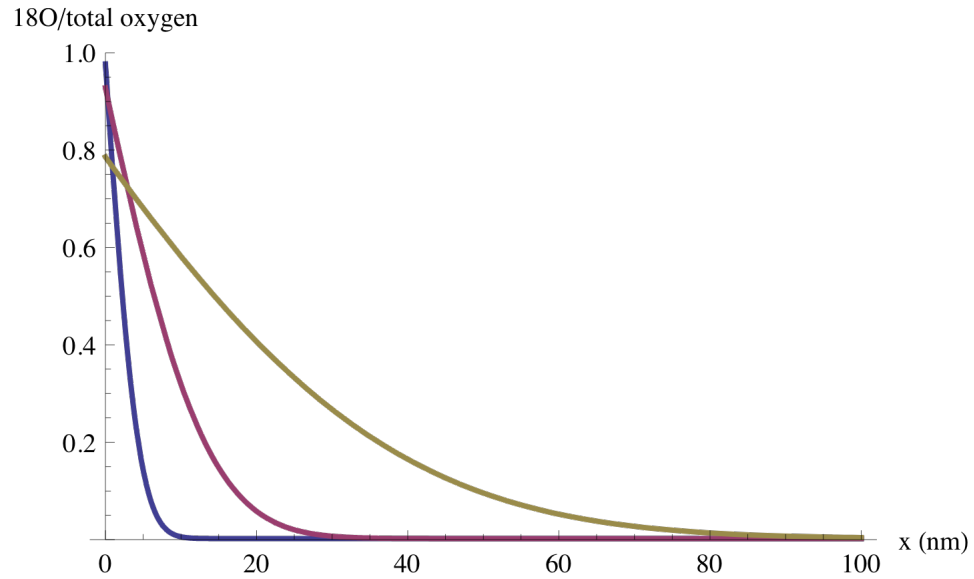


Figure 11: Semi-infinite diffusion profiles where $D = 10^{-13} \text{ cm}^2/\text{sec}$ (yellow), $D = 10^{-14} \text{ cm}^2/\text{sec}$ (red), and $D = 10^{-15} \text{ cm}^2/\text{sec}$ (blue). In all cases, $k = 10^{-7} \text{ cm/sec}$ and the exchange time is 60 seconds. Position $x=0 \text{ nm}$ represents the air/ film interface. Larger D values lead to greater isotope penetration in the same exchange time.

Variation in bulk diffusion coefficient, shown in figure 11, impacts the distance the isotope diffuses. Diffusion profiles with small D values decrease to background concentration near the surface of the material while diffusion profiles with large D values feature concentrations significantly above background levels further into the depth of the material.

The semi-infinite model does not account for the material having a finite thickness and ending at a substrate with insignificant diffusivity (as would be the case for any real experiment). For this model to be applicable to thin films, the diffusion

profile must have a concentration that is insignificantly different than background levels before reaching the film-substrate interface. To include this requirement within the modeled behavior examined in this thesis, the diffusion length is used. The diffusion length is defined here as $l = \sqrt{D^* t}$. For the semi-infinite model to be used with a thin film sample, the diffusion length was required to be, at most, one quarter the thickness of the film. By requiring a film thickness equal to or greater than 4 diffusion lengths, a concentration at the film-substrate that is insignificantly increased from background concentration was ensured. The semi-infinite solution to the diffusion equation thus remains valid in these cases. This limitation in the solution validity is shown in Chapter 3 to severely restrict the utility of the semi-infinite model in measuring useful surface exchange coefficients using thin films.

1.9 Plane Diffusion Model

The plane diffusion model is based on a medium bounded by two parallel planes lying at $x = +l$ and $x = -l$. At each boundary, the first order reaction boundary equation, equation 1-16, is applied. The solution to the diffusion equation is symmetric in this case. By symmetry this solution is equivalent to a boundary condition of zero flux at the midpoint, $x = 0$, figure 12. Using just one half of this solution, a relevant case is solved: a thin film bounded on one side by a first order exchange reaction and on the other side by a substrate with insignificant diffusivity (or, equivalently, insignificant surface exchange coefficient). For the remainder of this thesis, to allow easy visual comparison with the diffusion profiles shown before, we

model the film/surface interface at $x = 0$ (where l is the thickness of the material) and the film/substrate interface at $x=l$. This is a minor change to the initial equation, a repositioning of the x axis, however the added ease of comparison between the semi-infinite and plane diffusion solutions made the adjustment desirable.

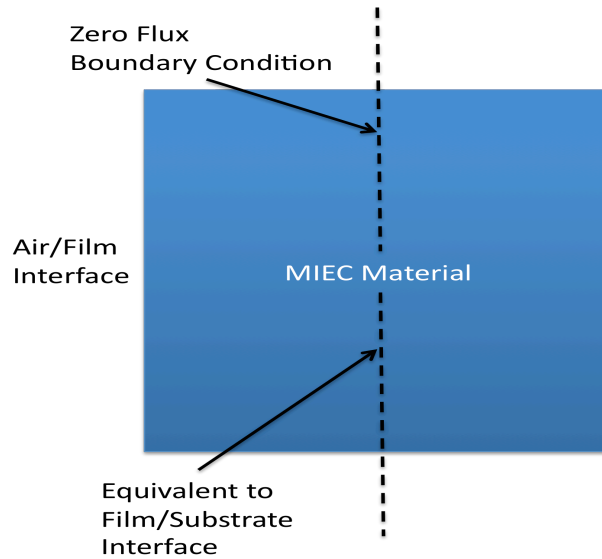


Figure 12: Schematic illustrating the mid-plane of a plane wall of material has the same zero flux boundary condition as a film with half the thickness of the plane wall deposited on a substrate with zero isotope diffusion.

The mathematical solution to the diffusion equation for this geometry was solved by Crank [27] and can be seen in equation 2-4. β_n is the n^{th} solution to equation 1-17 and L is the dimensionless quantity defined by the thickness of the film, l , the surface exchange coefficient, k , and the bulk diffusion coefficient, D , as seen in equation 1-18. The solution calls for an infinite sum however in most cases the

solutions change insignificantly after the first two terms. To ensure a sufficiently precise calculation, this work always used the first 6 terms in the series expression.

$$\frac{C - C_2}{C_0 - C_2} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x / l) e^{-\beta_n^2 D t / l^2}}{(\beta_n^2 + L^2 + L) \cos \beta_n} \quad (1-16)$$

$$\beta \tan \beta = L \quad (1-17)$$

$$L = l \frac{k}{D} \quad (1-18)$$

Plots of diffusion profiles showing the differences caused by variation in surface exchange coefficients, figure 13, and bulk diffusion coefficients, figure 14, were made using a routine written in Mathematica (version 8, Wolfram), see Appendix B. The surface exchange coefficient has a similar effect on the diffusion profile as in the semi-infinite model: larger k values yield higher surface concentrations. In contrast, the bulk diffusion coefficient has a different effect than what was observed in the semi-infinite model, where D changed the “penetration depth” of the diffusion profile. In the plane diffusion model, the material thickness can be small enough that even small diffusion coefficients allow a significant concentration of isotope to diffuse to the substrate. The concentration throughout the

material increases due to the zero flux condition of the substrate, making the concentration more constant throughout the thickness. As D/l approaches infinity, the diffusion profile becomes completely flat throughout the material, with the concentration determined solely by the exchange time and surface exchange coefficient. When D/l is large enough, it has no significant impact on the diffusion profile, and the system is in a fully surface exchange limited regime. This is a very desirable condition for the purposes of this work, because it effectively eliminates the impact of the bulk diffusion coefficient from the solution. The solution is based on just one unknown parameter: the surface exchange coefficient, and the known experimental constants: the exchange time and film thickness.

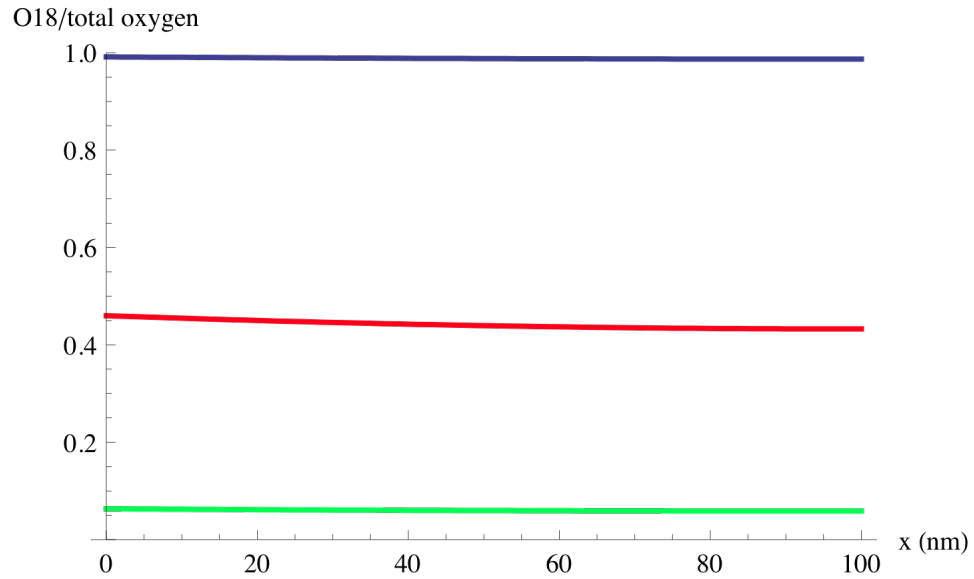


Figure 13: Plane diffusion profiles showing $k = 10^{-8}$ cm/sec (green), 10^{-7} cm/sec (red), and 10^{-6} cm/sec (blue) surface exchange coefficients all with a bulk diffusion coefficient of 10^{-11} cm²/sec an exchange time of 60 seconds and a film thickness of 100 nm. Re-plotted from traditional plane diffusion solution so that $x = 0$ nm represents the air/film interface and $x = 100$ nm represents the film/substrate interface.

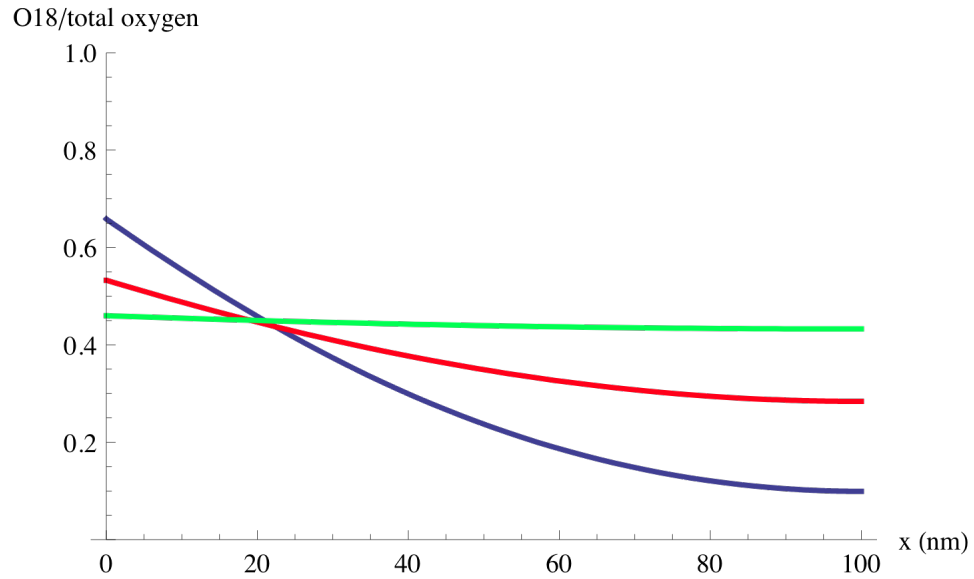


Figure 14: Plane diffusion profiles showing $D = 10^{-11} \text{ cm}^2/\text{sec}$ (green), $D = 10^{-12} \text{ cm}^2/\text{sec}$ (red), and $D = 10^{-12.5} \text{ cm}^2/\text{sec}$ (blue) bulk diffusion coefficients all with a surface exchange coefficient of $10^{-7} \text{ cm}^2/\text{sec}$, an exchange time of 60 seconds, and a thin film thickness of 100 nm. Re-plotted from traditional plane diffusion solution so that $x = 0 \text{ nm}$ represents the air/film interface and $x = 100 \text{ nm}$ represents the film/substrate interface.

Chapter 2

EXPERIMENTAL

2.1 Target Fabrication

The materials investigated in this work are LaCoO_3 and SrCoO_3 . These materials are both mixed ionic electronic conductors (MIECs) and have a perovskite-related crystal structure [42][43]. Perovskite materials feature the lattice structure shown in figure 15 and the chemical formula of ABO_3 . To investigate these materials using thin film methods, sputtering targets with corresponding compositions were fabricated using traditional ceramic processing methods [44].

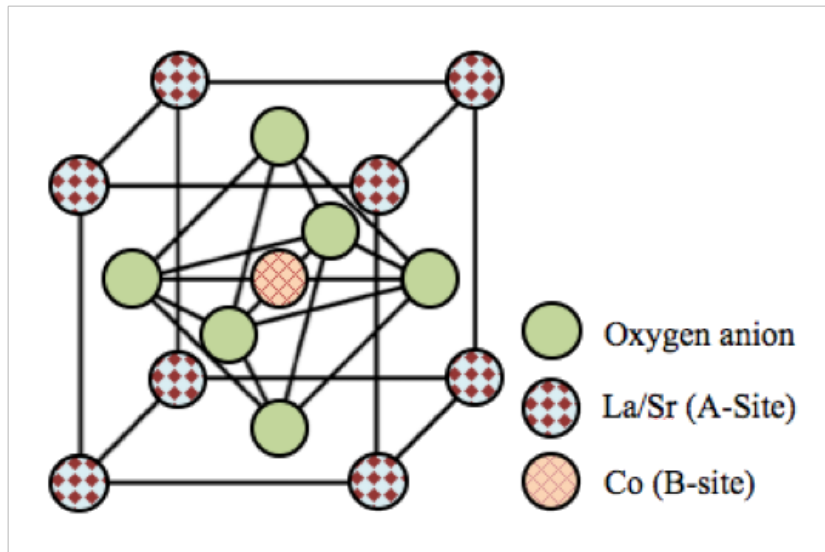


Figure 15: The cubic perovskite crystal structure

Sputtering source targets of the lanthanum cobaltite (LaCoO_3) and strontium

cobaltite (SrCoO_3) were made from high purity oxide and carbonate powder raw materials. Strontium carbonate, SrCO_3 , (99.5+% pure, Inframat Advanced Materials), lanthanum oxide, La_2O_3 , (99.99% pure, Alfa Aesar), and cobalt oxide Co_3O_4 (99.99% pure, Inframat Advanced Materials) powders were weighed to form the desired stoichiometry, described in equations 2-1 and 2-2, and ball milled in de-ionized (DI) water for 24 hours using yttrium-stabilized zirconia (YSZ) milling media.

$$x(\text{LaCoO}_3) = 0.327 * x(\text{Co}_3\text{O}_4) + 0.663 * x(\text{La}_2\text{O}_3) \quad (2-1)$$

$$x(\text{SrCoO}_3) = 0.761 * x(\text{SrCO}_3) + 0.413 * x(\text{Co}_3\text{O}_4) \quad (2-2)$$

Milling mixes the powders together and decreases particle sizes to aid the sintering of the material. After milling, the powders were sieved with a 500 μm nominal hole diameter to remove large powder agglomerates and the milling media. The water was evaporated from the milled powders by heating on a hot plate while continuously stirring to ensure the powders do not separate.

The dried powders were calcined in a high temperature furnace in an alumina boat. The powders for each target were each calcined at 1000 $^\circ\text{C}$ for 6 hours. Nominal heating and cooling ramp rates of 100 $^\circ\text{C/hr}$ were used (the use of passive cooling led to reduced cooling rate below about 400 $^\circ\text{C}$). The temperature ramp rate was chosen to be slow enough to ensure that the material would stay a consistent temperature

throughout. The powders remained fully oxidized during calcining by maintaining an atmosphere of flowing, standard purity oxygen through the furnace.

After calcining, the powders were believed to have reacted to form cobaltites with perovskite crystal structure, though this was not verified. Since the target is vaporized during the sputtering process, the crystal structure of the target was not directly important to this work. This material was then formed into a solid disc to fit the sputtering gun. Polyvinyl alcohol (PVA) (98-99% pure, Alpha Aesar) was added to the calcined powders to a total concentration of 1 weight percent. This mixture was then ball-milled in deionized water for 24 hours with YSZ milling media. The PVA was a sacrificial binder used to hold the powders in the desired shape before sintering. The PVA was removed by oxidation during the sintering process.

After milling, the material was filtered with a sieve to remove the milling media and any large particles of PVA and dried in the same manner as before. The

Sputtering Target Fabrication Process Flow

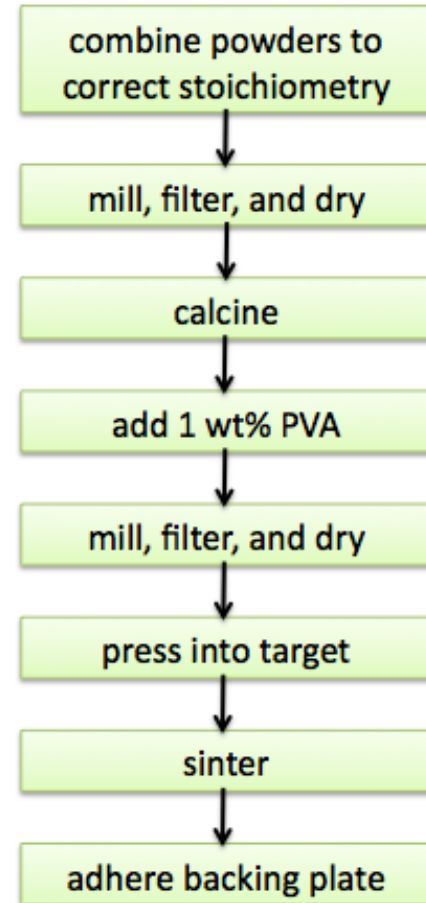


Figure 16: Process flow for fabrication of sputtering source targets using traditional ceramic processing methods

dried powders were pressed uniaxially in a 3-inch inner diameter cylindrical stainless steel die to a pressure of 1500 psi. Steric acid diluted in acetone was used as a lubricant for the dies. The pressed powder targets were removed from the dies and were sintered on an alumina plate at 1350 °C for 8 hours and 1250 °C for 4 hours for the lanthanum cobaltite and strontium cobaltite targets respectively. The heating and cooling ramp rate were identical to that used during calcining except for heating between 300 °C and 500 °C. In this temperature range, the PVA is oxidizing and the resultant gases are escaping through pores in the target. If this occurs too rapidly, the target can fracture. For this reason, the ramp rate between 300 °C and 500 °C was slowed to 20 °C/hr. The targets were also cooled at 100 °C/hr to avoid any thermal shock that may cause cracking. An atmosphere of slowly flowing oxygen was used during sintering to ensure the surface of the targets did not reduce. Once the sintering process completed, the targets had densified to be slightly larger than the desired 2-inch diameter and 0.25 inch thickness. The targets were then shaped using sandpaper until they met these required dimensions.

Since the targets were brittle and poor thermal conductors (and therefore prone to thermal shock), a backing plate made of copper was attached to provide structural support and a constant thermal profile. The copper plates were 2 inch in diameter and 1/8 inch thick. They were roughened with sandpaper on one side to aid adhesion. The back of the target and the copper plate were coated with silver paint to serve as an electronically and thermally conductive adhesive. The copper backed target was then put into a box furnace and held at 700 °C for one hour. This temperature allowed the

silver paint to flow and securely bond the copper plate to the target.

A small amount of powder from each of the sintered targets was obtained by removing a small section from the back before the copper backing plate was applied. This material was highly granular, so it was ground by hand using a mortar and pestle. The resulting powder was then analyzed by x-ray diffraction (XRD). Measurements were performed on PANalytical X'Pert Powder X-Ray Diffractometer in a standard $\Theta/2\Theta$ configuration from $5^\circ - 75^\circ$ with a step size of 0.001.

2.2 Sputtering

Magnetron sputtering, figure 17, is a common thin film fabrication technique. The process involves ionizing a gas (typically argon) to make a plasma and electrically accelerating the ions into the source material. Magnets, situated behind the source target, concentrate the plasma near the target surface to increase process efficiency. The accelerated ions have enough energy to remove atoms of the source material. These atoms deposit onto a substrate forming a thin film of the source material. Sputtering is performed in a vacuum chamber, in part to minimize contamination. This means the thin film can be nominally identical in composition to the source target. Adding a reactive gas in with the ionizing gas is another method of ensuring the deposited film is the desired composition. This process, known as reactive sputtering [37], is often used for thin film depositions. For example, sputtering with oxygen as the reactive gas can ensure the film does not reduce during the deposition. The deposition rate of materials by sputtering depends on many variables, most notably the

pressure of the operational gas, gas composition, and power applied. These processing conditions are discussed below.

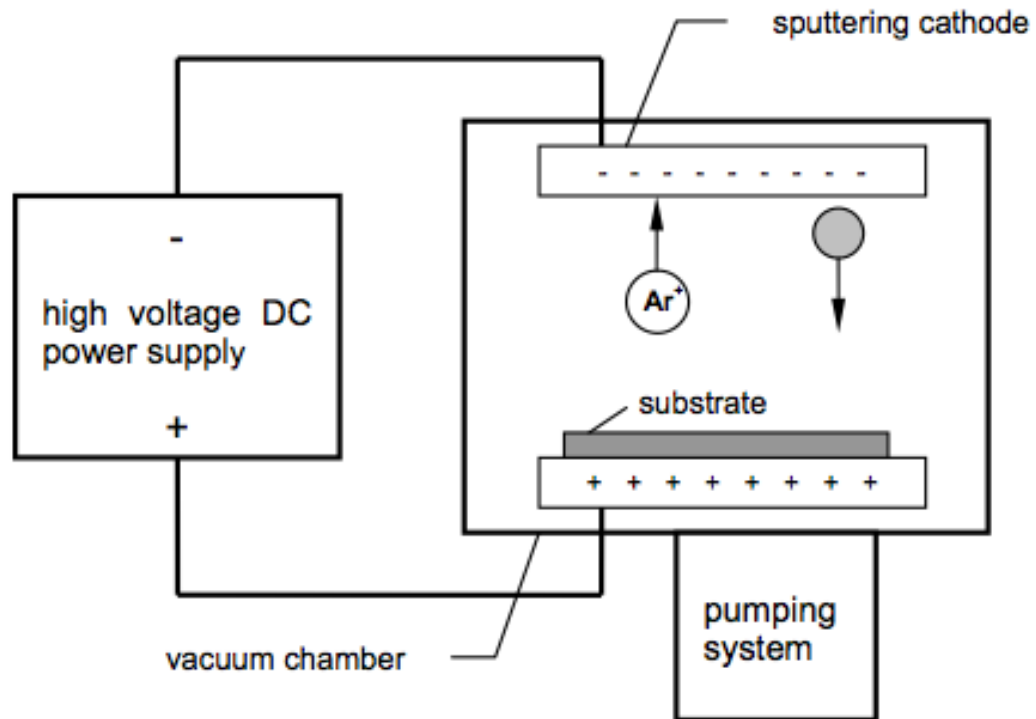


Figure 17: Schematic of typical DC sputtering. Argon ions are accelerated towards the sputtering cathode and the impact releases atoms of the cathode to be deposited on the substrate.

2.2.1 Basics of the Sputtering System

The sputtering system used to create the thin films is a magnetron sputtering

system designed by PVD products. While many of these capabilities are not used in this thesis, they are necessary for combinatorial analysis of thin films, a future extension of this work. For this reason the full capabilities of the system are noted below. The system consists of two chambers: the load lock and the main sputtering chamber. The base pressure of the main sputtering chamber is roughly 10^{-8} Torr. The load lock is used to exchange substrates so that multiple depositions can be done without venting the main chamber. The sputtering system has four magnetron sputtering guns. RF power supplies power to three of the guns. These guns are physically separated within the chamber by 120 degrees for symmetry. The fourth gun is powered by a DC power supply. The substrate holder accommodates up to a 4-inch diameter substrate although more often a substrate holder with a circular array of 10 mm x 10 mm square substrates was used. The substrate holder has the capability to spin with constant rotational speed to produce a film with radially uniform thickness or can be held fixed which produces a gradient of thickness which decreases from the location where the gun was directed to the substrate holder.

2.2.2 Fixed Sputtering Variables

To sputter there must be an operating pressure of a gas. Argon and oxygen can be used as the operating gases. Argon is the standard gas used for sputtering. It was desired that the ceramic materials in this work (both the source targets and the deposited thin films) remain fully oxidized, so a combination of argon and oxygen was used. The effects of operating pressure was previously measured [39] in order to

optimize the deposition rate. Ceramic materials generally have low deposition rates; adjusting these variables within the allowable ranges to provide maximum deposition rate was needed to provide reasonable film thicknesses over experimentally achievable time scales. Operating pressures of 5 mTorr and 10 mTorr and argon to oxygen ratios of 9:1 and 4:1 were compared. As described in the Results, an operating pressure of 10 mTorr with an argon to oxygen ratio of 4:1 was found to provide the largest deposition rate and thus used for subsequent experiments. Previous experimentation [39] used nominally the same materials as in this work, however different sputtering targets were used. Therefore, qualitative deposition rate comparisons can be made but the exact deposition rates found in this work are shown in Chapter 3.

Even with the argon to oxygen ratio set to ensure the sputtered material is fully oxidized, the surface of the sputtering source target can become chemically reduced over time. A reduced surface deposits at a different rate than a fully oxidized surface. To ensure a consistent surface, the targets were pre-sputtered, meaning they were sputtered without opening the shutter such that material is removed from the source target but not deposited on the substrate. Both ceramic targets were pre-sputtered for an hour before every deposition.

The power being applied to the target heats the target up. If the ramp rate of the applied power is too large, the target may crack from thermal shock. The copper backing plate helps prevent thermal shock by adding some mechanical support, however further precautions were taken. A ramp rate of 50 W/hr was chosen for the ceramic targets, which was slow enough to ensure that thermal shock did not occur.

2.2.3 Deposition Rates

The primary methods of changing the film thickness were to adjust the power applied and the total sputtering time. To measure the sputtering deposition rates, both LaCoO_3 and SrCoO_3 films were deposited for 3 hours at both 25 W and 50 W. SrCoO_3 was sputtered from the gun in position 1 and LaCoO_3 was sputtered from the gun in position 2, figure 18. The sputtering gun used for each target was kept the same throughout the entirety of these experiments. Even though the sputtering guns and power supplies have identical specifications, slight differences in magnet strength can change deposition rates. All deposition rate measurements were done on 10 mm x 10 mm x 0.5 mm polished silicon substrates.

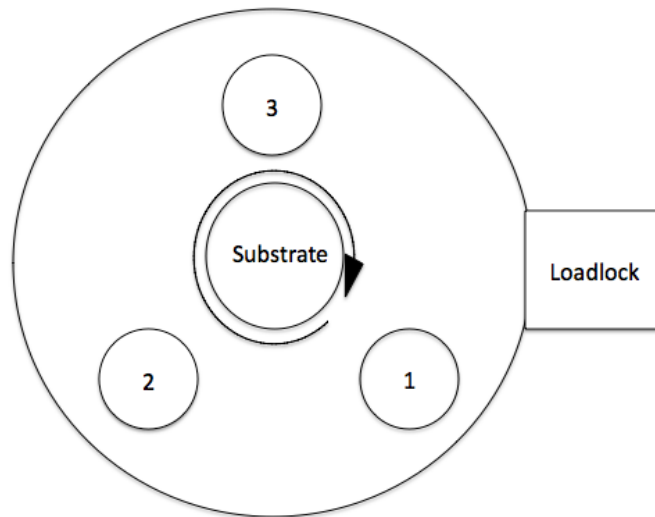


Figure 18: Diagram of the sputtering chamber showing the positions of the sputtering guns with respect to the rotating substrate and the loadlock.

Cleanliness of the chamber, and in particular the substrate, is a concern for physical vapor depositions. Dust, residue, and other contaminants can prevent the film from depositing smoothly on the substrate. The standard cleaning procedure for cleaning substrates used here was a “triple rinse”. The triple rinsing procedure consisted of ultrasonically washing the substrate in a bath of acetone for one minute, then rinsing successively with isopropyl alcohol and deionied water. Then the substrate was blown dry with filtered compressed air. Once the substrate was triple rinsed, it was covered with vacuum tape over half of the polished surface. The vacuum tape acts as a mask so that a step height can be made, figure 19. Sputtering of the material was then performed with the desired forward power applied and the substrate under constant rotation of 30 rpm. After 3 hours, the target and substrate shutters were closed, the sputtering power was ramped down to zero, and then the sample was removed from the sputtering chamber. The vacuum tape was then removed carefully to create a clean edge and the sample was triple rinsed to remove any tape residue. Returned to the sputtering system, the sample was coated with a thin layer of reflective metal. The reflective layer is important for measuring the size of the step height in the optical interferometer, as described below. The metals that were used were titanium or chromium. Both provide a sufficiently smooth and reflective layer, so either was used. The metal was sputtered over the entire substrate, both the earlier deposited film and the surface previously covered by the vacuum tape. The metals were deposited at a power of 100 W and a chamber pressure of 0.01 Torr. Argon was used as the ionizing gas. The metal was deposited for less than 10 minutes to ensure the metal layer was

thin. The sample was removed from the sputtering chamber and triple rinsed a final time to remove any dust particles before analysis in the interferometer.

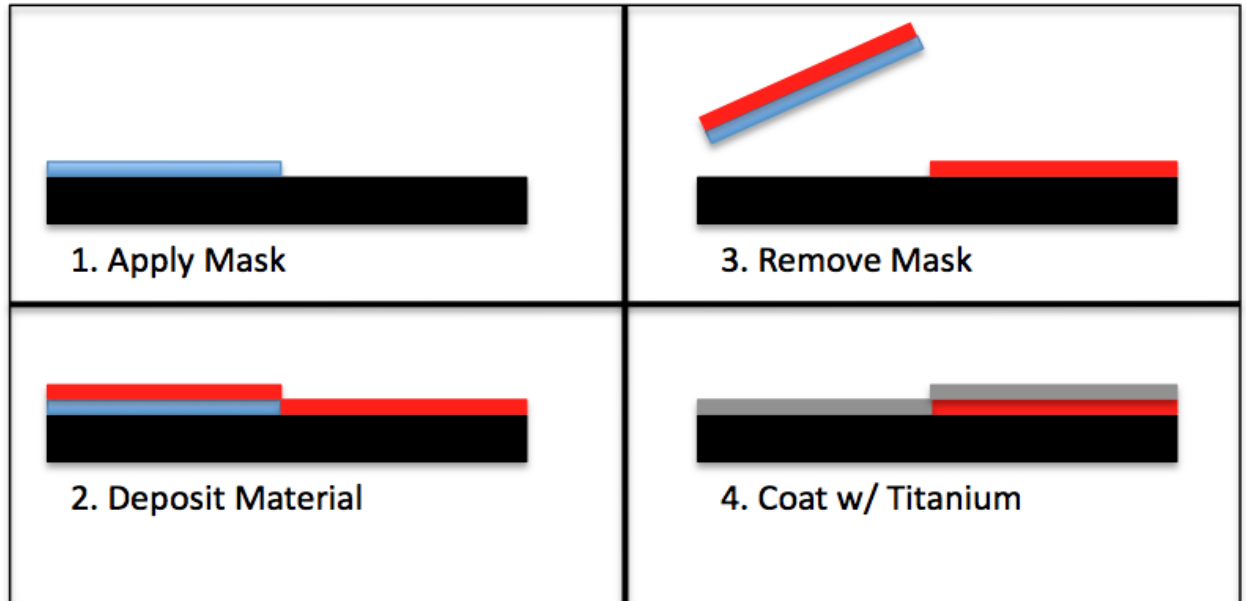


Figure 19: Mask method used to create a step height for deposition rate measurements in the interferometer

2.2.4 Interferometry

A Veeco Wyko N9100 interferometer was used to measure the step height. The interferometer uses reflected light to measure the relative height of a surface. This is particularly useful in measuring step heights where the change in the surface is abrupt. To measure, the brightness was first manually adjusted in order to make the sample well lit but not to overload the detector. Samples were placed on the stage and the step height brought into focus. Focus was found by adjusting the orientation of the stage to an angle that provided an optical interference banding pattern across the step height.

The banding is important to the measurement because as the band of light crosses the step height it is phase-shifted. This shift corresponds to the difference in the wavelength of light as it reflects off of surfaces of two different heights. A measurement is taken of the surface when the interferometer moves the focal point through the current focus, which moves the optical interference bands over the surface. The interferometer can analyze this information to give an image of the surface.

Since this was a measurement of relative height, the side of the step without perovskite film was normalized to have an average baseline height of zero, figure 20. The step height was measured by plotting a histogram of surface height each measured point. A 640 x 480 array of points was measured representing an area of 238 μm x 315 μm . The difference in the heights at the step height location can be seen in the 3D plot of the surface, figure 21. The histogram was bimodal, corresponding to the distribution of heights on each of the two surfaces, figure 22. The step height, and therefore the thickness of the perovskite film, is the span distance between the peaks of the two distributions.

Y Profile

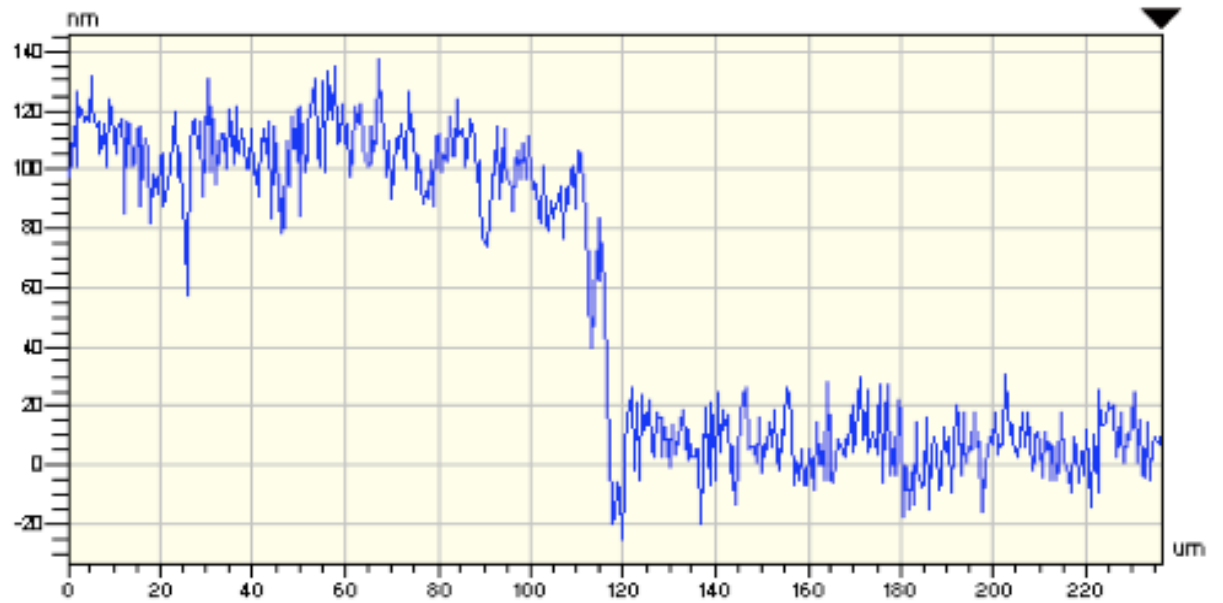


Figure 20: The step height created in the film. The data is adjusted to remove any tilt in the film.

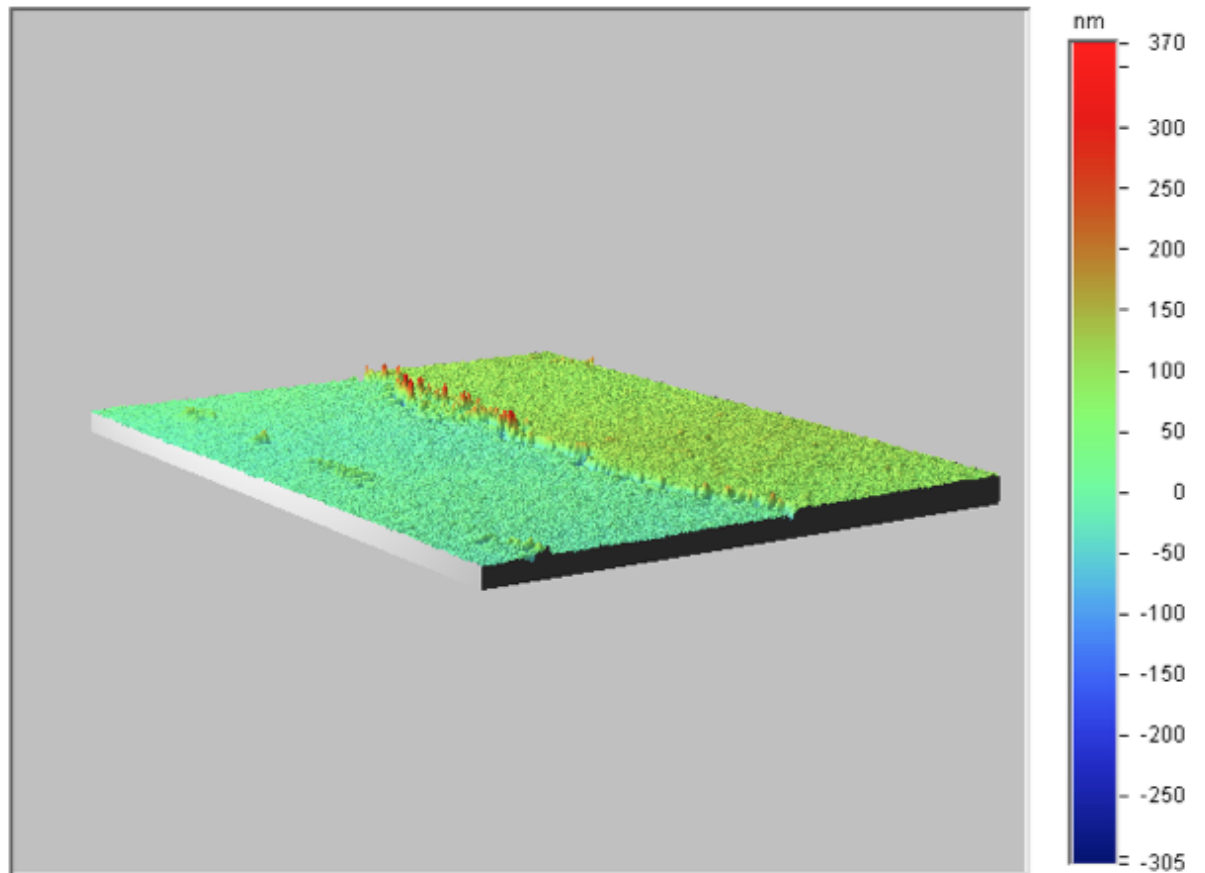


Figure 21: 3D plot showing the step height in the film

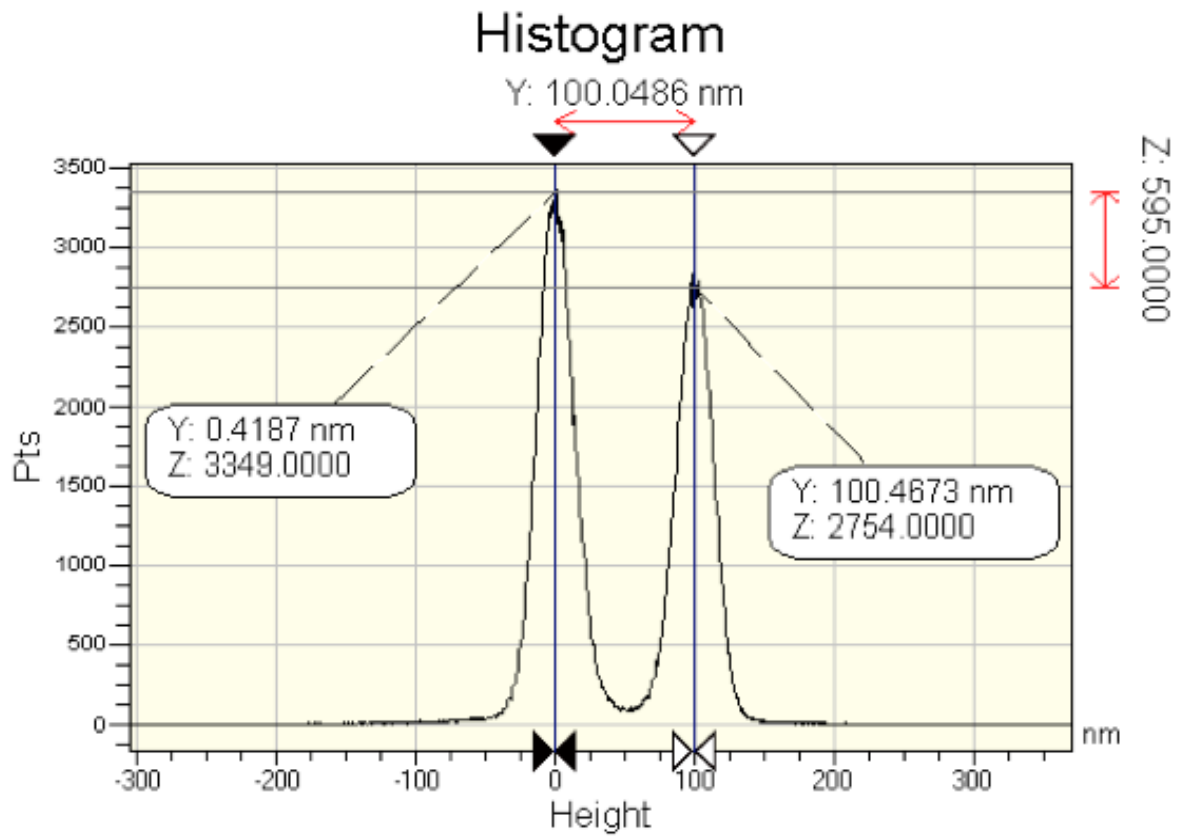


Figure 22: Histogram showing the step height as the difference in the two peaks. The step height is 100 nm.

This analysis technique was used to measure the film thickness of all of the deposition samples. The deposition rates for both materials (given in more detail in Chapter 3) were slow, in the range of 5 – 10 nm/hr. For depositing reasonably thick films, the fastest rate possible was desired. This corresponded to the highest power used: 50 W, a working pressure of 10 mTorr and a sputtering gas composition of [4:1] Ar:O₂. Higher powers than 50 W likely would have lead to greater deposition rates;

however, they were not investigated because higher powers increase the potential of cracking the targets from thermal shock. The goal of this work was not to optimize the deposition rates of these materials but to produce thin films with consistent thickness. The deposition rates achieved were deemed sufficient for this work. This thesis focuses on the pure LaCoO_3 and SrCoO_3 thin films, however doped thin films for combinatorial analysis could be fabricated by adjusting the applied power for each target to produce relative deposition rates that matched the desired dopant concentration.

2.3 Thin Film Surface Structure and Thermal Stability

Films of both LaCoO_3 and SrCoO_3 were deposited to thicknesses of 100 nm. This thickness is within the thin film range, described in Section 1.7, while having a reasonable deposition time of 696 minutes and 1284 minutes for LaCoO_3 and SrCoO_3 respectively. To ensure that the samples had a smooth, clean surface for isotope exchange, scanning electron microscopy (SEM) was used to observe the surface structure of both newly deposited films and films that were exposed to the elevated temperatures of testing conditions. SEM micrographs were taken on a JSM 7400F high-resolution scanning electron microscope. Samples of newly deposited films were not coated, however some charging was seen in the micrographs so samples that were exposed to elevated temperatures were imaged with a sputtered coat of gold palladium. The micrographs are shown in Chapter 3.

Isotopic exchanges were performed at elevated temperature in order to provide

experimentally measurable values of the diffusion and surface exchange coefficients. Crack testing was done to ensure that the films would remain mechanically stable during isotopic exchange. Nominally identical thin films to those used during isotope exchange were heated in an atmosphere of air to 500 °C at a rate of 150 °C/hr. The samples were held at this temperature for one hour, which was the longest ^{18}O isotopic exchange time used. The films were then pulled out of the furnace and quenched rapidly to room temperature with flowing dry air. This test simulated the rapid thermal treatment used during the isotope exchange procedure where a rapid quench is used to lock in the oxygen profile after high temperature exchange.

Initial crack testing showed delamination of the films when deposited on silicon substrates. Stress induced by the thermal expansion difference between the film and the substrate was a suspected cause of the delamination. The CTE of LaCoO_3 within the temperature range is between $8 \cdot 10^{-6} \text{ K}^{-1}$ and $23 \cdot 10^{-6} \text{ K}^{-1}$ [45]. This is a mismatch with silicon which has a CTE between $3 \cdot 10^{-6} \text{ K}^{-1}$ and $5.5 \cdot 10^{-6} \text{ K}^{-1}$ [46]. Magnesium oxide (MgO) substrates were chosen because of its higher CTE, $13.9 \times 10^{-6} \text{ K}^{-1}$, more similar to the assumed values for the films [47]. The reduced mismatch in thermal expansion coefficient was believed to have reduced stress in the film during heating and cooling cycles.

To further improve the films' thermomechanical stability, the films were deposited at a substrate temperature of 500 °C. Depositing the films at the same elevated temperature to be used during subsequent isotope exchanges increased their stability in that temperature range. After performing the crack testing described above,

films deposited on MgO substrates at 500 °C had a polished, reflective appearance to the naked eye and exhibited no visible cracks under the optical microscope figure 23.

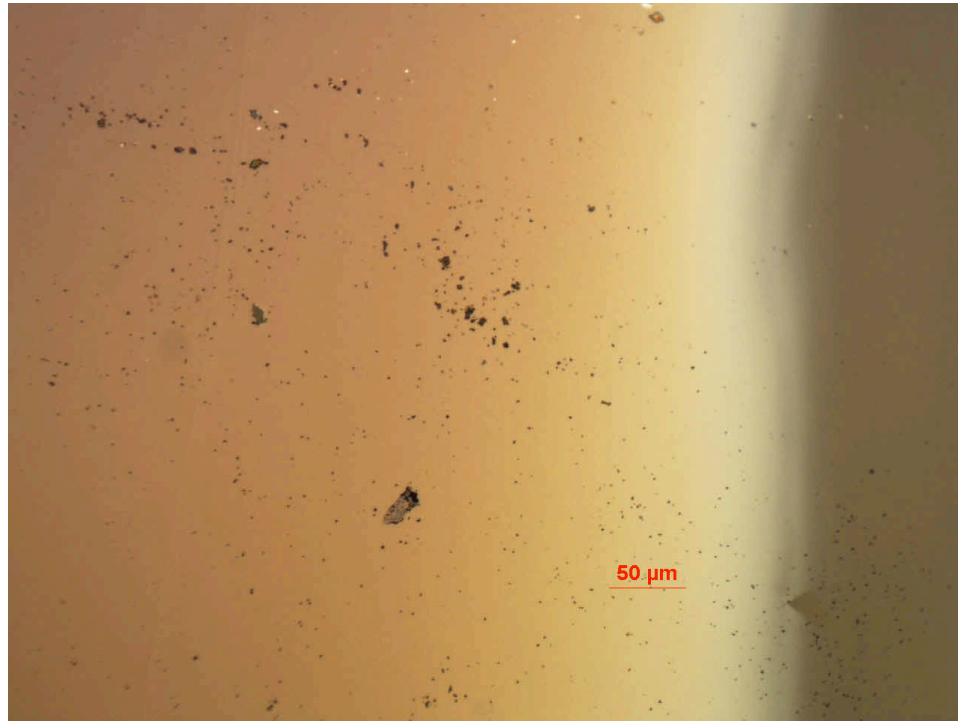


Figure 23: An optical micrograph of the edge of the SrCoO₃ film. The film appears dark brown on the left portion of the image, tapering in thickness in the brighter section to the right of center. A portion of uncovered MgO substrate is at far right. No cracks are visible in the films; dark spots are believed to be dust.

Increased substrate temperature during deposition can affect the deposition rate due to densification in the film, similar to sintering. This effect can cause measured film thickness to be reduced from what is measured under otherwise identical sputtering conditions at room temperature. Deposition rates were re-measured for

depositions at 500 °C so that a known film thickness could be deposited for later experimentation.

2.4 Oxygen Exchange Chamber

A very small amount of $^{18}\text{O}_2$ isotopically enriched oxygen gas was needed to conduct the exchanges, so a low volume oxygen exchange chamber was fabricated, figure 24. The chamber was a stainless steel tube with 0.5-inch inner diameter and 24 inch length. This length was required so that the sample could be placed in the center of the tube furnace. Connected to the tube on the exterior of the furnace was a pressure gauge to measure vacuum pressure in the chamber when evacuating internal gases and a burst valve to ensure pressure in the chamber did not increase above atmospheric value. A T-valve was used to switch an inlet to the tube between a vacuum pump and a gas inlet. The exchange chamber was kept airtight using PTFE tape at all of the joints outside of the furnace. The end cap inside the furnace experienced temperatures that were too high for PTFE tape, so it was sealed with Resbond 907GF high temperature sealant, (Cotronics Corporation). To periodically test the chamber for airtightness, the chamber was pumped to a rough vacuum, the T-valve was closed to seal off the chamber, and then the pressure gauge was monitored over an extended period of time. Any gradual increase in pressure indicated a gas leak. To reduce the amount of expensive $^{18}\text{O}_2$ gas needed to fill the chamber, the majority of the volume of the tube was filled with a solid stainless steel rod. There was ample space around the rod for gas flow to reach the sample at the end of the chamber. The entire chamber was

made of stainless steel to be able to withstand the high temperatures. Before performing any isotope exchanges, the chamber was cleaned with liquid solvents and then heat treated to remove any volatile impurities from the chamber walls by putting it in the furnace at 1000 °C for 10 hours. This treatment was significantly hotter and longer than any isotopic exchanges performed in this work.

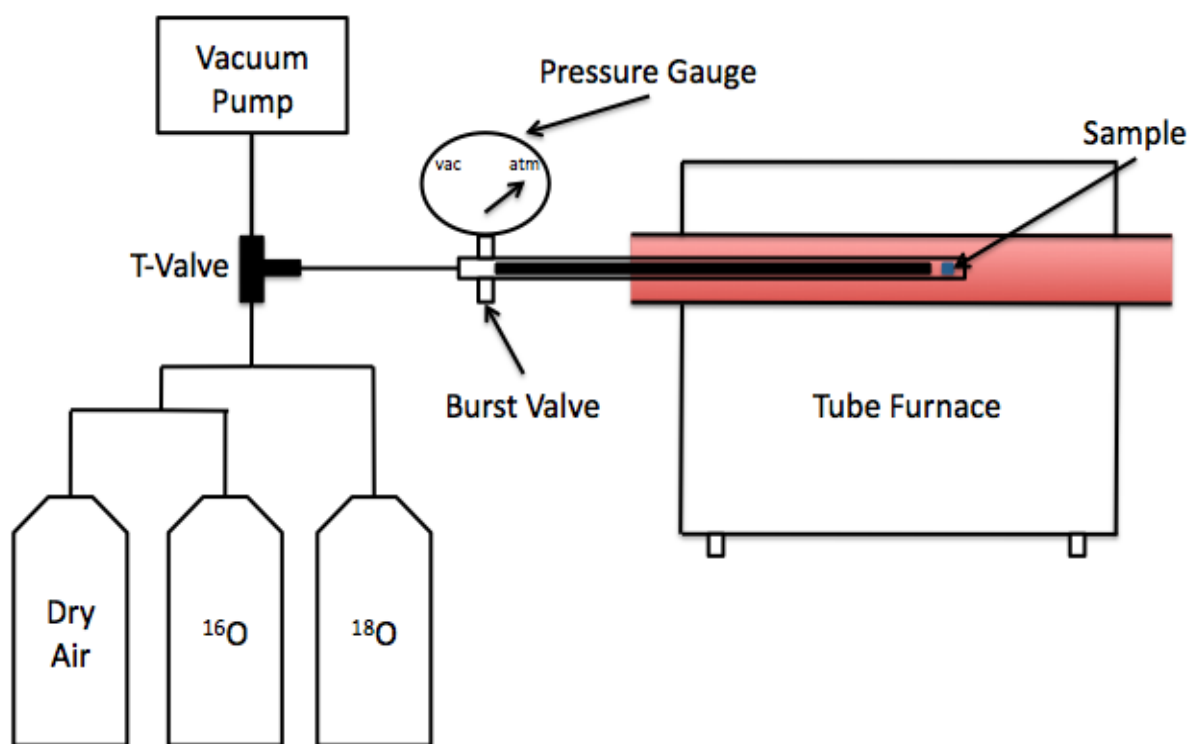


Figure 24: Experiment setup for ^{18}O exchange

The temperature inside the chamber was measured with a k-type wire thermocouple. It was found that a furnace temperature of 540 °C was required to achieve a chamber internal temperature of 500 °C. This difference is likely due to heat

loss along the exchange chamber. All temperatures listed in this thesis correspond to calibrated operational temperatures inside the exchange chamber.

2.5 Oxygen Isotopic Exchange

The films used for the isotope exchange were 100 nm thick and deposited on 10 mm x 10 mm MgO substrates using sputtering conditions as described in section 2.2. Each substrate was then broken into four quarters using a diamond scribe. This allowed for more data to be gathered from material that was deposited in identical conditions.

The isotope exchange procedure, figure 25, began with placing the samples into the chamber and sealing the chamber for air-tightness. Often one sample of LaCoO_3 and one sample of SrCoO_3 were placed in the chamber at the same time. There was no worry of cross-contamination because the vapor pressures of the film and substrate materials are exceedingly small at the temperatures used. Exchanging multiple samples at one time conserved $^{18}\text{O}_2$ gas, which is very expensive.

^{18}O Isotope Exchange Process Flow

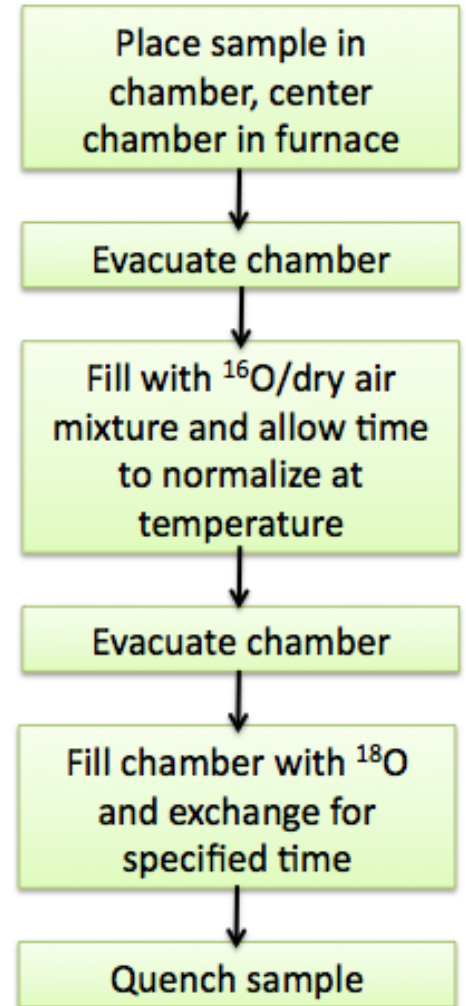


Figure 25: Process flow for ^{18}O isotope exchange experiment. This process is used for all exchanges with the only variables being operation temperature and exchange time.

Once the samples were loaded, the chamber was placed into the tube furnace, centering the samples in the heated zone. The chamber was then evacuated using the vacuum pump. Once evacuated, the chamber was filled with a mixture of standard, non-isotopically enriched O₂ gas and dry air. The mixture was such that it matched the oxygen partial pressure in the ¹⁸O cylinder. The ¹⁸O cylinder used was 57% ¹⁸O₂ gas and 43% dry air. This initial step was performed in order to ensuring that the diffusion and surface exchange were not driven by a chemical driving force. To do this, the material had to be equilibrated first in an atmosphere with the same partial pressure of oxygen as in the exchange atmosphere. The material was allowed to chemically stabilize in this atmosphere for, at a minimum, an amount of time equal to the exchange time to be used. The furnace was then heated to the desired operation temperature. Despite the volume expansion of the gases, the chamber was kept at atmospheric pressure during heating by the burst valve. After the furnace had heated and the stabilization time had concluded, the chamber was re-evacuated with the vacuum pump and quickly filled with the ¹⁸O₂ gas mixture. As soon as the chamber reached atmospheric pressure, a stopwatch was started to measure the exchange time. At the end of the desired exchange time (60 seconds, 75 seconds, 10 minutes, and 60 minutes) the chamber was quickly pulled from the furnace and the samples were removed.

The samples were quenched by quickly removing the chamber from the furnace, removing the samples from the chamber, and then blowing room temperature dry air on them. The samples reached room temperature in less than a minute. Even

with the quench, there was likely a small time period where the sample was exposed to air and hot enough to re-exchange oxygen with the atmosphere. At room temperature, the oxygen mobility in the material is negligible and therefore the diffusion profile is locked in the material over very long time scales. Still, the samples were analyzed by secondary ion mass spectrometry (SIMS) within a few days of the exchange.

2.6 Secondary Ion Mass Spectrometry Analysis

Secondary ion mass spectrometry (SIMS), figure 26, is commonly used to measure diffusion profiles in isotope exchange depth profiling (IEDP) experiments. The measurement involves using an ion beam to sputter away the surface of a material of interest and then an ion beam to analyze the material within that sputtered area. This is done by rastering a larger area than will be analyzed. In some cases the primary ion beam can be used for both sputtering and the analysis of material and in other cases a different beam is used to sputter an area to a depth and then the primary ion beam is used to collect a spectra of ionized atoms from the material. This spectra of ionized atoms, the secondary ions, are then analyzed by mass spectrometry. SIMS does not give absolute values for atomic concentration in a material, as the signal depends on the probability of an element's removal from the surface by sputtering and ionization to a specific charge state. These processes all depend on specifics of the chemistry of the analyzed material as well as the analysis parameters. On the other hand, this work focused on the relative concentration of ^{18}O to total oxygen ($^{16}\text{O} + ^{18}\text{O}$), which can be measured accurately and repeatably by SIMS.

SIMS was measured using two instruments: LaCoO₃ samples were analyzed on a CAMECA IMS-6F by Fred Stevie's group at North Carolina State University and SrCoO₃ samples were analyzed on a TOF-SIMS IV (ION-TOF, Munster Germany) by the Beebe research group at the University of Delaware. Two instruments were used due to their availability. Each material was only analyzed on one machine to make comparison easier of data gathered at temperature. The LaCoO₃ samples were rastered and the spectra was collected with a Cs⁺ primary ion beam. The raster was done with the primary ion beam at 8 nA over an area of 220 μm x 200 μm and the spectra collection was a 60 μm diameter area in the center of the raster. The SrCoO₃ samples were sputtered by a 5 keV Cs ion beam rastered over an area of 300 μm by 300 μm with a beam current of 5 nA. Spectra were collected using a 25 keV monoisotopic ⁶⁹Ga primary ion beam rastered over an area of 150 μm x 150 μm with a beam current of 1 pA.

The oxygen isotopic ratio $^{18}\text{O} / (^{16}\text{O} + ^{18}\text{O})$ as a function of depth into the film was fitted to the known solution to the diffusion equation using routines written in Mathematica (version 8, Wolfram Software). This routine, Appendix B, is discussed in detail in the results section. SIMS depth analysis is determined initially as a function of time that the sample is within the primary ion beam. Absolute depth values through the thickness were calculated from this by noting when the SIMS ion beam had penetrated through the entire film to the substrate. This point was clear from the SIMS signal because of a sharp decrease in oxygen ions, both ¹⁶O and ¹⁸O, being detected. The depth of this point was known from the thickness of the deposited film. The

amount of material sputtered away by the SIMS ion beam was assumed to be constant with time so that an absolute depth vs. oxygen isotopic ratio could be derived from the SIMS signal.

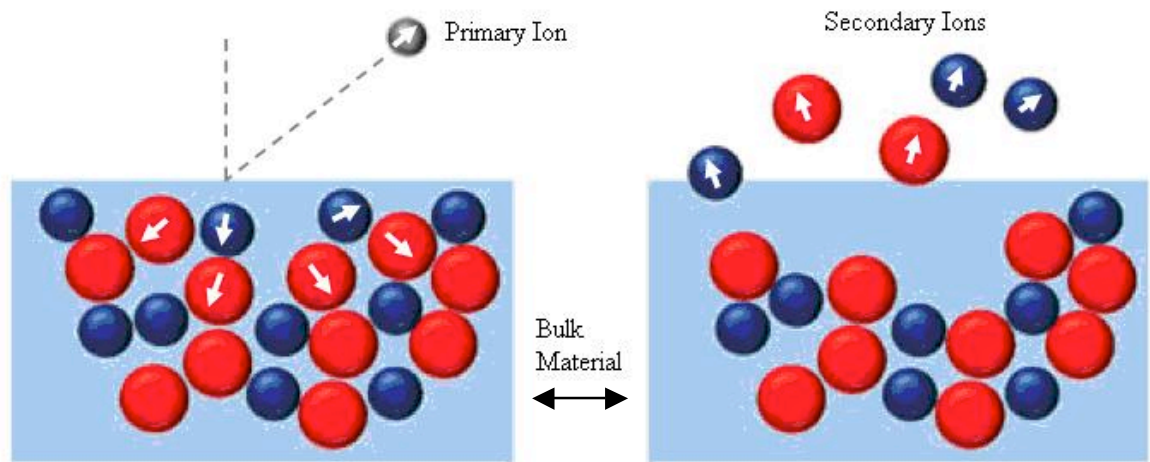


Figure 26: SIMS showing primary ion bombarding the bulk material and atoms of the material, the secondary ions, being released. Adapted from [22]

Chapter 3

RESULTS

This chapter will examine the surface exchange-limited and diffusion-limited regimes of both the semi-infinite and plane diffusion models. The experimental requirements to reliably measure surface exchange coefficients will specifically be shown. In addition, robust experimental determination of surface exchange coefficients using thin films fabricated in this work will be presented.

3.1 Modeling of Isotope Diffusion in Thin Films

The semi-infinite model is investigated first. To define what surface exchange coefficients are measurable using this model, the space of measurable bulk diffusion values and exchange times must be found based on the semi-infinite boundary conditions. Then within this defined space, surface exchange coefficients can be determined, giving the entire range of measurable surface exchange coefficients. To visualize this space, a plot is created with bulk diffusion on the x-axis and exchange time on the y-axis, figure 27. The outer boundaries of the space form a parallelogram shape; they arise from the experimental limitations defined in Chapter 1. The bottom and top bounds of the parallelogram are defined by the minimum and maximum reasonable exchange times, respectively. The boundaries on the left and right sides of the space are defined by the semi-infinite boundary condition that requires the isotope

concentration to reach near background levels before it reaches the substrate. This boundary condition was met by requiring the film thickness to be 4 times the diffusion length. This means that a thinner film requires a smaller bulk diffusion coefficient. Therefore the left bound of the space is defined by the smallest measurable bulk diffusion coefficients measurable on the thinnest film, 10 nm, and the right boundary of the space is the largest bulk diffusion coefficients measurable on the thickest film, 10 μm . With the measurable space defined by the boundary conditions of the model, the measurable surface exchange coefficients within this space can be found.

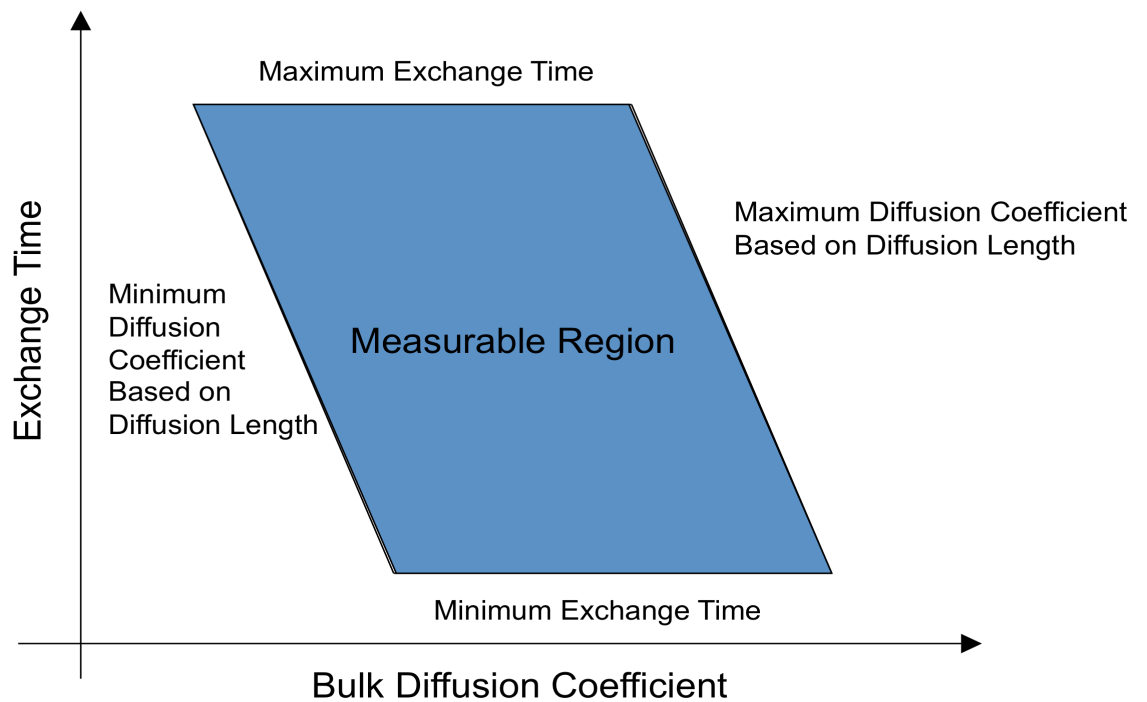


Figure 27: The measurable region of bulk diffusion coefficients and exchange times for the semi-infinite model.

Contours of surface exchange coefficient were plotted over the measureable bulk diffusion coefficient and exchange time region. These contour plots were created using a software routine programmed in Mathematica (version 8, Wolfram). The software routine is given in Appendix B. The routine evaluates the semi-infinite diffusion model for the surface exchange coefficient at each point in an array corresponding to all combinations of a range of bulk diffusion coefficients and exchange times within the measurable region. To create the array, the minimum and maximum bulk diffusion coefficients were found for the exchange times of 60 seconds, 1 hour, 1 day, 1 week, 1 month and 3 months. These points correspond to points on the left and right boundaries of the measurable region. These points were found by using the diffusion length boundary condition of the semi-infinite model and evaluating for the minimum and maximum film thickness. For each exchange time, points of evaluation in-between the minimum and maximum bulk diffusion coefficients are added with three points for each order of magnitude of diffusion coefficient. Along with this array of bulk diffusion coefficient and exchange time, the concentration of ^{18}O /total oxygen at the surface is required to solve the semi-infinite diffusion model for the surface exchange coefficient. Two contour plots were created, one using the minimum measureable surface concentration and one using the maximum surface concentration, 0.44% - 90% ^{18}O /total oxygen. The plots correspond to the minimum and maximum measurable surface exchange coefficients.

The contour plots of the maximum and minimum measurable surface exchange coefficients are given in figures 28 and 29. The surface exchange values that are

measurable using the semi-infinite model are shown as contours inside the parallelogram. For each combination of bulk diffusion coefficient and exchange time, the minimum and maximum measurable surface exchange coefficients for a given diffusivity and time are proportional to each other, $k_{\max} \approx 2800 * k_{\min}$. That means that for a given bulk diffusion constant and exchange time, the range of surface exchange coefficients that are measurable is over three orders of magnitude. This holds true over the entire experimental region. The contours are only shown in the region where the boundary conditions of the semi-infinite model are met. Outside this region, the model is no longer valid.

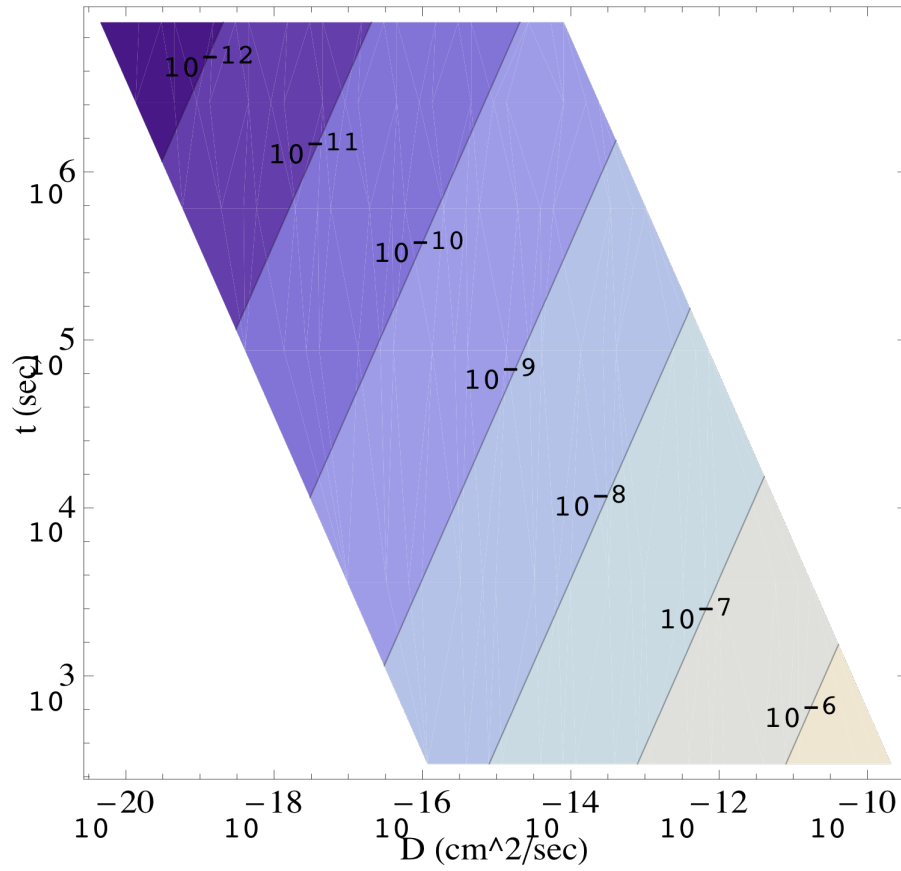


Figure 28: Contour plot of the maximum measurable surface exchange coefficient for a given diffusivity, D , and isotopic exchange time, t . The boundary conditions for the semi-infinite diffusion model are assumed and required for validity. These surface exchange values are the maximum because they correspond to the maximum measureable surface concentration of 90%.

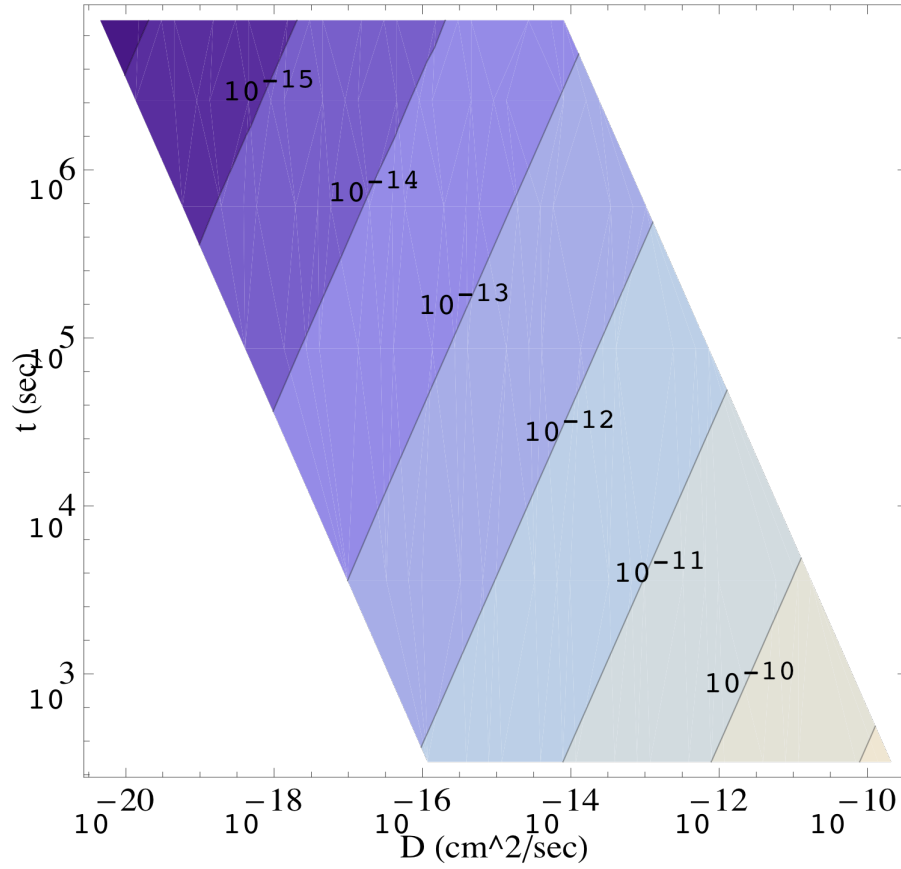


Figure 29: Contour plot of the minimum measurable surface exchange coefficient for a given diffusivity, D , and isotopic exchange time, t . The boundary conditions for the semi-infinite diffusion model are assumed and required for validity. These surface exchange values are the minimum because they correspond to the maximum measureable surface concentration of 0.44%.

The contour plots show clearly that the semi-infinite model is a valid model for measuring the surface exchange coefficients over a significant region of bulk diffusion and exchange times. However, over the entire range of accessible

experimental conditions for thin films considered here, including film thicknesses ranging between 10 nm and 10 μm , only materials with diffusion coefficients of $1.04 \cdot 10^{-9} \text{ cm}^2/\text{sec}$ or smaller have measureable surface exchange coefficients. Even using the thickest film (10 μm) and the shortest diffusion time (60 s), materials with faster diffusion coefficients will have significantly exceeded the background concentration of the isotope at the film-substrate interface, thus invalidating the boundary condition for this solution to the diffusion equation. This measurement limitation is a significant restriction on the use of the semi-infinite model with thin films, because the majority of the mixed ionic electric conductors of interest have bulk diffusion coefficients faster than the measurable range of this model. For this reason, the semi-infinite model will often be unsatisfactory as a means of modeling isotope exchange experiments using thin films.

The plane diffusion model is more appropriate for typical thin films of interest, because it does not suffer from the diffusion length concerns. As shown in figure 14, the plane diffusion model can solve for surface exchange coefficients with a wide range of bulk diffusion coefficients even, theoretically, infinite bulk diffusion. A plot of the measurable region of bulk diffusion and exchange times is shown in figure 30. As can be seen on this plot, there is no boundary on the D axis; the measurement of surface exchange coefficient is valid even as the bulk diffusion coefficient goes to infinity. The top and bottom of the measurable region are bounded by the maximum and minimum exchange times as in the semi-infinite diffusion model. The boundary on the left side of the measurable region is defined the transition between a surface

exchange limited system and a bulk diffusion limited system. As the boundary is approached the values of the surface exchange coefficient become indistinguishable from each other. This thesis is concerned with surface exchange limited systems and therefore the boundary is defined by the line $L=1$. This is the dimensional quantity, defined by equation 1-18, that defines if a system is surface exchange limited or bulk diffusion limited. A surface exchange limited system is required for accurate measurement of the surface exchange coefficient, so an L value of 1 or less is required. The maximum L value boundary is not as universal as the boundaries for the semi-infinite diffusion however it clearly defines the region of interest in this thesis.

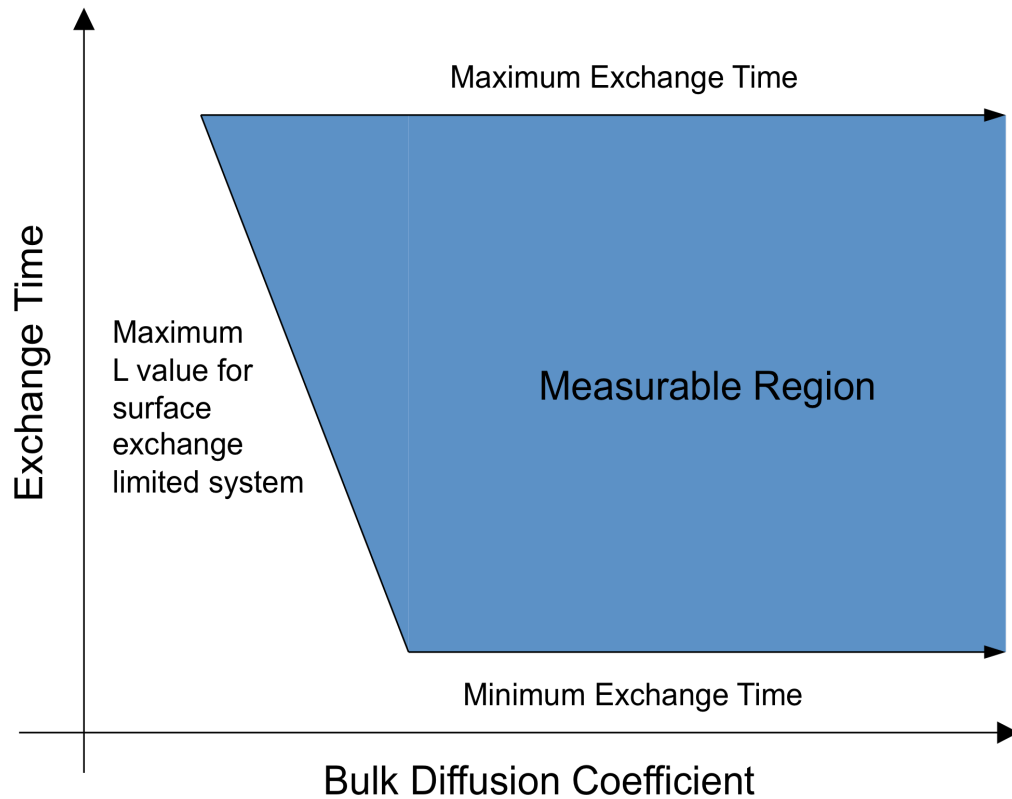


Figure 30: The measurable region for bulk diffusion coefficients and exchange times for the plane diffusion model.

Figure 31 and 32 show the minimum and maximum measurable surface exchange coefficient values for a film that is 100 nm thick. All contour plots for the plane diffusion model were made with the Mathematica routine in Appendix B. This routine differed from the semi-infinite routine in two ways. First, this solution of the diffusion equation depends on the film thickness, so each film thickness investigated was used to create a different contour plot. Second, beta values, the roots of equation

1-17, are required to evaluate this diffusion equation solution. The plane diffusion model calls for an infinite series, each with a different beta value, however in surface exchange limited systems only the first few terms of the summation are needed to provide an accurate solution. Beyond the first few terms of the series the impact of additional terms in the sum on the solution of the diffusion model is negligible, the terms in the summation rapidly go to zero. This is only true for surface exchange limited systems, bulk diffusion limited systems require many more terms in the summation to provide a significantly accurate solution. For thoroughness, six summation terms are used in the routine. These beta values are related to the ratio of the surface exchange and the bulk diffusion coefficients. Due to this interdependence of the diffusion coefficients, the surface exchange coefficient cannot be found by easily solving the model for a specified bulk diffusion and exchange time like in the solution to the semi-infinite model. Evaluating the model for combinations of bulk diffusion and surface exchange coefficients and solving for the exchange time surpasses this difficulty. Large ranges of possible bulk diffusion and surface exchange coefficients are made with three points per order of magnitude. Every combination of these coefficients is taken and the respective beta values are solved. With ranges of surface exchange coefficient, bulk diffusion coefficients and the appropriate beta value, the final inputs required are the surface concentration and the film thickness. To evaluate over the range of experimental parameters for thin films, plots are made for the minimum and maximum surface concentration values for thicknesses of 10 nm, 100 nm, 1 μm and 10 μm . The plots of the 100 nm solution are shown and all other

plots are included in the appendix. Evaluating the routine gives a list of points that are solutions to the diffusion equation. These points consist of a surface exchange coefficient, a bulk diffusion coefficient and an exchange time. While the points are valid solutions to the diffusion equation, they do not all fall within the boundary conditions. All solutions with exchange times greater than 3 months, less than 60 seconds, or L values greater than 1 are removed from the list of solutions and contours are created from the measurable subset.

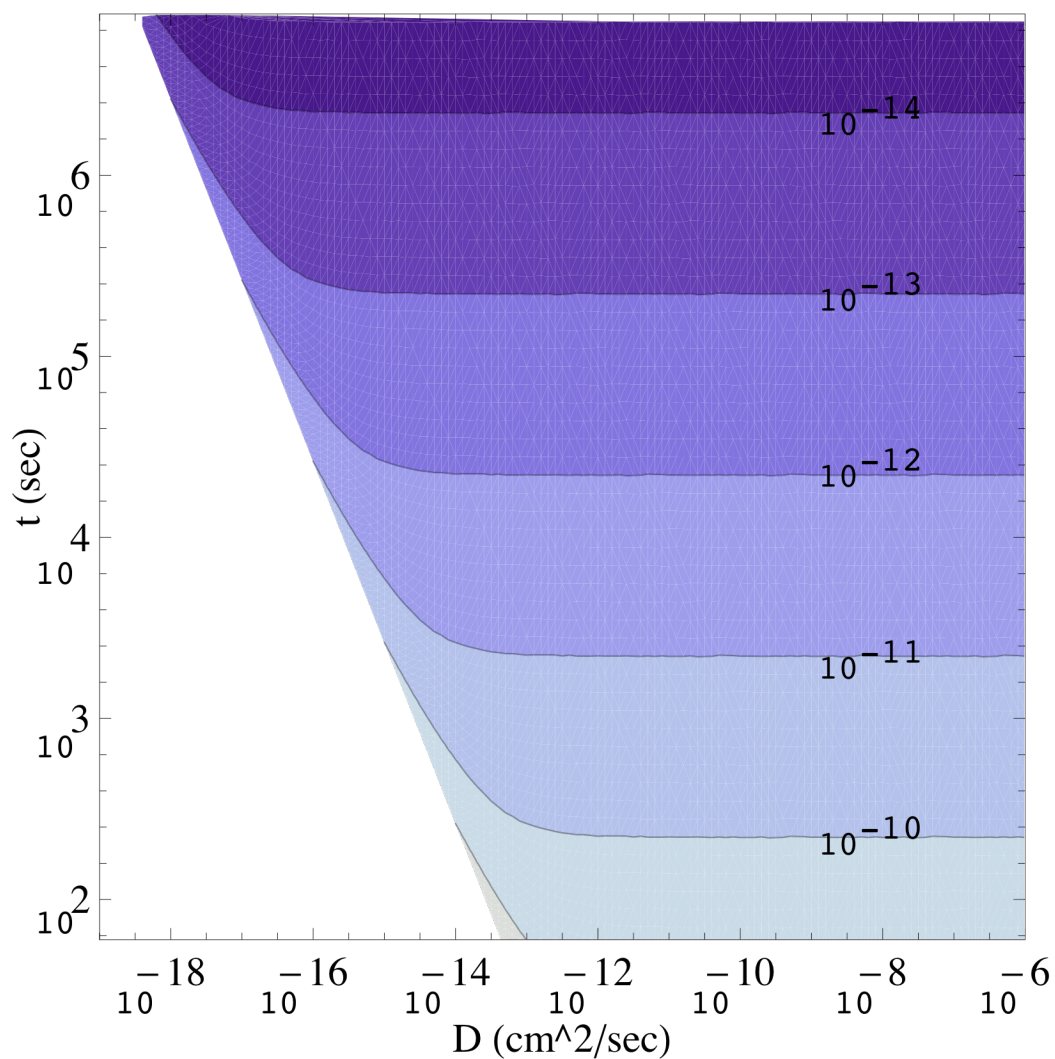


Figure 31: Contour plot of the minimum measurable surface exchange coefficient for a given diffusivity, D , and isotopic exchange time, t , using a 100 nm thick film. The boundary conditions for the plane diffusion model are assumed and required for validity.

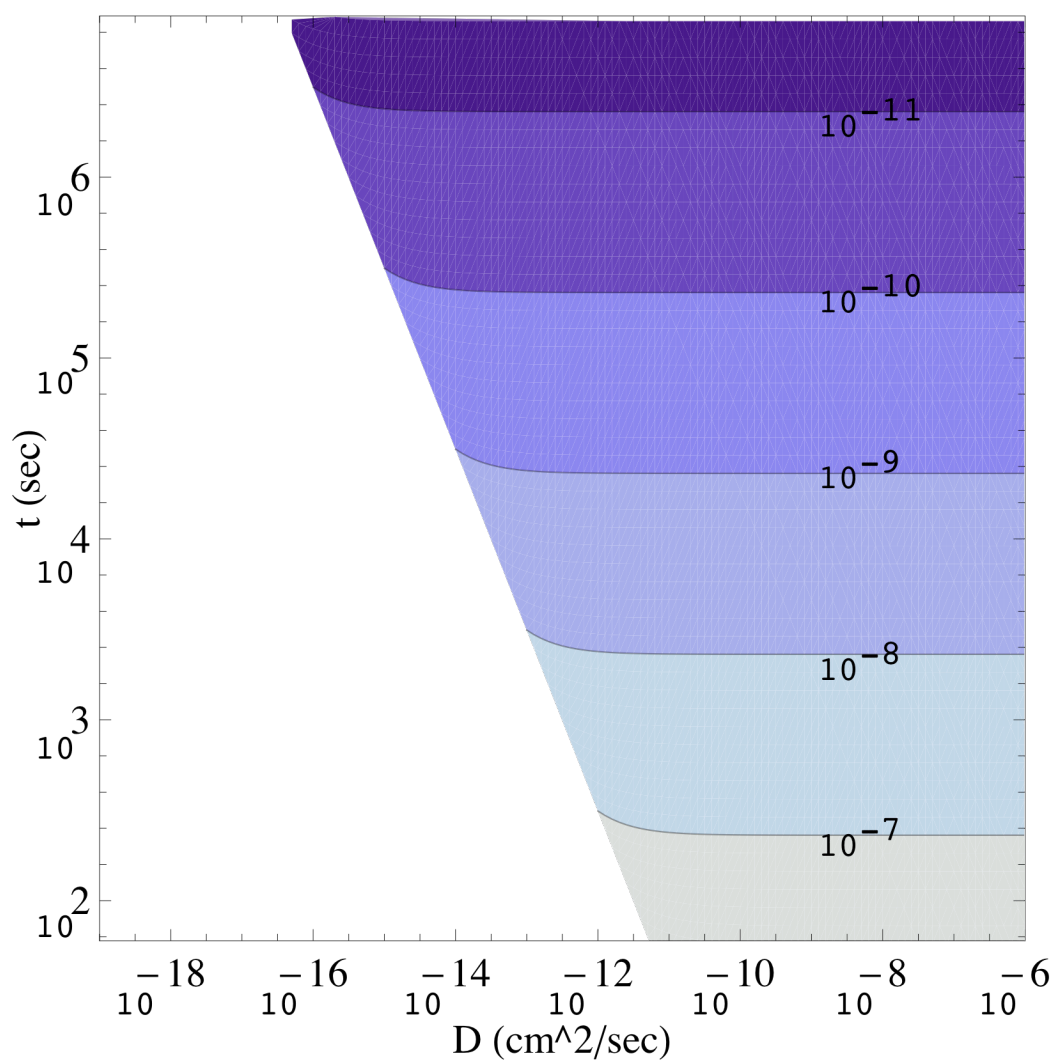


Figure 32: Contour plot of the maximum measurable surface exchange coefficients for a given diffusivity, D , and isotopic exchange time, t , using a 100 nm thick film. The boundary conditions for the semi-infinite diffusion model are assumed and required for validity.

This plot can be very useful for choosing the correct test conditions to measure the surface exchange coefficient for a material with a known bulk diffusion coefficient. For example, the 100 nm film contour plots above show combinations of bulk diffusion coefficients and exchange times that give the minimum and maximum measurable surface exchange coefficient for that combination of test parameters. If one had a material that had a known bulk diffusion coefficient of $10^{-10} \text{ cm}^2/\text{sec}$ and an expected surface exchange coefficient also around 10^{-10} cm/sec then by using the contour plots above it would be clear to use an exchange time of 10^4 seconds. This amount of exchange time will give a range of measurable surface exchange coefficients $\sim 5 \cdot 10^{-9} \sim 5 \cdot 10^{-12}$. This would put the expected value well within the range of measurable surface exchange coefficients for the test parameters. If the exchange causes the sample to be saturated with isotope, then a faster exchange time can be picked to measure surface exchange coefficients larger than $5 \cdot 10^{-9}$. The same holds true if the isotope concentration in the sample is below the measurable amount – in this case, a longer exchange time can be chosen to measure a range of surface exchange coefficients smaller than $5 \cdot 10^{-11}$.

To better investigate surface exchange limited systems and why an L value of 1 is the differentiating factor between diffusion and surface exchange limited systems, this data was re-plotted such that the y-axis is the surface exchange coefficient and the contours indicate the minimum and maximum exchange times. Unlike the plots above, where data is excluded for L values greater than 1, all solutions to the diffusion

equation where $L < 100$ are plotted. This is done because as L increases above 100, the model requires significantly more terms in the infinite sum to produce an accurate solution. By plotting only where $L < 100$, the diffusion limited region can be seen without having to increase the number of terms in the infinite sum to an unreasonable number. While the remainder of the diffusion limited region is not shown in the plots, it is clear that the contour lines are approaching vertical and will continue so as the surface exchange coefficient goes to infinity. These plots, which are again for a 100 nm thick film, are shown in figures 33 and 34.

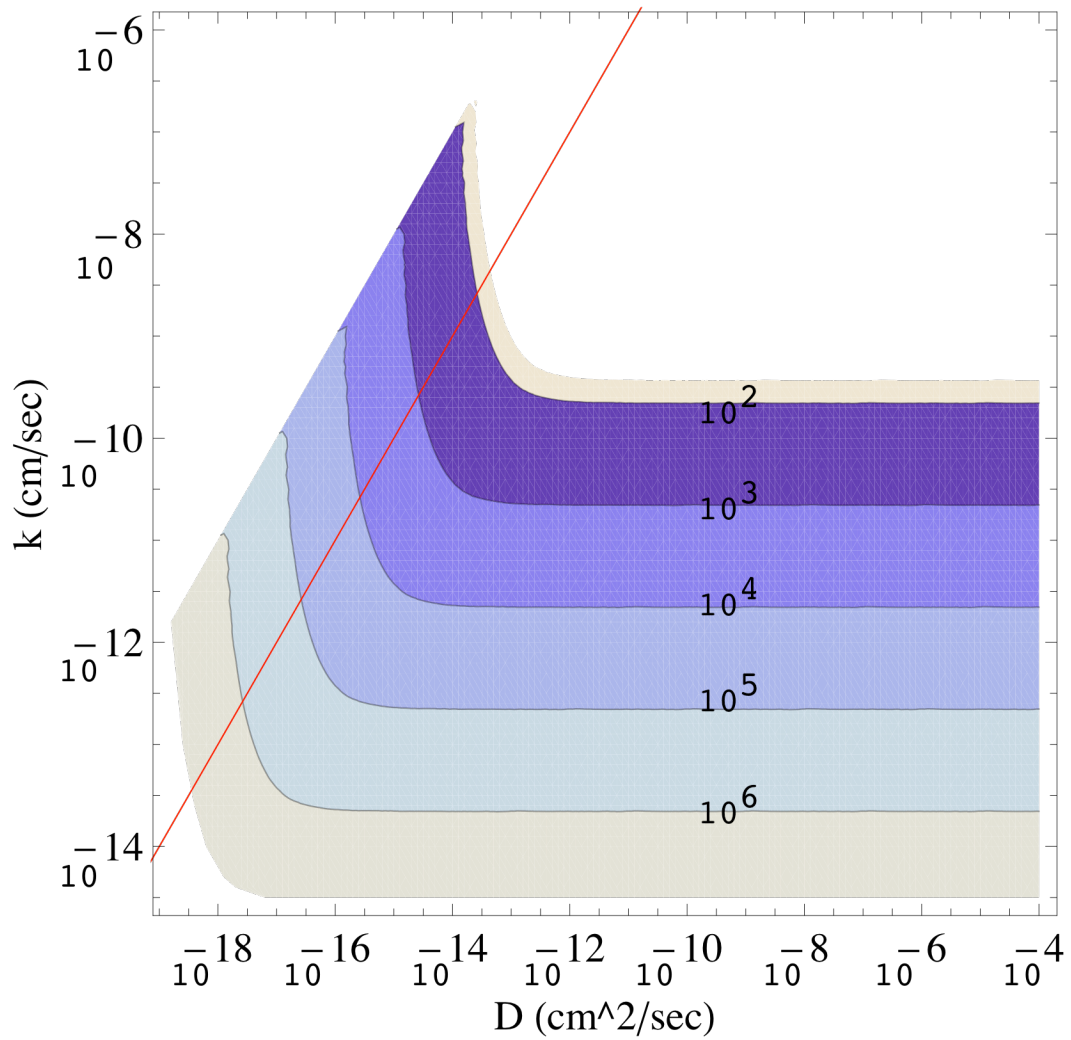


Figure 33: Contour plot of the minimum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 100 nm thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

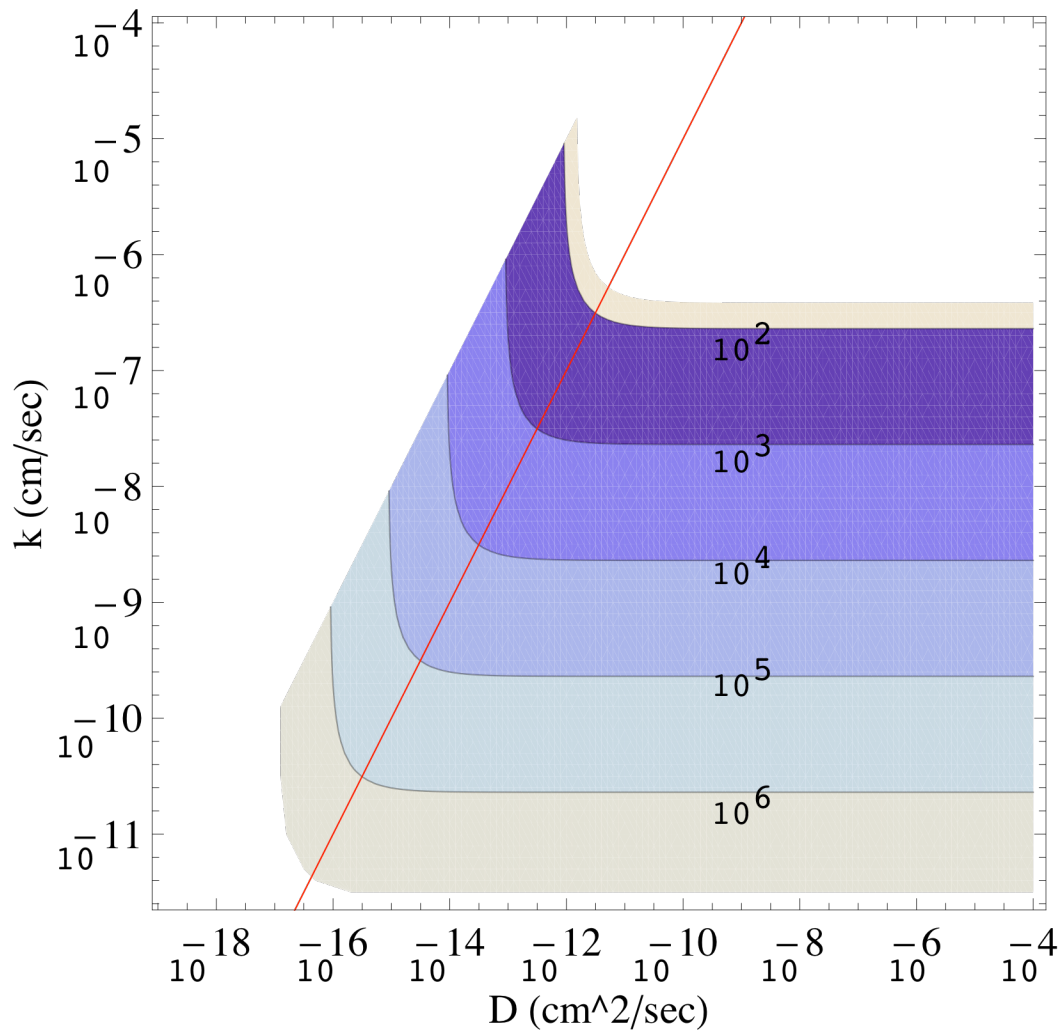


Figure 34: Contour plot of the maximum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 100 nm thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

The contour plots show two distinct regions: a vertical region and a horizontal region. In the vertical region, the solution to the diffusion equation is largely independent of the surface exchange coefficient. The measured concentration profile is thus governed predominantly by the diffusion coefficient and exchange time. A solution of the diffusion profile with values taken from this region would correspond to a diffusion profile that is completely saturated with ^{18}O at the surface after the specified diffusion time. Such a diffusion profile is shown in figure 35. The surface exchange coefficient would be extremely difficult to measure in such cases, because it is nearly indistinguishable from infinite. At best, a lower bound could be placed on the surface exchange coefficient in these cases. This region can be described as diffusion-limited, because the bulk diffusion coefficient and exchange time are the two key variables for describing the concentration depth profile. Since the goal of this work is to measure surface exchange coefficients, this is an undesirable situation and experiments will be designed to avoid this region.

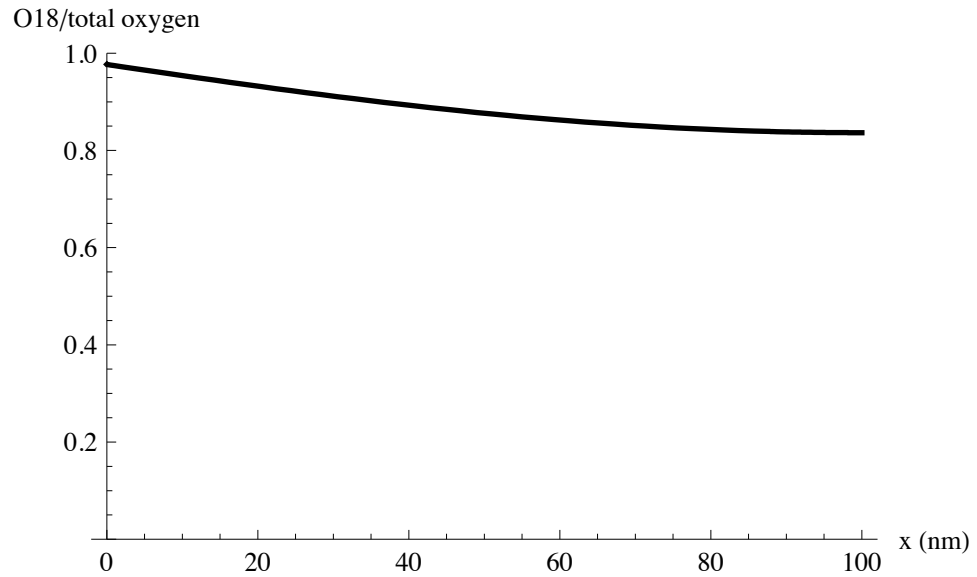


Figure 35: Diffusion profile of a 100 nm film that is saturated with isotope at the surface ($x=0$ nm) making it impossible to determine the surface exchange coefficient. This diffusion profile was created with $k=10^{-9}$ cm/sec, $D=10^{-15}$ cm²/sec, and $t=10^5$ sec; these correspond to the black dot in figure 37. This diffusion profile has an L value of 10.

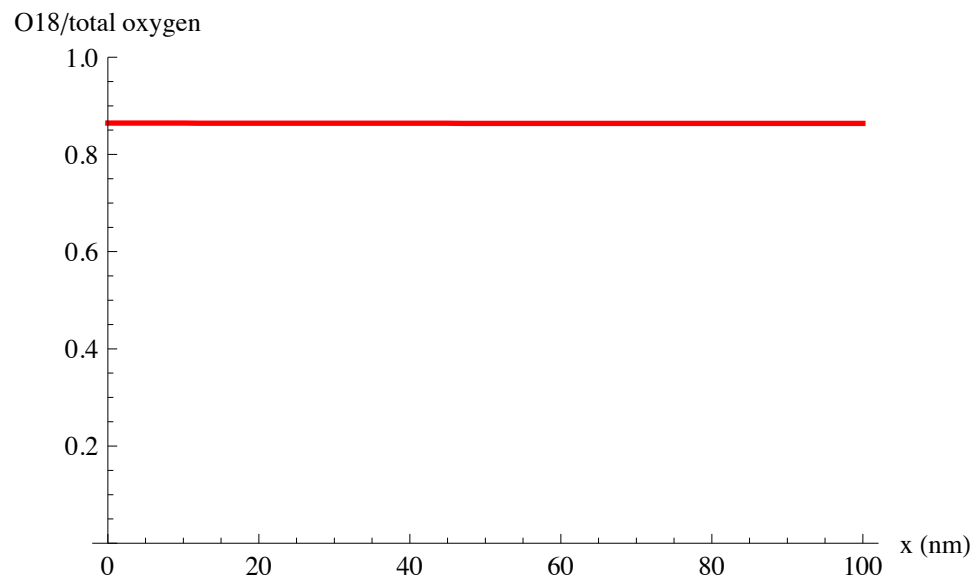


Figure 36: Diffusion profile of a 100 nm film that is not saturated at the surface ($x=0$ nm) meaning the surface exchange coefficient is measurable. This diffusion profile corresponds to the blue dot in figure 37. This diffusion profile has an L value of $1/50$.

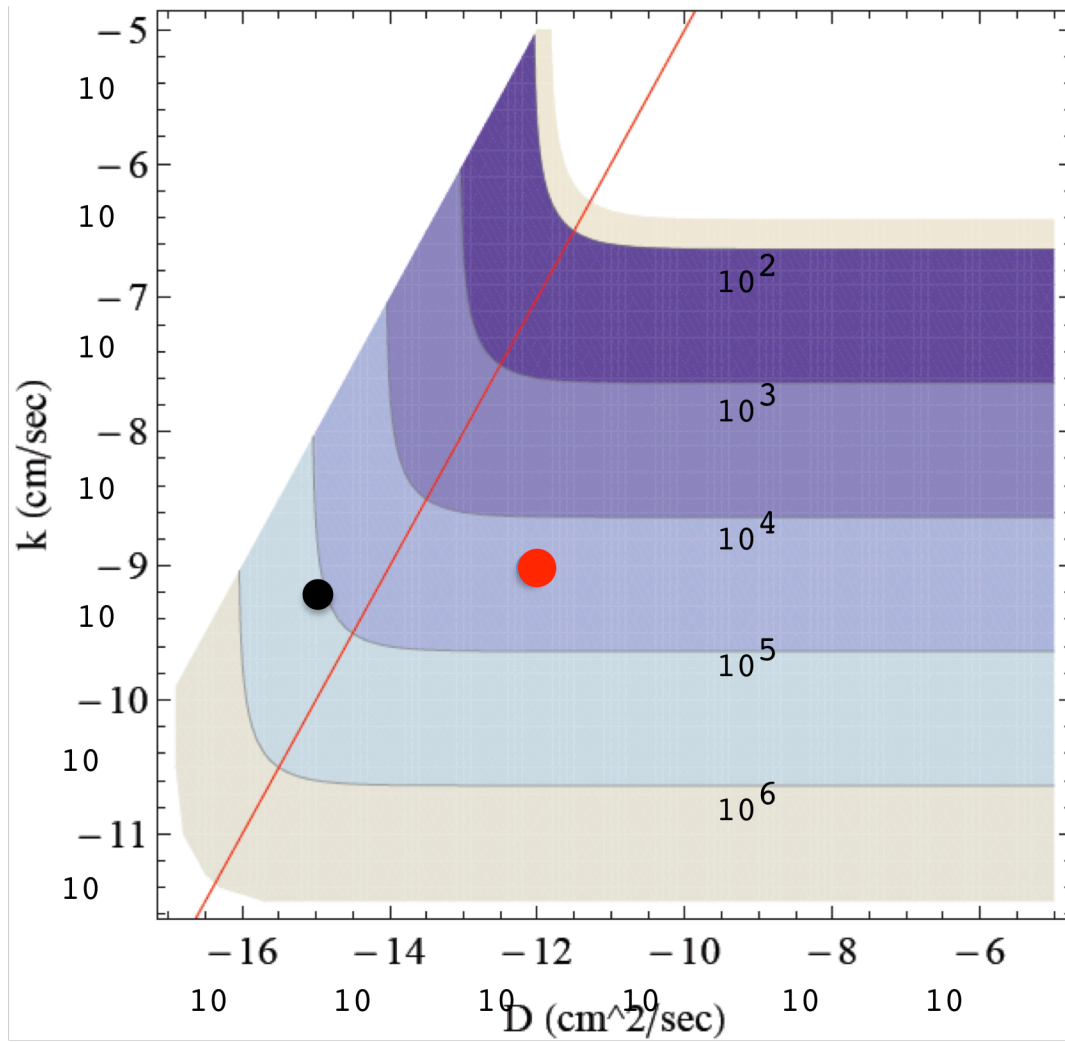


Figure 37: Plane diffusion contour plot for the maximum measurable surface exchange coefficients. The black dot indicates the diffusion profile in figure 35 and the red dot indicates the location of the diffusion profile in figure 36. The red dot is in the surface exchange limited region and has a measurable surface exchange coefficient while the black dot is in the bulk diffusion limited region and the diffusion profile is saturated at the surface. The surface exchange coefficient is thus indeterminable.

The horizontal region is the surface exchange limited region. This region is largely independent of bulk diffusion coefficient such that the solution of the diffusion equation is determined almost exclusively by the surface exchange coefficient and the exchange time. A diffusion profile that is independent of the bulk diffusion coefficient has an isotopic concentration that is homogeneous throughout the film. Such a diffusion profile is shown in figure 36 (the values used are depicted as a red dot in figure 37). The bulk diffusion coefficient is large enough that an insignificant concentration gradient is created. The surface exchange limited region will provide the most accurate measurement of the surface exchange coefficient, albeit with limited ability to measure the diffusivity. The experiments described in this thesis were intended to be within this surface exchange limited region.

The boundary between the surface exchange limited and diffusion-limited regions is given by the dimensionless parameter L , defined in equation 1-18. The red line in the contour plots in figures 33 and 34 indicate an L value of 1. L values much greater than 1 correspond to systems that are diffusion limited region, while L values much less than 1 correspond to systems that are surface exchange limited. When L is close to 1, the system is co-limited and a robust measurement of both the surface exchange coefficient and diffusivity may be possible. While the bulk diffusion coefficient and surface exchange coefficient are essentially invariable for a given material, the film thickness, l , can be experimentally tailored to provide a system that is surface exchange limited, diffusion limited, or co-limited, as desired. While co-limited systems offer the greatest power in terms of being able to measure both

coefficients in one isotope exchange, the focus of this work is to robustly measure the surface exchange coefficient.

Thin film isotope exchange depth profiling has great ability to measure surface exchange coefficients in a surface exchange limited region. Using the experimental parameters discussed in Chapter 1, film thickness between 10 nm and 10 μm and exchange times between 60 seconds and 3 months, this method has the ability to measure surface exchange coefficients from $5 \cdot 10^{-16}$ cm/sec to $5.5 \cdot 10^{-5}$ cm/sec assuming the material has the appropriately fast bulk diffusion coefficient to produce a surface exchange limited system. This is a very large range of measurable values for one test method. This range is large enough to cover all of the most researched MIEC materials that have a known surface exchange coefficient.

3.2 Experimental Results

3.2.1 Thin Film Characterization

X-ray diffraction patterns of the sintered targets are given in figure 38. The peak positions are indicative of the cubic perovskite lattice structure. In general, the diffraction patterns indicate that the predominant phase of the targets is the perovskite structure. At a number of expected peak locations, two peaks are found in close proximity. The most likely cause of this is that the perovskite structure is not in an ideal cubic form, but rather is tetragonal or orthorhombic. These structures are two common non-cubic variants that are little more than slight distortions of the lattice. In

this work, the variant of perovskite is not a concern so the peak splitting is not investigated further.

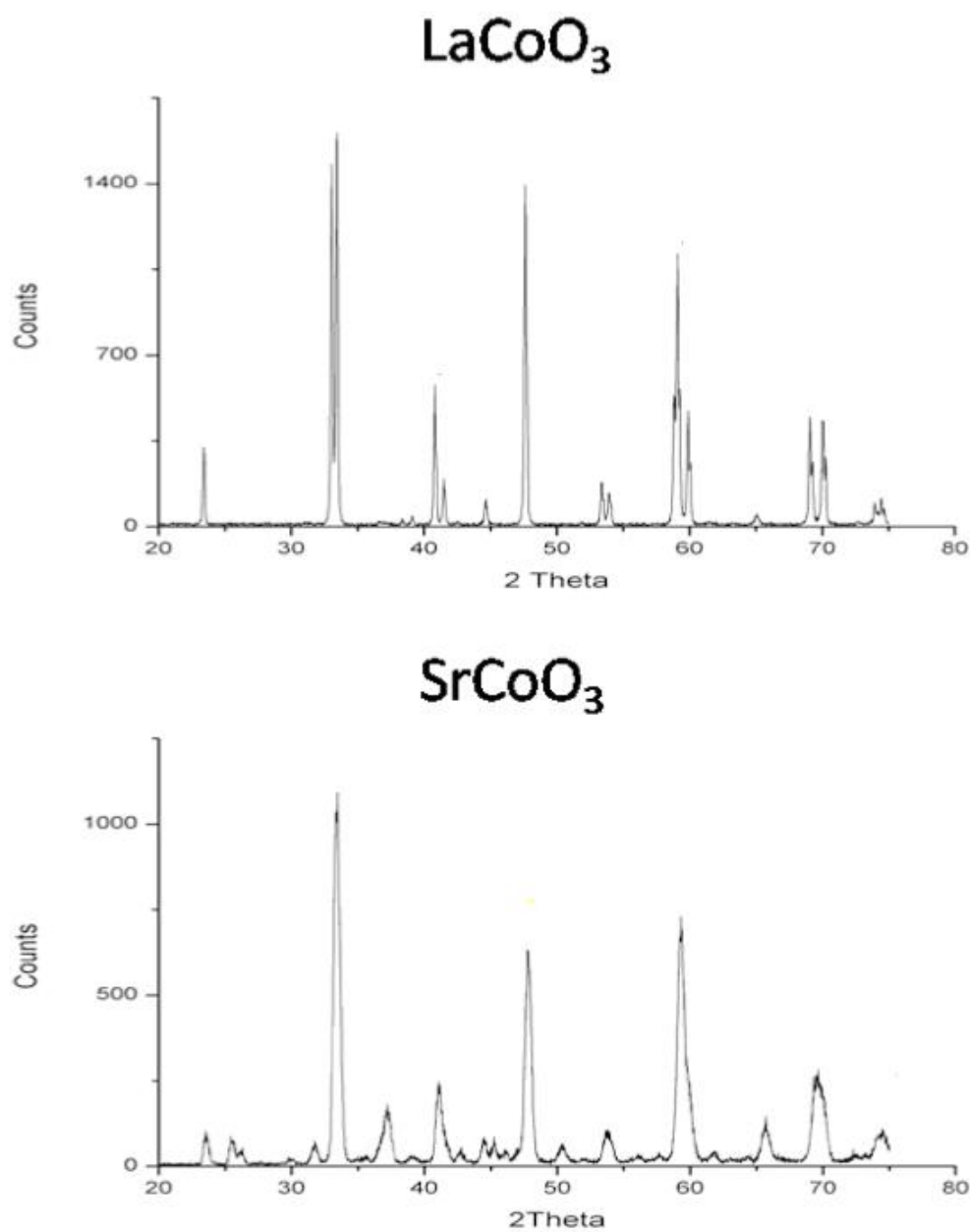


Figure 38: X-ray diffraction patterns of powder samples of LaCoO_3 and SrCoO_3 used in the manufacture of sputtering targets. The major peaks correspond to a perovskite crystal structure. [48] [43]

Deposition rates from the sputtering targets at 25 W and 50 W are given in figure 39. These rates are extremely slow; under all conditions they are less than 10 nm/hour. For this reason, thin films of 100 nm were chosen to provide a reasonably thick film without taking an excessive amount of time to fabricate. This thickness was shown to be sufficient for measuring the isotope exchange within LaCoO_3 and SrCoO_3 while maintaining a surface exchange limited system. While process parameters were chosen to produce 100 nm thick films the large standard deviation in deposition rate produced films that were not exactly 100 nm thick. The LaCoO_3 samples were 86 nm and 83 nm thick for the 400 °C and 500 °C samples respectively and the SrCoO_3 samples were 102 nm and 140 nm thick for the 400 °C and 500 °C samples respectively. The thickness of the SrCoO_3 samples are different thicknesses because they were created during two different depositions. The thickness of the samples did not inhibit the measurability of the surface exchange coefficients. Each sample provided a system that was able to accurately measure the surface exchange coefficient of the material. The thickness of each sample was taken into account when fitting the diffusion data and calculating the L value of the system. If precise thickness of samples was desired steps could be taken to provide a more accurate deposition rate such as increasing the deposition time in the deposition rate experiments or etching of samples to the desired thickness.

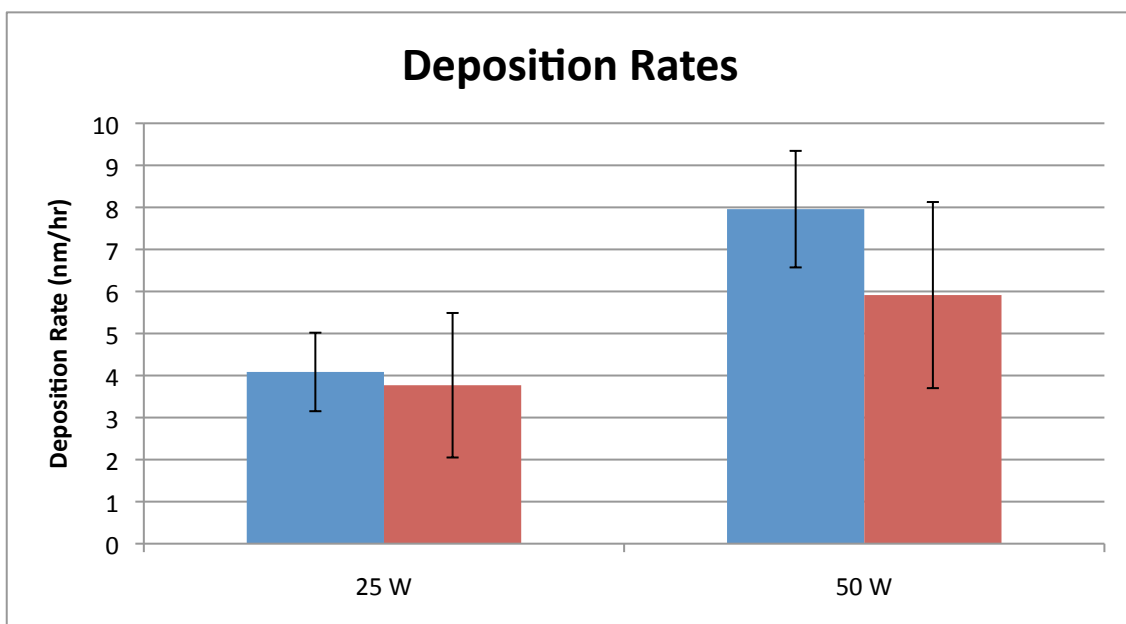


Figure 39: Deposition rates of LaCoO₃, blue, and SrCoO₃, red, at 25 W and 50 W applied power. The error bars represent one standard deviation based on three measurements of a single sample.

It is critical for this experimentation that the thin films are fully dense, since open porosity allows diffusion of the isotopically enriched gas by convection and not, as desired, purely by solid state diffusion. Surface micrographs, figures 40 and 41, were taken of the deposited thin films with a JSM-7400F high-resolution scanning electron microscope. Samples were not coated prior to imaging. For this reason, some charging of the sample occurred, visible as darker regions within the image. This charging of the surface is not permanent, and did not affect any other measurements or

usage of the samples. The micrographs of freshly deposited samples show smooth surface with small grain size, < 70 nm. No cracks or pores were found in the samples, ensuring that the isotopic concentration depth profiles represent solid state diffusion within the films.

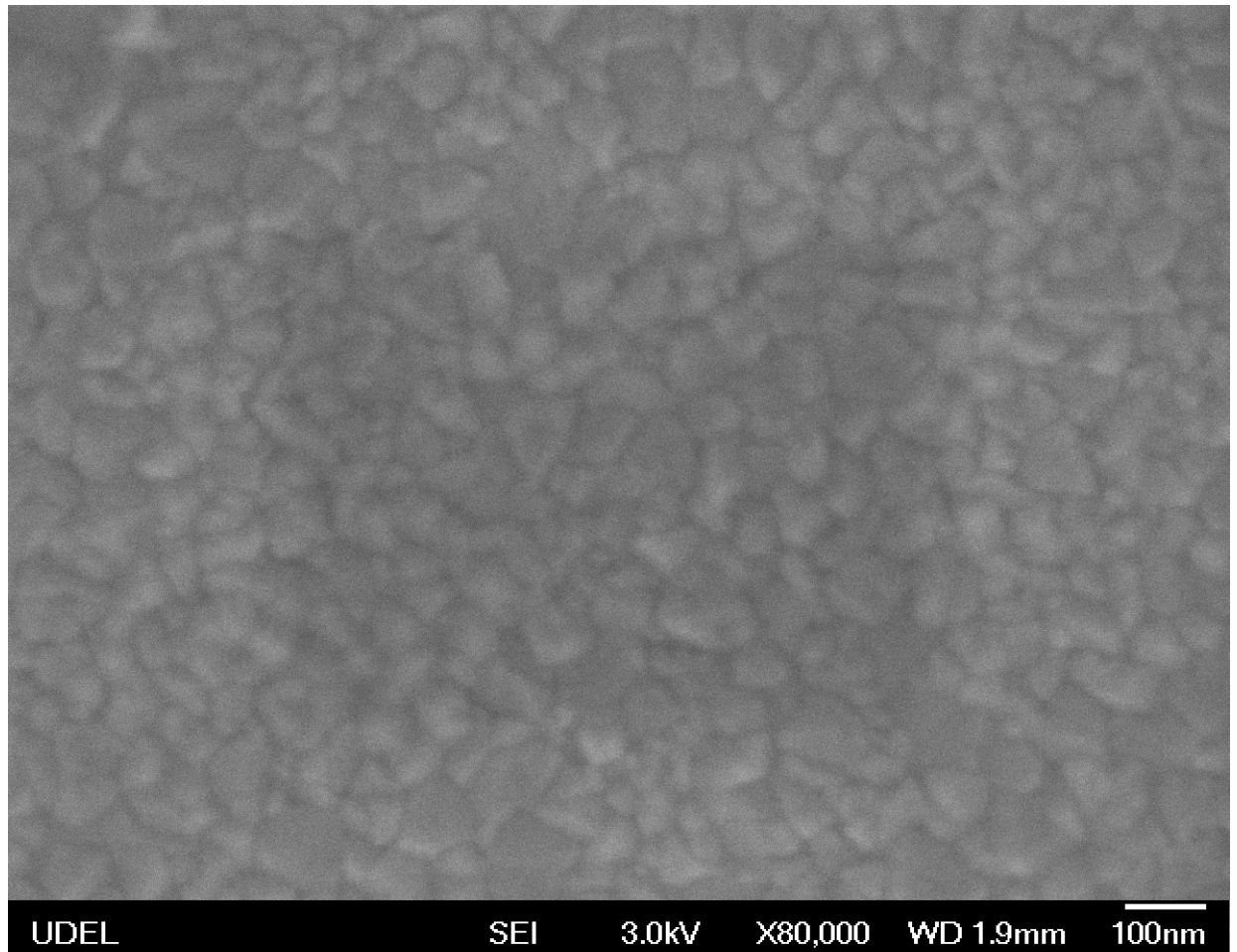


Figure 40: Scanning electron micrograph of a LaCoO₃ film, as deposited on an MgO substrate. The features are believed to be grains, approximately 70 nm in diameter. (The darker region in the center is due to sample charging from the electron beam during imaging)

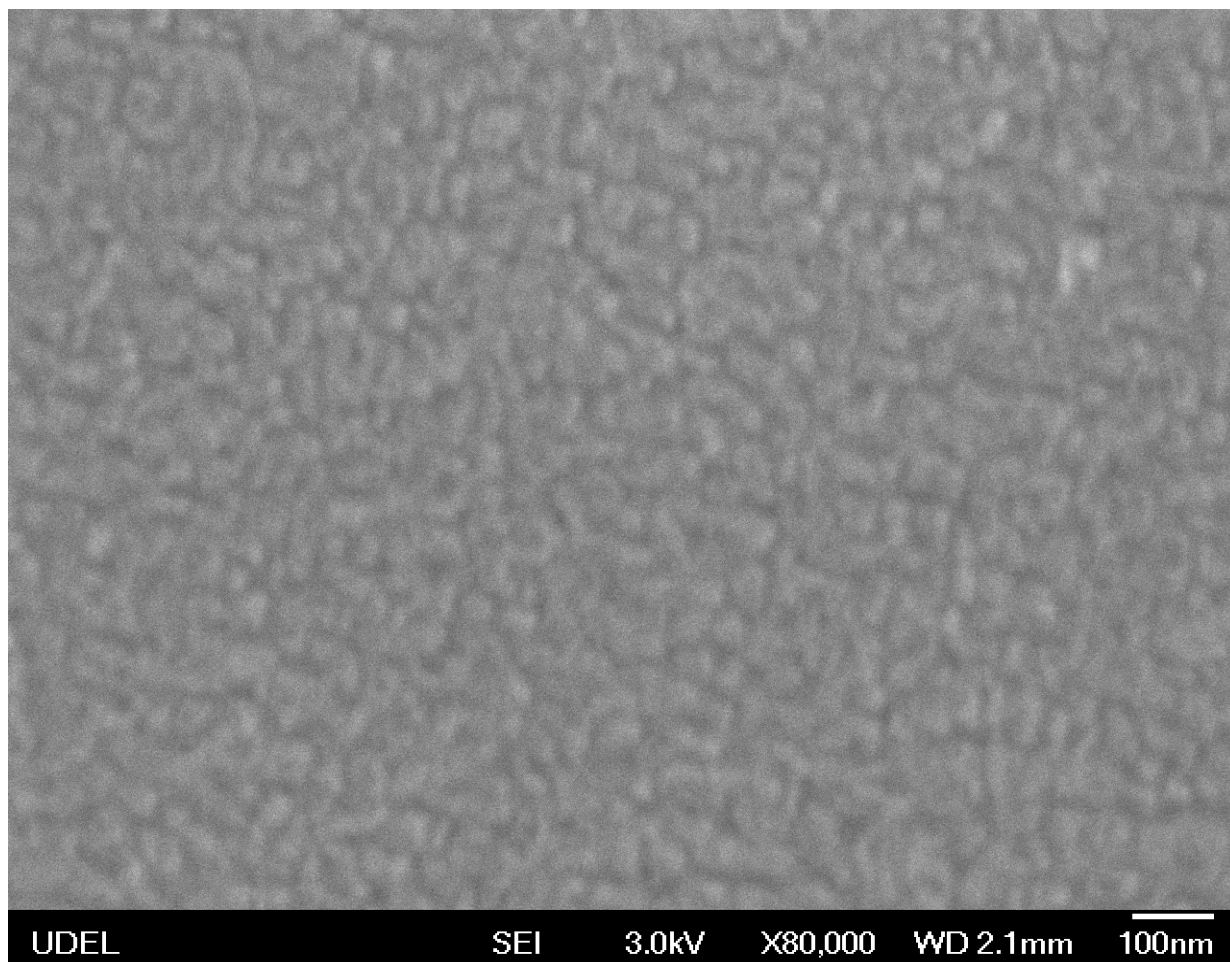


Figure 41: Scanning electron micrograph of a SrCoO₃ film, as deposited on an MgO substrate. The features are believed to be grains, approximately 25 nm in diameter.

Additional micrographs were taken of the samples after heating for two hours at 500 °C and quenching rapidly to room temperature. This is representative of an isotope exchange of one hour: the sample would be at temperature for one hour to equilibrate in an isotopically unenriched oxygen environment and then one hour in

^{18}O -enriched environment for isotopic exchange. Micrographs of these samples are shown in figures 42 and 43. No major cracking was seen in the films after heating and quenching.

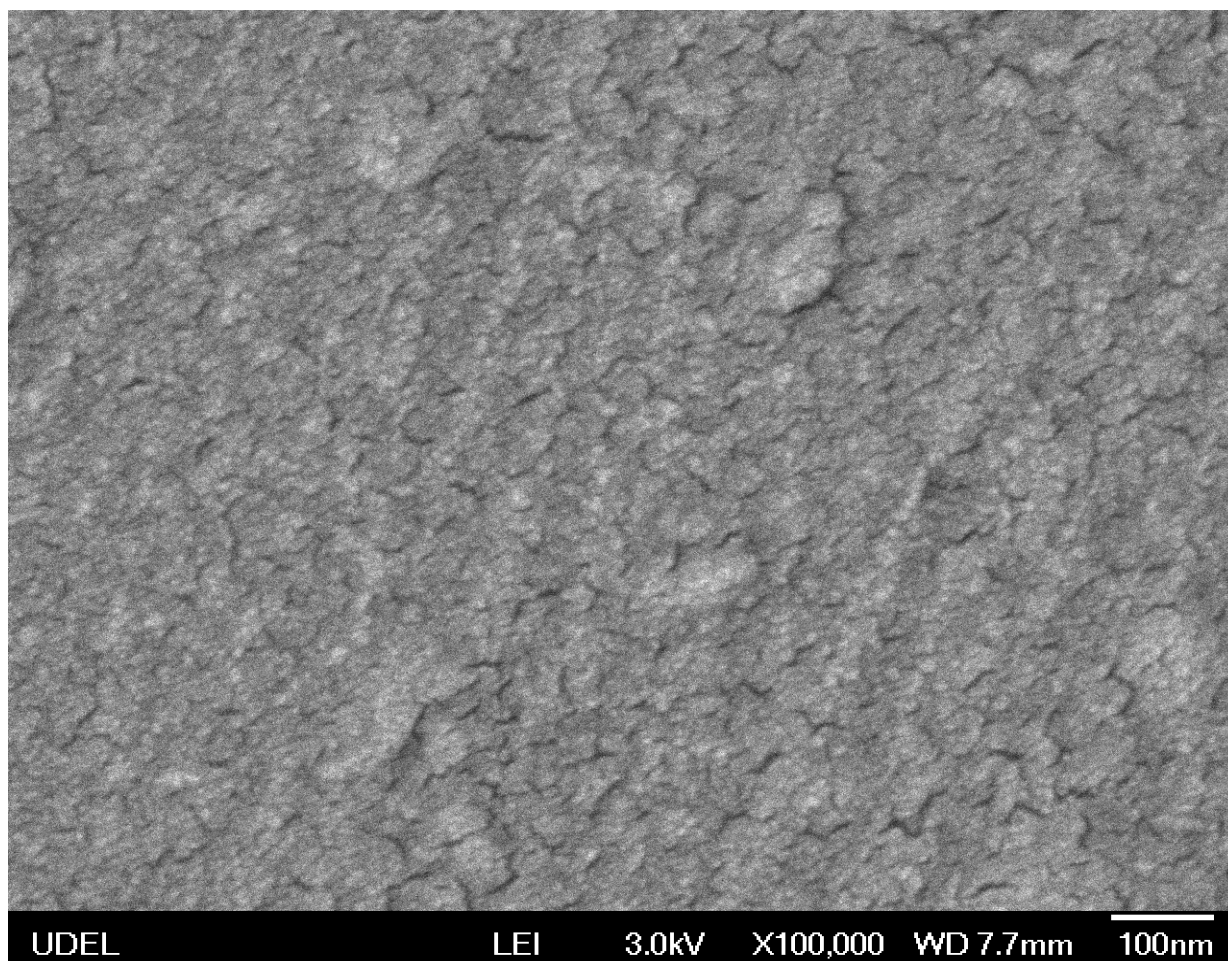


Figure 42: Scanning electron micrograph of a LaCoO₃ film after heating. The surface shows no major cracking which could lead to unexpected isotope penetration. The features are believed to be grain boundaries.

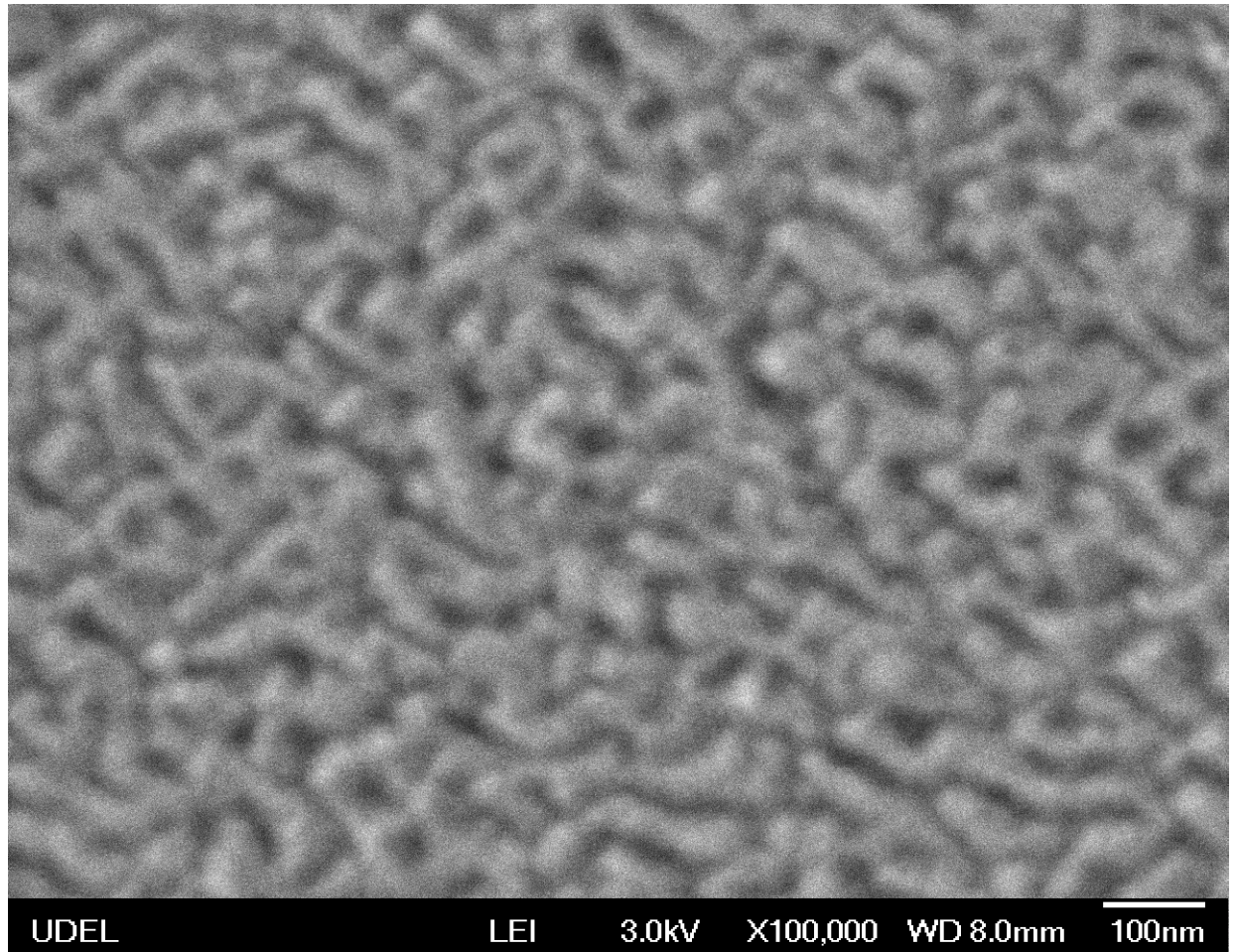


Figure 43: Scanning electron micrograph of a SrCoO₃ film after heating. The surface shows no major cracking which could lead to unexpected isotope penetration. The features are believed to be grain boundaries.

3.2.2 IEDP and SIMS Analysis

An example of the raw data taken from the secondary ion mass spectrometry

(SIMS) analysis can be seen in figure 44. The data shown was measured from an 83 nm thick LaCoO_3 thin film that was in an ^{18}O enriched environment for 60 seconds at 500 °C before being quenched. The raw data gathered shows integrated counts for peaks related to the oxygen species (^{18}O and ^{16}O) and to various cation-related species of the thin film material. The drastic increase in Mg-related intensity and coincident decrease in Co-related intensity found on the right side of the plot indicates the thin film – substrate interface. The data is plotted as a function of the depth into the film based on an estimate of the material removal rate of the primary ion beam.

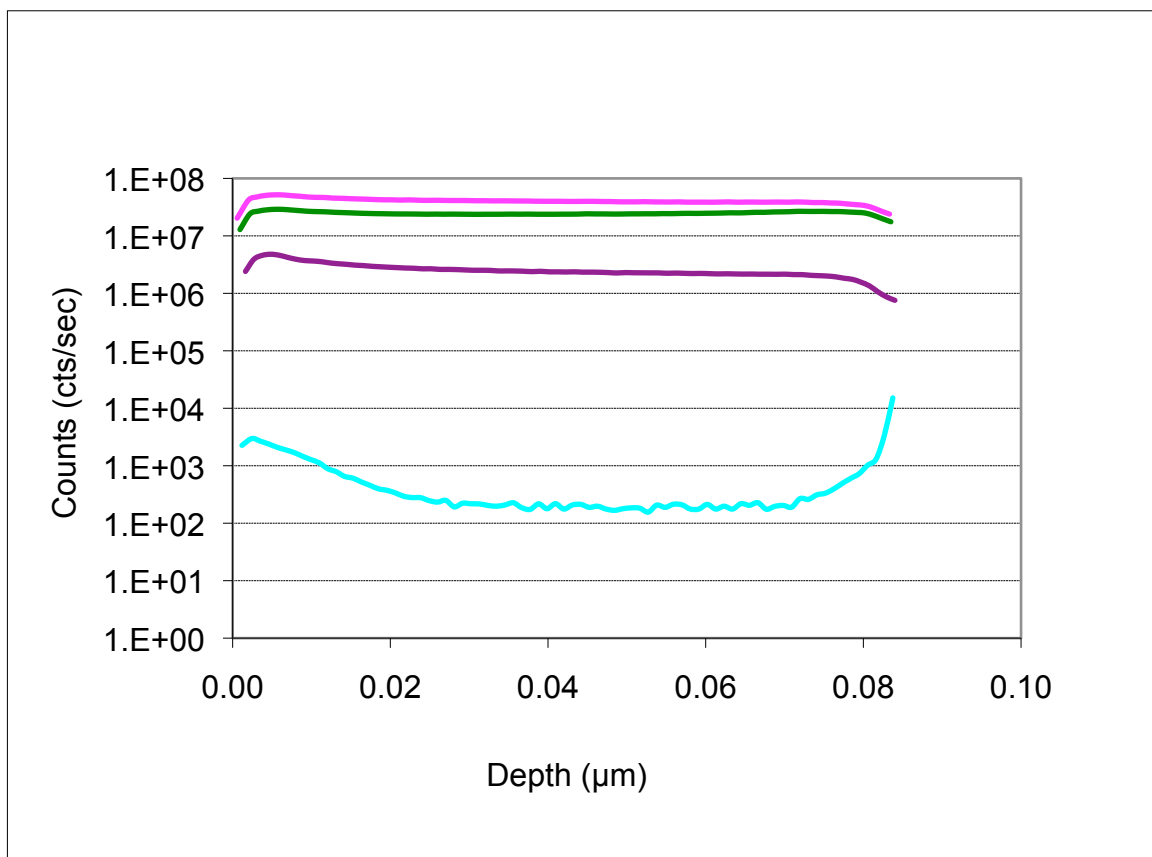


Figure 44: Integrated raw SIMS data from a LaCoO_3 film following isotopic exchange for 60 seconds at 500°C . ^{16}O (pink) and ^{18}O (green) as well as other constituents of the film $^{59}\text{Co}^{16}\text{O}$ (purple) and $^{24}\text{Mg}^{16}\text{O}$ (blue) are plotted. The substrate/film interface can be seen as a drop in oxygen and a sharp increase in magnesium. This film is 83 nm thick.

The peak intensities cannot be directly correlated to an elemental concentration. Despite this, a *ratio* of peak intensities for two isotopes can be used as a direct measurement of a compositional ratio. In figures 45(a)-(d) plots of the oxygen

isotopic ratios $^{18}\text{O}/(^{16}\text{O} + ^{18}\text{O})$ as a function of depth into the film are given for LaCoO_3 and SrCoO_3 films, following isotopic exchanges at 500 °C and 400 °C. The exchange times are listed in the captions.

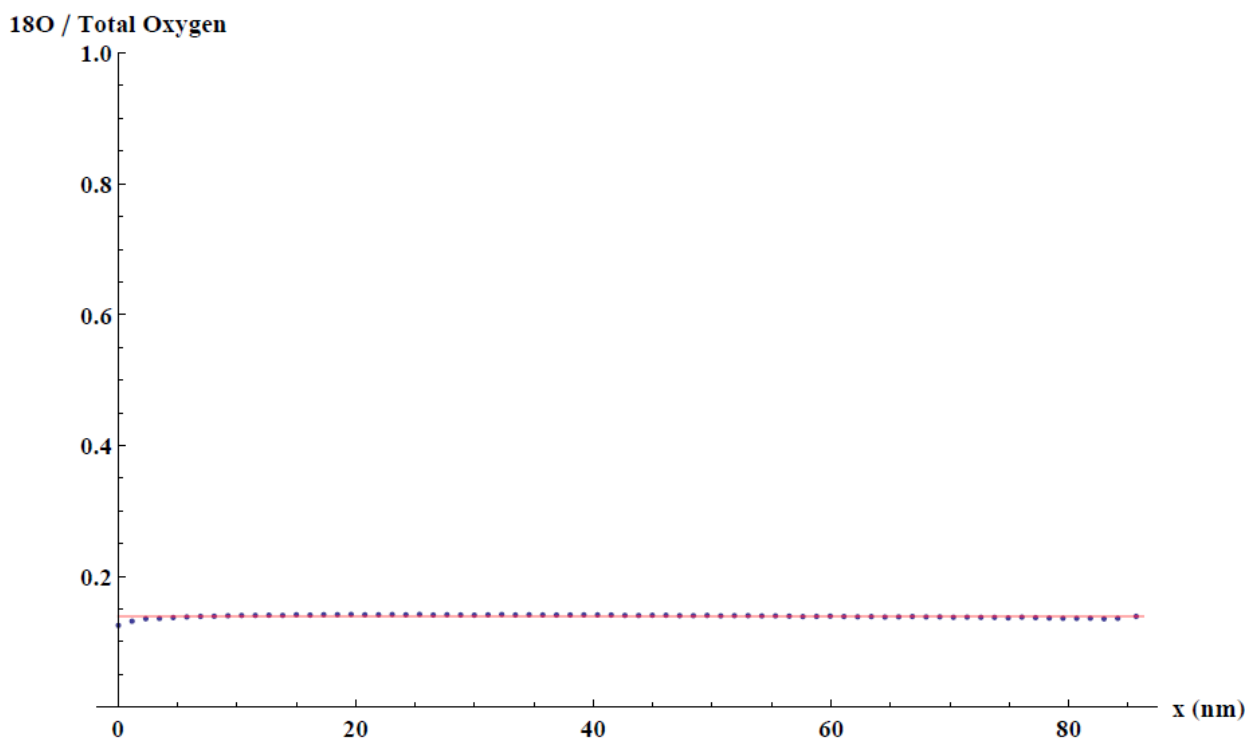


Figure 45a: Oxygen isotopic ratios as a function of depth into the film for a LaCoO_3 film, following isotopic exchange at 400 °C for 75 seconds. Blue dots indicate measured values; the red line indicates the fit to the model according to equation 1-16. The data has been re-plotted such that the film/air interface is at $x = 0$ nm.

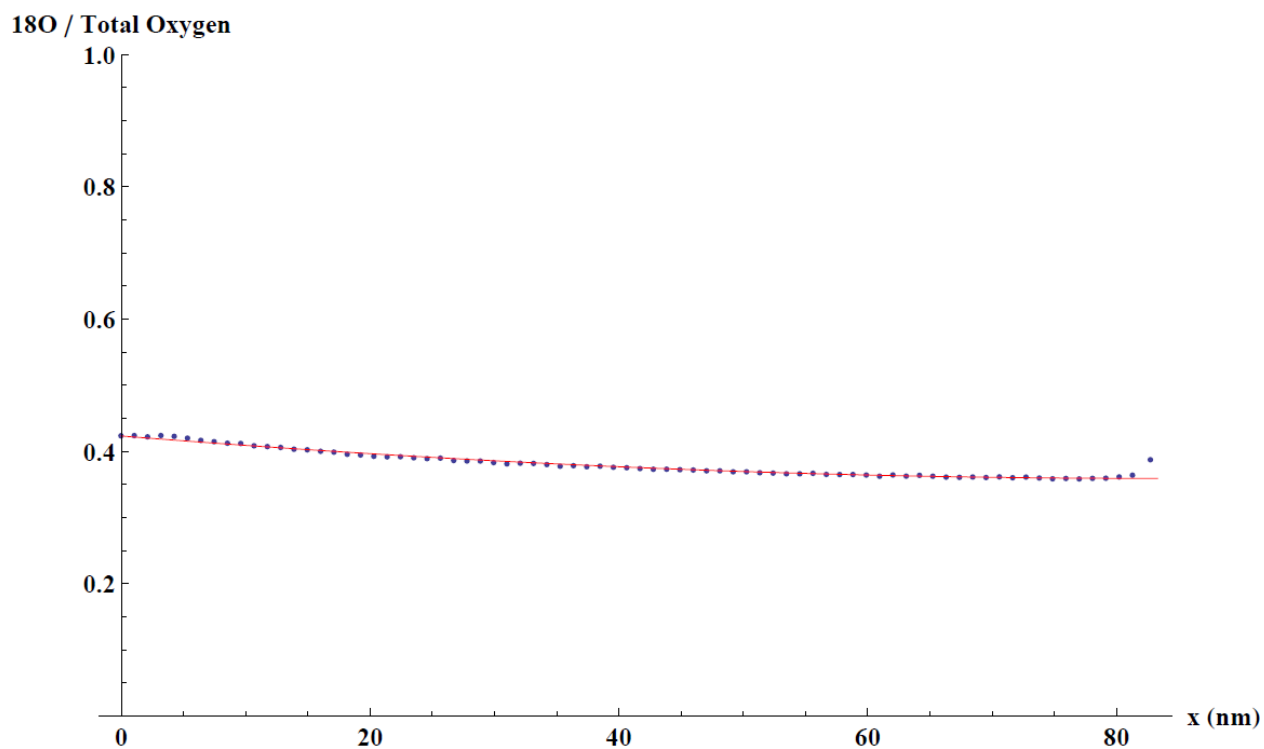


Figure 45b: LaCoO_3 diffusion profile at $500\text{ }^\circ\text{C}$ with an exchange time of 60 seconds.

The red line shows the fit to the model.

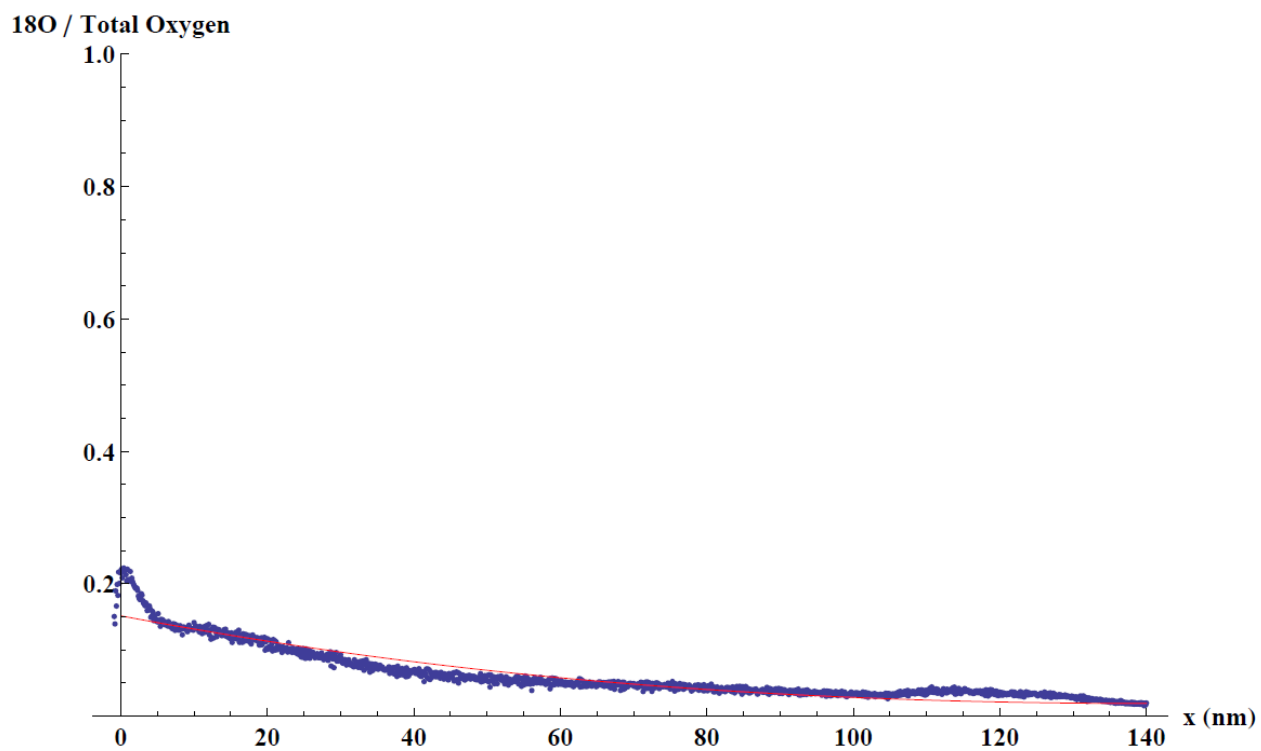


Figure 45c: SrCoO_3 diffusion profile at 500 °C with an exchange time of 10 minutes.

The red line shows the fit to the model.

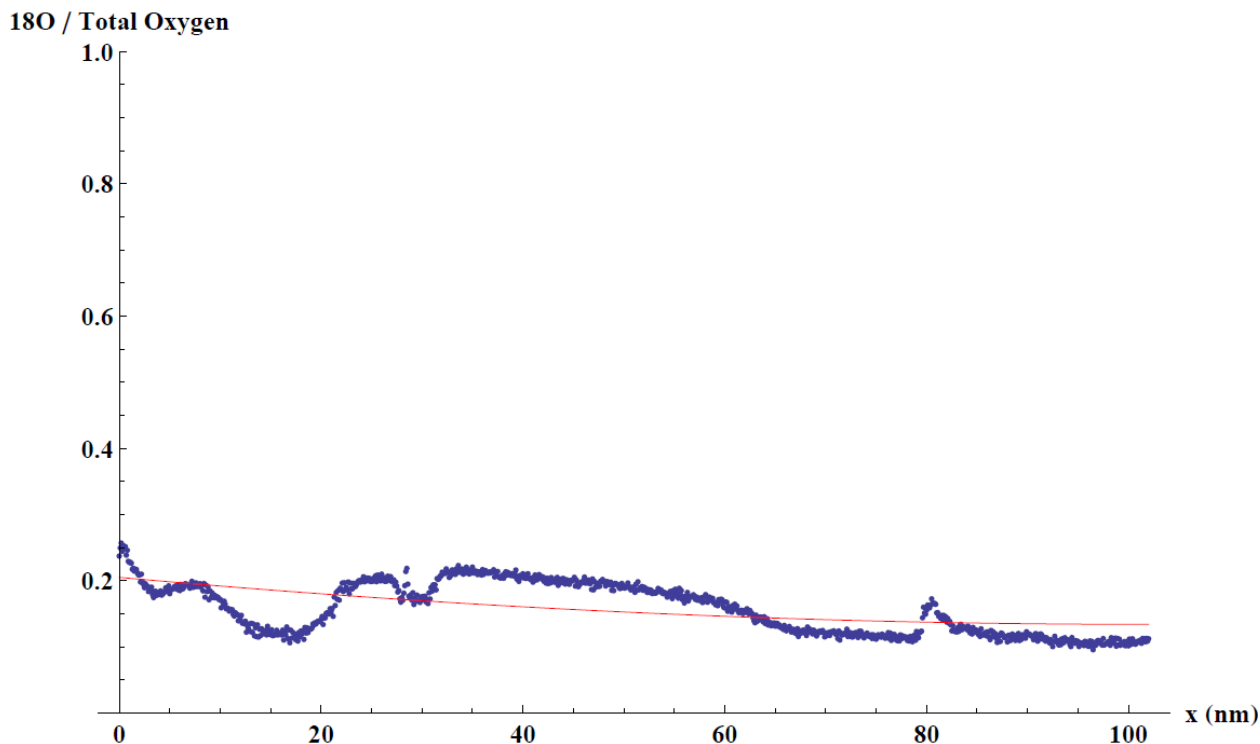


Figure 45d: SrCoO₃ diffusion profile at 400 °C with an exchange time of 60 minutes.

The red line shows the fit to the model.

A fitting routine programmed in Mathematica (version 8, Wolfram) was used to solve for the surface exchange coefficient and the bulk diffusion coefficient from the SIMS data. The code is provided in Appendix B. Each data set was highly overdetermined, vastly exceeding the benchmark of 25 points set in Chapter 1 to provide a reasonable fit. A table of the surface exchange coefficients, bulk diffusion coefficients, L values as defined by equation 1-18, and confidence intervals for each is

shown in table 1.

Table 1: The measured values for surface exchange and bulk diffusion coefficient with standard error.

Material	Temperature (°C)	k_{surf} (cm/sec)	Standard Error, k_{surf}	D (cm ² /sec)	Standard Error, D	L value
LaCoO ₃	400	$2.274 \cdot 10^{-8}$	$4.120 \cdot 10^{-9}$	$1.805 \cdot 10^{-9}^+$	$5.457 \cdot 10^{-8}^+$	$1.04 \cdot 10^{-4}^+$
LaCoO ₃	500	$1.061 \cdot 10^{-7}$	$3.21 \cdot 10^{-10}$	$2.431 \cdot 10^{-12}$	$5.238 \cdot 10^{-14}$	0.375
SrCoO ₃	400	$9.891 \cdot 10^{-10}$	$6.315 \cdot 10^{-12}$	$3.431 \cdot 10^{-14}$	$1.807 \cdot 10^{-15}$	0.404
SrCoO ₃	500	$2.117 \cdot 10^{-9}$	$1.324 \cdot 10^{-11}$	$6.133 \cdot 10^{-14}$	$9.238 \cdot 10^{-16}$	0.344

⁺ This value is not determined with statistical significance, as described in the text.

The SrCoO₃ samples exhibited an unexpectedly large amount of noise in the diffusion profile. This noise could point to morphology irregularities such as grain boundaries or slight contamination in the film. The SrCoO₃ samples were analyzed on a different SIMS machine. The different operating conditions could also have lead to increased noise in the data. Despite the reduced signal-to-noise ratio, the fitting routine was able to determine a good fit to equation 1-16.

The L values indicate that all of the systems were in a surface exchange limited regime. For three of the data sets, L was sufficiently large that a bulk diffusion coefficient could be reasonably determined, albeit with less confidence than the

surface exchange coefficient. The fitting routine was unable to determine a diffusion coefficient with statistical significance for the flattest diffusion profile: LaCoO_3 at 400 °C. As seen in Table 1, the error in the bulk diffusion coefficient exceeds the determined value, allowing for a non-physical, negative diffusion coefficient. This relative independence of the modeled solution upon the diffusion coefficient is expected, as this system is the most surface exchange limited with $L \ll 1$. It is important to note that while the bulk diffusion coefficient was not determinable in this instance, a relatively robust determination was made for the surface exchange coefficient. Since the focus of this work was the surface exchange coefficients, this result remains highly useful. If the bulk diffusion coefficient of this material is desired in the future, one of the techniques discussed in the introduction, such as bulk isotope exchange depth profiling, could be used.

Other exchange times, 20 minutes, 3 hours, and 10 hours, were measured on the LaCoO_3 sample at 500 °C. These samples showed completely saturated diffusion profiles having a concentration of ^{18}O /total oxygen at the midpoint of 0.748, 0.765, and 0.762, near the concentration of the enriched atmosphere used during the exchange. The plane diffusion model predicts this. Figure 46 shows the concentration measured for each of the 4 exchange times. The blue line shows the concentration predicted by the plane diffusion model given the surface exchange coefficient and bulk diffusion coefficient determined above. Future experimentation would benefit from additional measurements near 100 s because they are in a measurable concentration range. A different concentration profile will be created for the different

exchange time however the model will fit the same surface exchange coefficient and bulk diffusion coefficient.

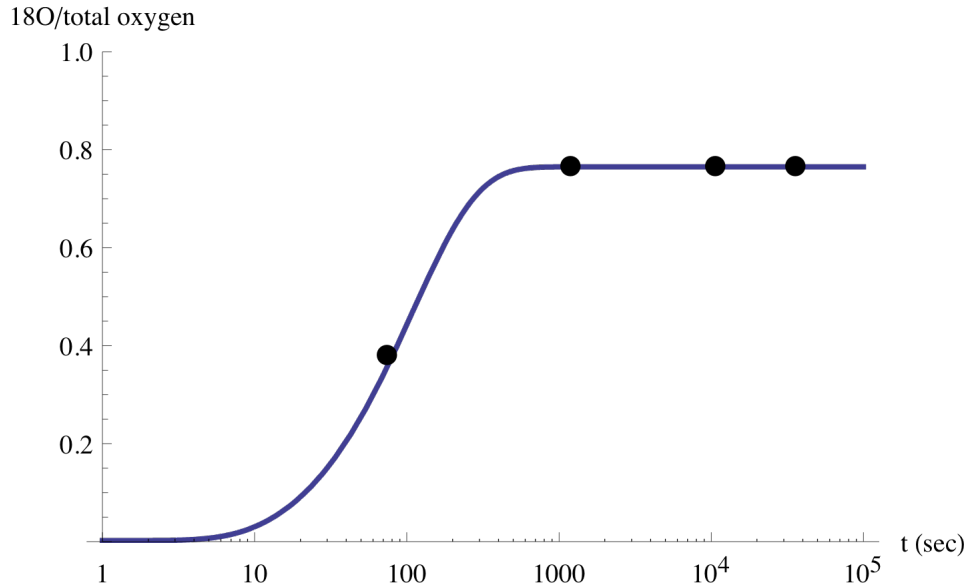


Figure 46: Plotted points indicate concentration of ^{18}O at the midpoint in LaCoO_3 samples with exchange times of 60 seconds, 20 minutes, 3 hours, and 10 hours at 500 °C. The blue line shows the modeled concentration of ^{18}O as a function of time based on the bulk diffusion and surface exchange coefficients found in the 60 seconds exchange sample. The three longest exchange times showed completely saturated diffusion profiles.

Figure 47 shows the surface exchange coefficients for LaCoO_3 compared to literature values. SrCoO_3 is often considered only a dopant material so there is no literature on the surface exchange coefficient to compare against, however for

comparison the values are also plotted in figure 47. Literature values for the surface exchange coefficients for LaCoO_3 range from 10^{-6} cm/sec to 10^{-10} cm/sec in a small range of temperatures. This may be due to the low accuracy with which these coefficients were measured as all of the literature values shown were measured using traditional isotope exchange on bulk samples. However the range of literature values could also be due to the different oxygen partial pressures used during the experiments or the crystallinity of the samples produced by the different fabrication methods. Although none of these articles list the characteristic length it is likely that with the techniques used the measurements were made in a bulk diffusion limited system. The values of the coefficients found in this work are higher than extrapolation of literature values to the measurement temperatures used here would predict. There are a number of possible reasons for this. This work focused on thin films where mechanical stresses from thermal expansion mismatch with the substrate could have an impact on the oxygen diffusion. The bulk samples to which these measurements are being compared have no such substrate and thus are likely to be stress-free. In addition, sputtering the samples may produce different microstructures such as different grain sizes. Samples in this work may also have a higher purity as they are sputtered under high vacuum instead of sintered for long times in a high temperature furnace. All of these could affect the measured surface exchange and diffusion coefficients relative to literature values.

Error bars are shown on the data obtained in this work. The x-axis error bars show possible error in the temperature of the substrate compared to the temperature

measured by the thermocouple. While a thermocouple was used internal to the exchange chamber to measure the air temperature, this temperature could be different than the temperature of the film particularly for short exchange times. To increase this accuracy the thermocouple could be adhered to the substrate using a silver paste however to provide quick removal of the sample from the exchange chamber for quenching, this was not done. The error bars show up to 10 degrees different from the measured temperature. The y-axis error bars show error in the measured coefficient value. For this work it is assumed that error in this is primarily due to errors in the exchange time. The exchange times used were, in some cases, the minimum measurable exchange time. This means small errors in the time measured for the exchange contribute to a large percentage of the total exchange time. For this reason the error bars for the LaCoO_3 samples are larger than the SrCoO_3 samples because shorter exchange times were used on the LaCoO_3 samples. The magnitude of the error bars was estimated using the contour plots discussed above.

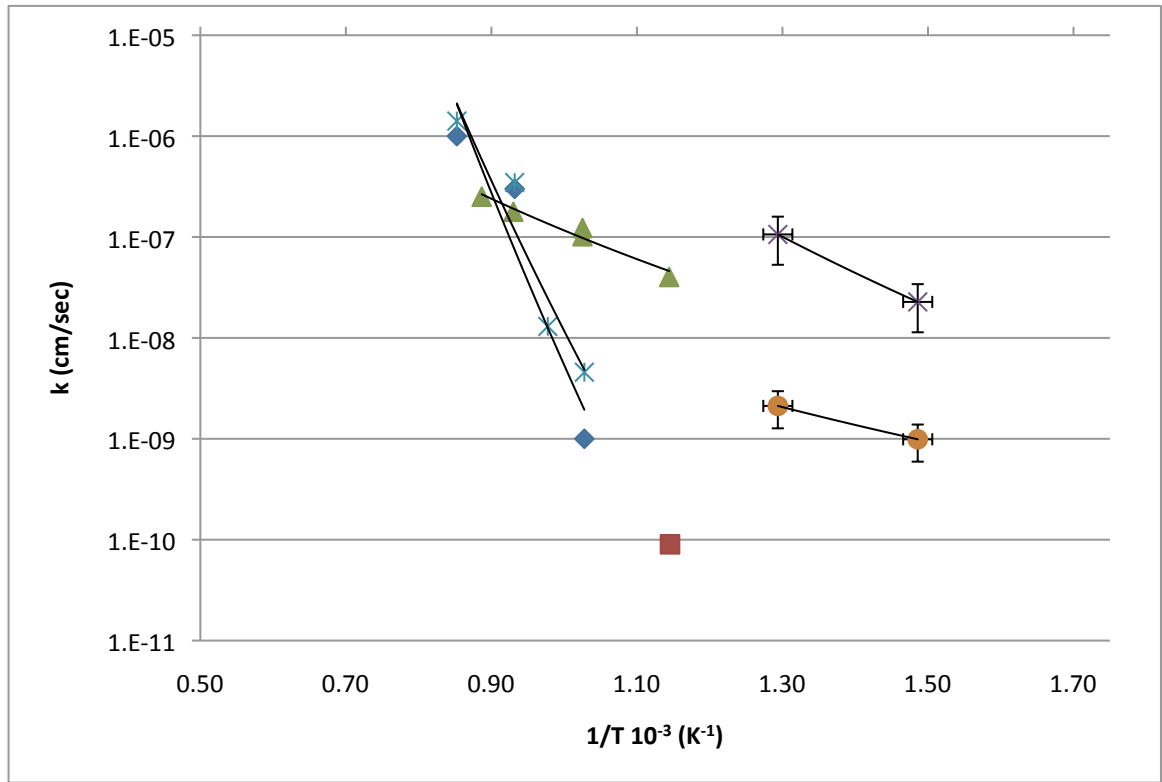


Figure 47: Comparison of reported surface exchange coefficients of LaCoO₃ from this work, (purple x measured at an oxygen partial pressure of $p_{O_2} = 577.6$ torr), and from Ananyev et. al. [49] (green triangles, $p_{O_2} = 5$ torr), Bouwmeester et. al. [32] (blue diamonds, $p_{O_2} = 33.75$ torr T. Ishigaki (blue asterisk, $p_{O_2} = 34$ torr) [50], and Berenov et. al. [51] (red square, $p_{O_2} = 159.6$ torr). Also shown are the values measured in this work for SrCoO₃ (orange circles, $p_{O_2} = 577.6$ torr).

Bulk diffusion coefficient values were also compared to literature values.

Figure 48 shows the literature values for LaCoO₃ as well as the bulk diffusion coefficient for LaCoO₃ at 400 °C and the SrCoO₃ at both 400 °C and 500 °C measured

in this work. The value for LaCoO_3 at 400 °C was not plotted as it was not determined with statistical significance. As with the surface exchange coefficients a range in literature values is seen. The bulk diffusion coefficients measured in this work fell within the range of literature values. The possible causes for higher bulk diffusion coefficient values than the literature trend would predict are the same as stated above for the surface exchange coefficient.

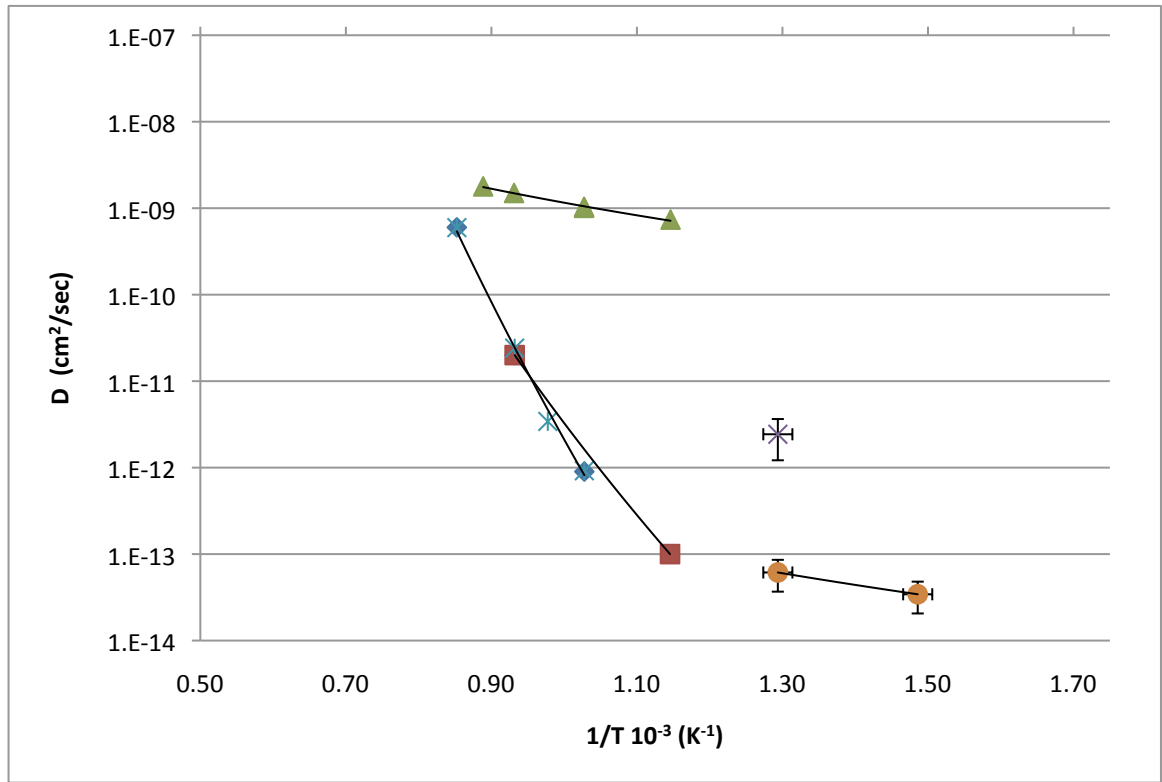


Figure 48: Comparison of reported bulk diffusion coefficients of LaCoO₃ from this work, (purple x, measured at an oxygen partial pressure of $p_{O_2} = 577.6$ torr), and from Ananyev et. al. (green triangles, $p_{O_2} = 5$ torr) [49], Bouwmeester et. al. (blue diamonds, $p_{O_2} = 33.75$ torr) [32], T. Ishigaki (blue asterisk, $p_{O_2} = 34$ torr) [50], and Berenov et. al. (red square, $p_{O_2} = 159.6$ torr) [51]. Also shown are the values measured in this work for SrCoO₃ (orange circles, $p_{O_2} = 577.6$ torr).

The values measured in this work show that LaCoO₃ and SrCoO₃ have insufficient diffusion coefficients to be used as a low temperature SOFC cathode material. Significantly higher bulk diffusion and surface exchange coefficients would

be required at the low temperatures for it to be considered for low temp applications. While there are no defined thresholds for minimum diffusion coefficients, materials considered for low temperature applications generally have bulk diffusion and surface exchange coefficients on the order or 10^{-10} cm/sec or larger [9] [52] [53]. Doping LaCoO_3 with SrCoO_3 has been shown to increase the bulk diffusion coefficient significantly making it attractive at low and high temperatures, figure 49. Now with an accurate measurement method for surface exchange coefficients similar studies on how doping changes the surface exchange coefficient can be performed. If a relationship between dopant concentration and both the bulk diffusion coefficient and the surface exchange coefficient can be determined, higher performance low temperature MIEC cathode materials for SOFCs can be found.

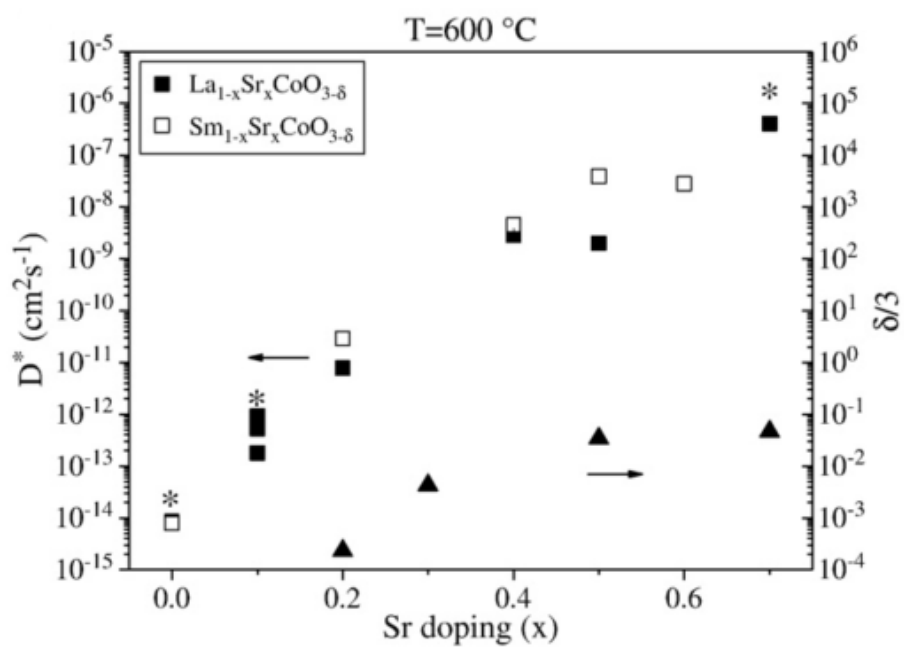


Figure 49: Doping of LaCoO_3 with strontium shows increased bulk diffusion coefficient. Reprinted from [51]

Chapter 4

CONCLUSION

Mixed ionic electronic conductors (MIECs) are a promising set of materials for a number of electrochemical devices. While it is known that dopant concentration plays a big part in the ion exchange and diffusion properties, a direct relationship between the two has not yet been found. Work has been done in finding techniques to measure the bulk diffusion coefficient of MIECs however little has been done in finding the surface exchange coefficient, a key performance parameter – especially as thin film fabrication becomes more prominent. Surface exchange coefficients have been historically difficult to measure using traditional techniques for measuring diffusion parameters.

In this work, a test method was created for measuring surface exchange coefficients using isotope exchange depth profiling of thin films. Modeling of isotope diffusion using routines created in Mathematica showed large range of measurable surface exchange coefficients provided measurements were conducted on a surface exchange limited system. A plane diffusion model was shown to best model a thin film system because of the zero flux boundary condition at the substrate. Isotope exchange experiments were conducted on LaCoO_3 and SrCoO_3 perovskite thin films. The thin films of these materials were deposited using magnetron sputtering of source materials targets fabricated and analyzed in house. Secondary ion mass spectrometry

was used to analyze the isotope diffusion. Surface exchange coefficients of LaCoO_3 and SrCoO_3 were measured at both 400 °C and 500 °C and showed a good fit to the model. LaCoO_3 has a surface exchange coefficient of $2.274 \cdot 10^{-8}$ cm/sec and $1.061 \cdot 10^{-7}$ cm/sec at 400 °C and 500 °C respectively. SrCoO_3 has a surface exchange coefficient of $9.891 \cdot 10^{-10}$ cm/sec and $2.117 \cdot 10^{-9}$ cm/sec at 400 °C and 500 °C respectively. These values were shown to be higher than the literature trends would predict at the experiment temperatures. The possible source of differences was predicted to be mechanical stresses in the thin films as well as microstructure differences between sputtering and traditional ceramic fabrication methods. The modeling and experimental results show that isotope exchange depth profiling of thin films is a feasible test method of accurately measure surface exchange coefficients from $5 \cdot 10^{-16}$ cm/sec to $5.5 \cdot 10^{-5}$ cm/sec of surface exchange coefficients of MIECs. Thin film combinatorial deposition techniques provide the opportunity to quickly measure a wide range of dopant concentrations from a single thin film sample. Thin film isotope exchange depth profiling and combinatorial deposition techniques can aid in the understanding of dopant concentration's impact on diffusion kinetics as well as offer a method of material optimization.

Future work on this topic should include finding relationships between dopant concentration and surface exchange coefficients. Dopant concentration has been shown to increase the bulk diffusion coefficient. A relationship between dopant and surface exchange coefficient will allow the optimization of the MIEC material based on the ALS model. To determine this relationship, a number of dopant compositions

will need to be deposited, exchanged and analyzed. This can be done efficiently using combinatorial analysis. Combinatorial analysis is a co-deposition technique that will allow a gradient of dopant concentration on a single substrate. This decreases the amount of time needed in the fabrication of thin films of doped materials. To proceed with combinatorial analysis there must be some work done with the deposition rates of each material to determine a dopant concentration as a function of position on the substrate. Special care must also be taken to ensure that during SIMS the position of the analysis spot is correctly aligned to the correct position on the substrate since dopant concentration changes as a function of position. Neither of these is a difficult task to overcome given the experimenter is familiar with the sputtering and SIMS equipment.

For modeling, plane diffusion is a good model for the surface exchange limited region however struggles in the bulk diffusion limited region. This is because the plane diffusion model would require increasingly large amount of terms in the infinite sum to accurately model L values greater than 1. By combining the semi-infinite model, which has been shown to be good at measuring diffusion limited systems with traditional IEDP, and the plane diffusion model, one model could be used to evaluate both diffusion limited and surface exchange limited systems. This could then be used to investigate the co-limited region where the diffusion profile is limited by both the bulk diffusion coefficient and the surface exchange coefficient.

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Appendix A

DIFFUSION PLOTS

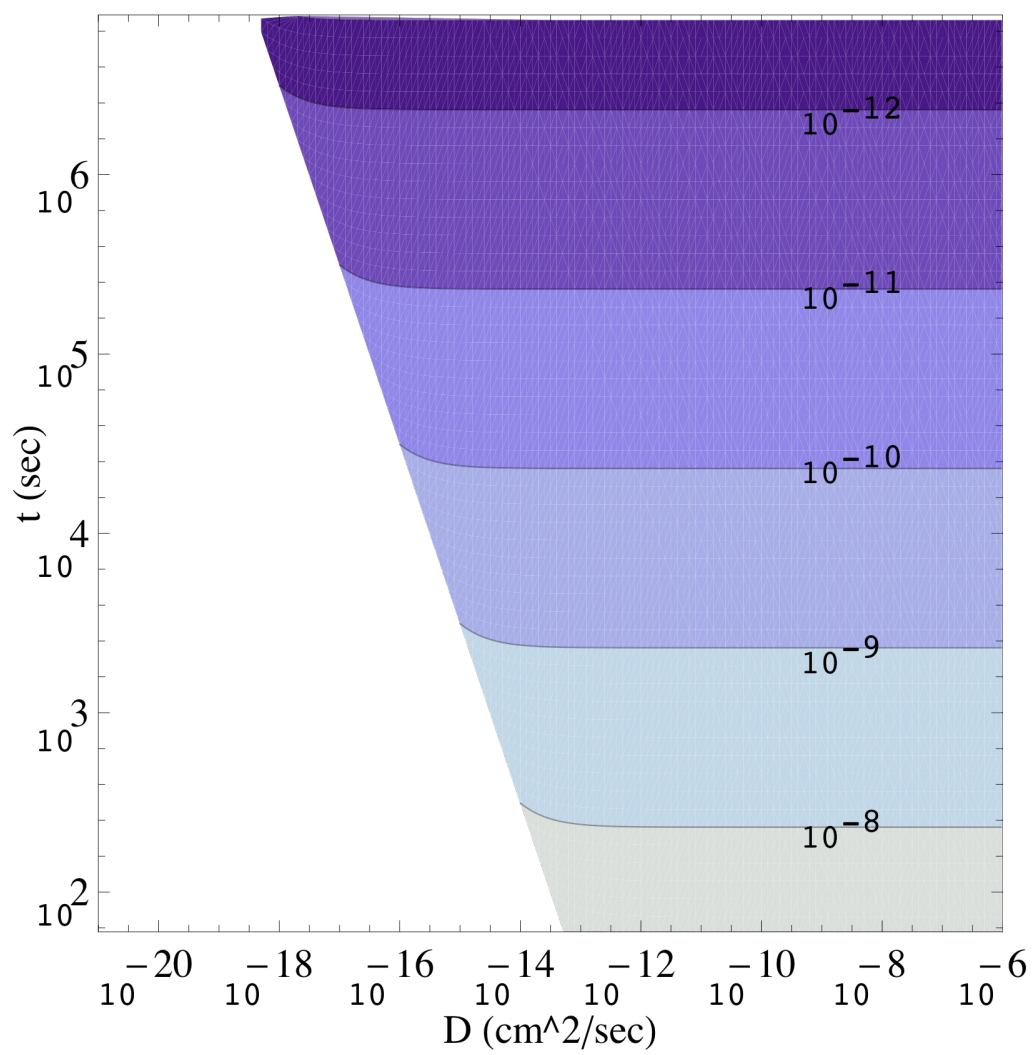


Figure A.1: Contour plot of the maximum measurable surface exchange coefficients for a 10 nm thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

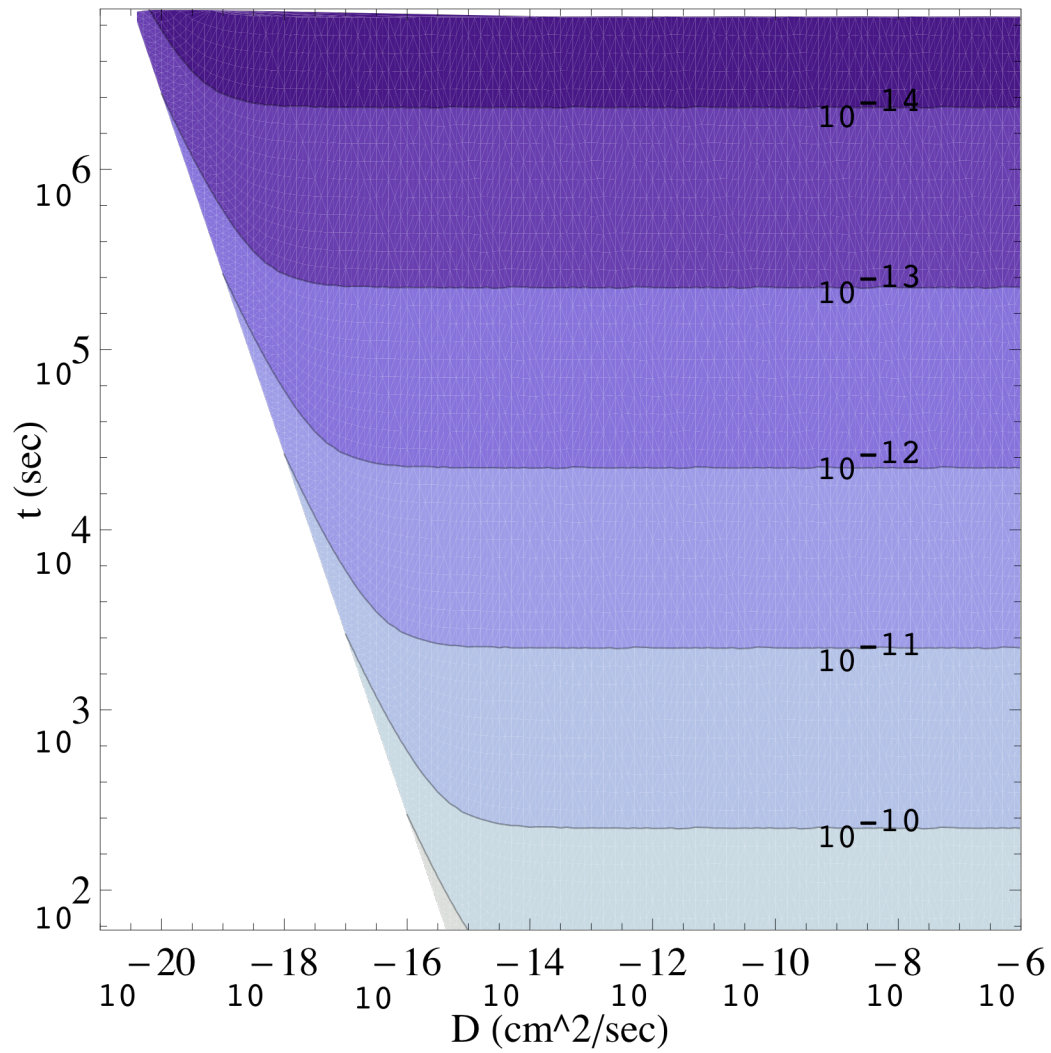


Figure A.2: Contour plot of the minimum measurable surface exchange coefficients for a 10 nm thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

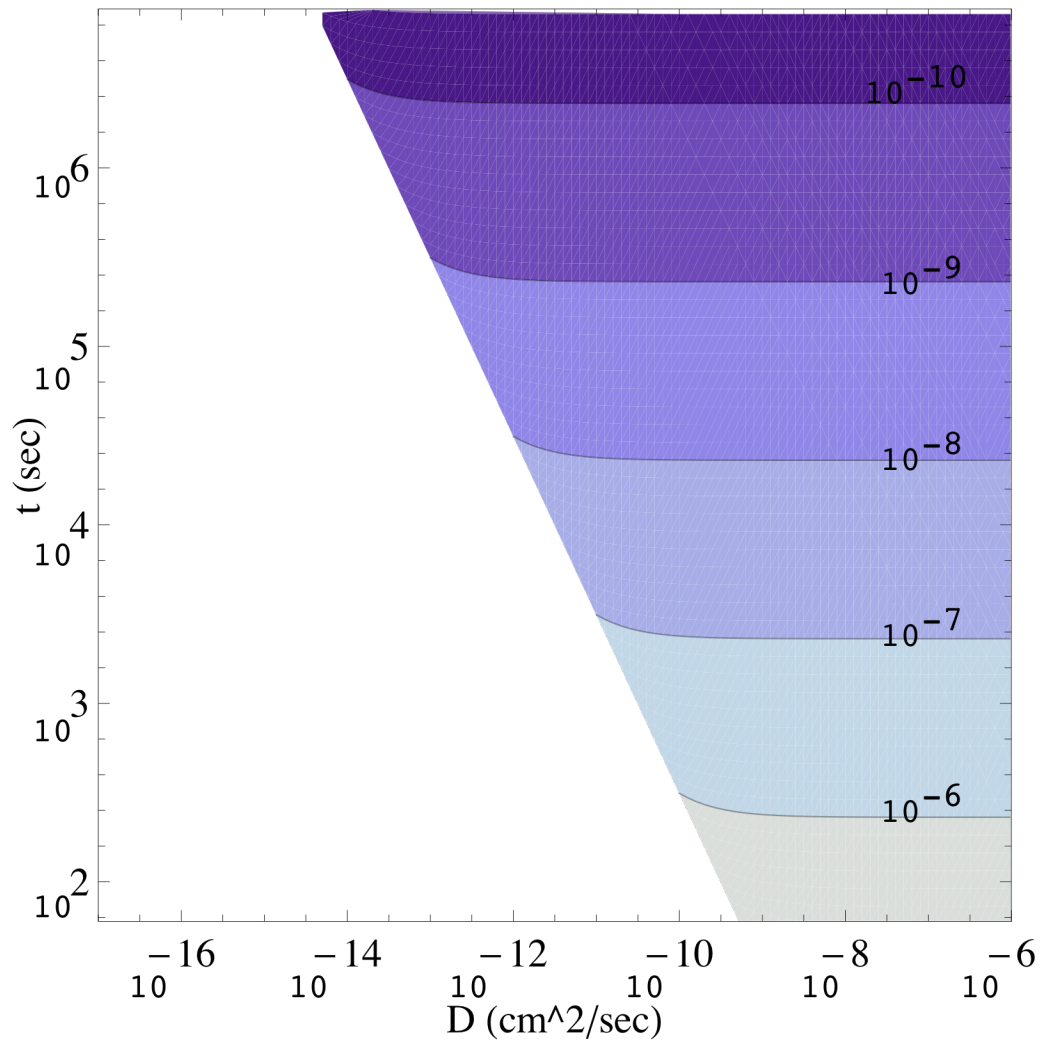


Figure A.3: Contour plot of the maximum measurable surface exchange coefficients for a 1 micron thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

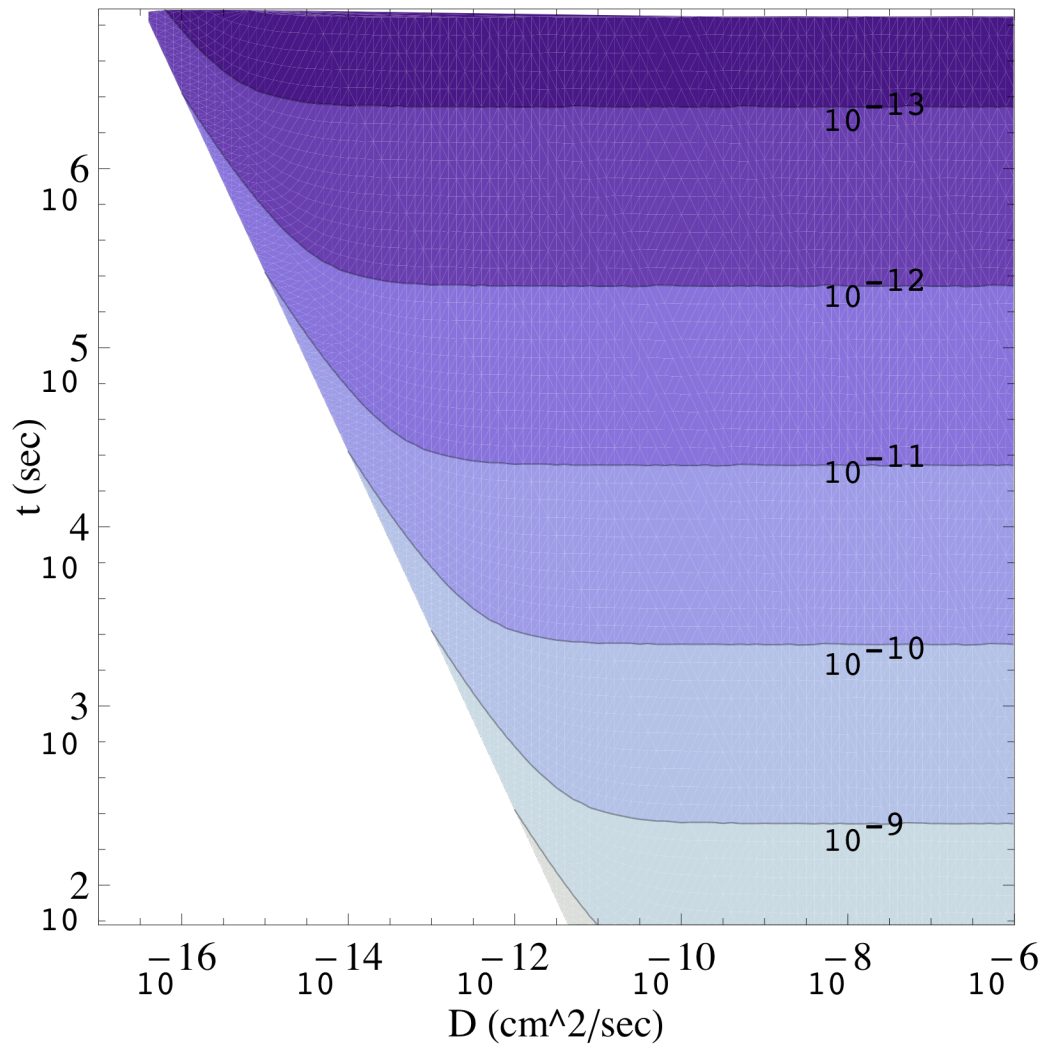


Figure A.4: Contour plot of the minimum measurable surface exchange coefficients for a 1 micron thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

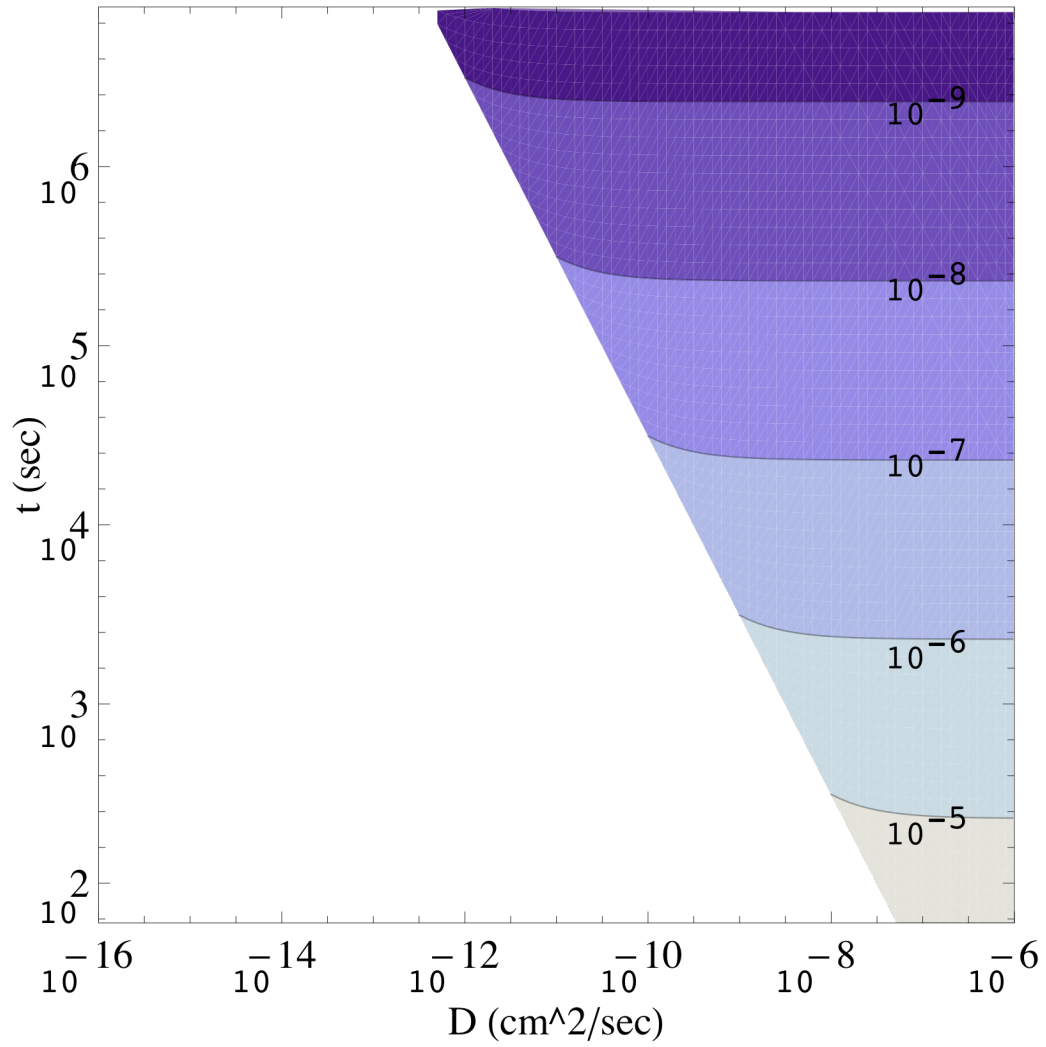


Figure A.5: Contour plot of the maximum measurable surface exchange coefficients for a 10 micron thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

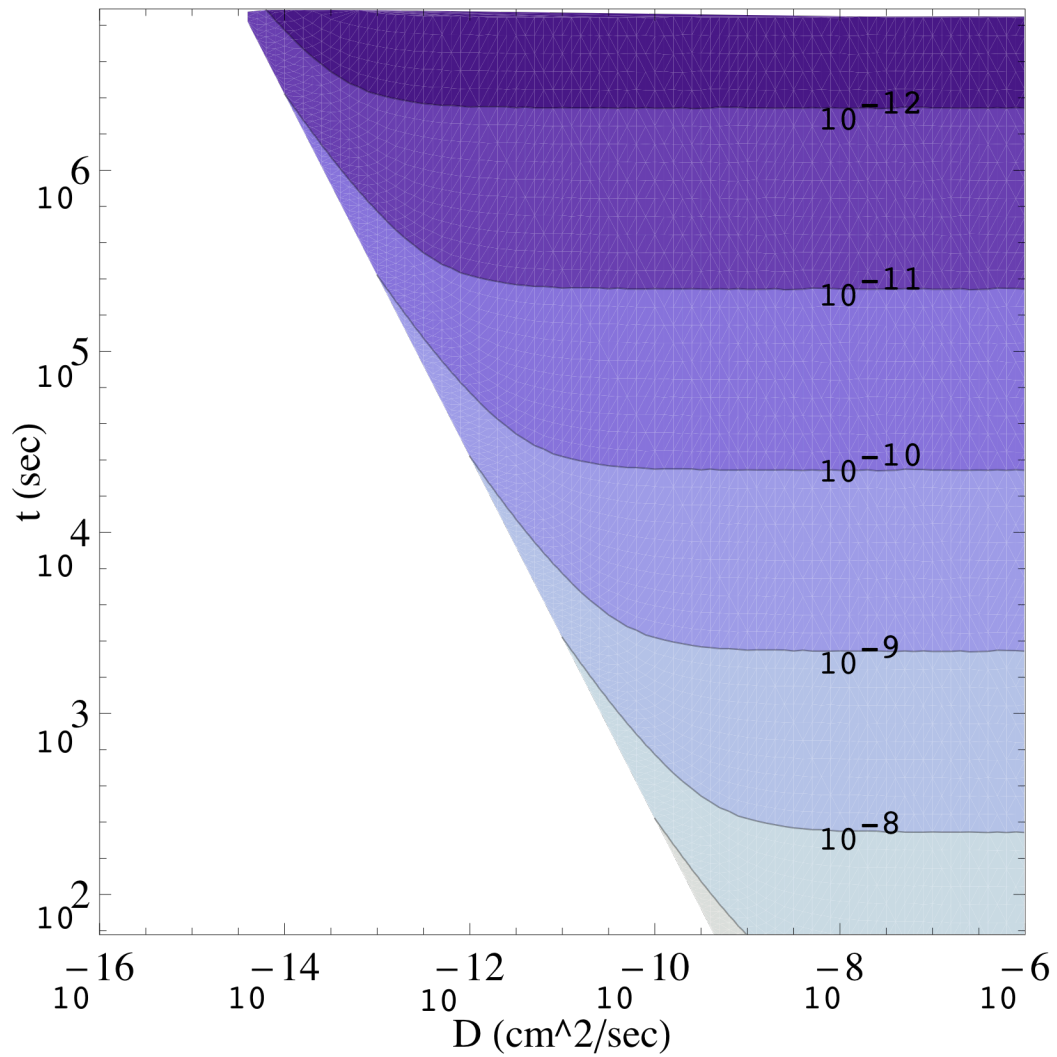


Figure A.6: Contour plot of the minimum measurable surface exchange coefficients for a 10 micron thick film given the bulk diffusion coefficient and exchange time. This plot is calculated using the plane diffusion model assuming a 100% enriched atmosphere of ^{18}O . The left boundary is defined by an L value of 1.

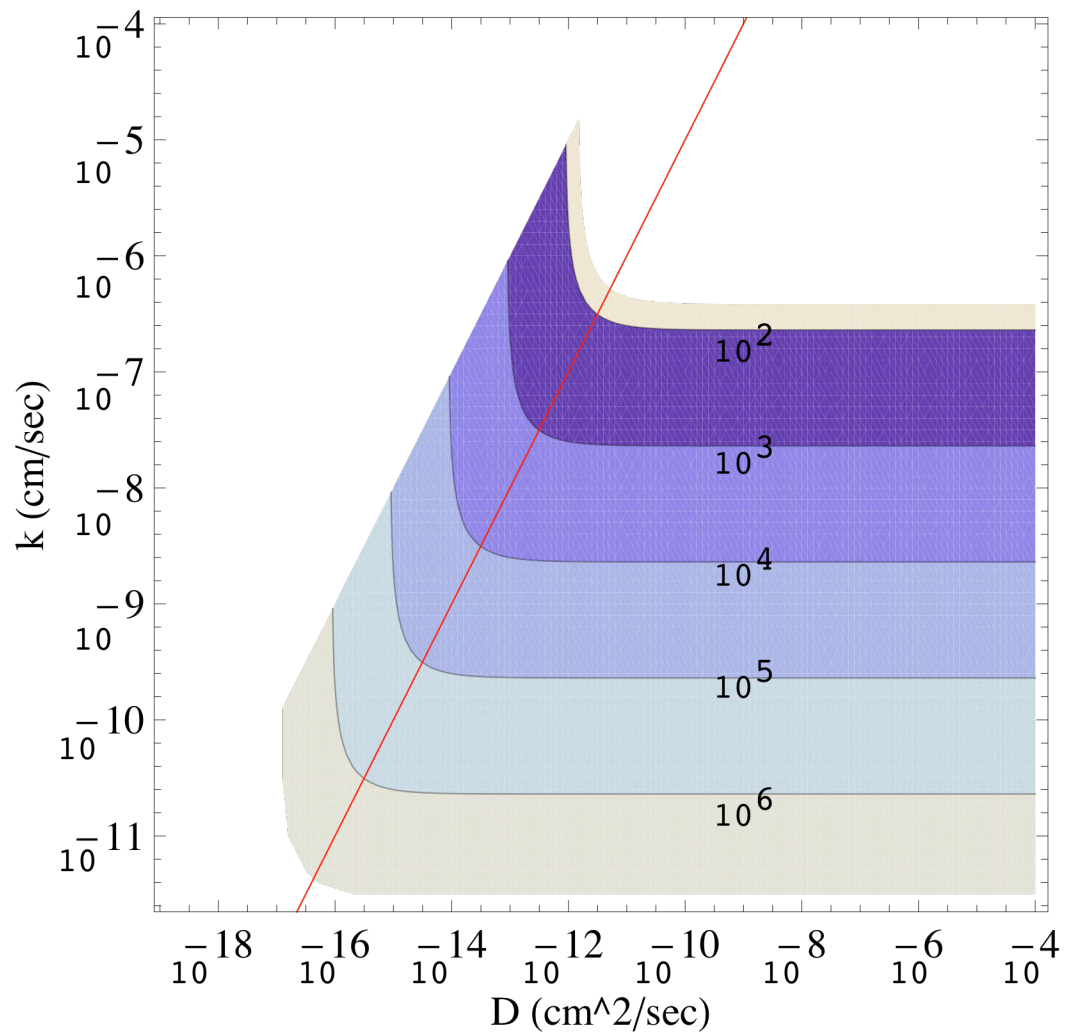


Figure A.7: Contour plot of the maximum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 10 nm thick film.

The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile.

An L value of 1 is marked with a red line.

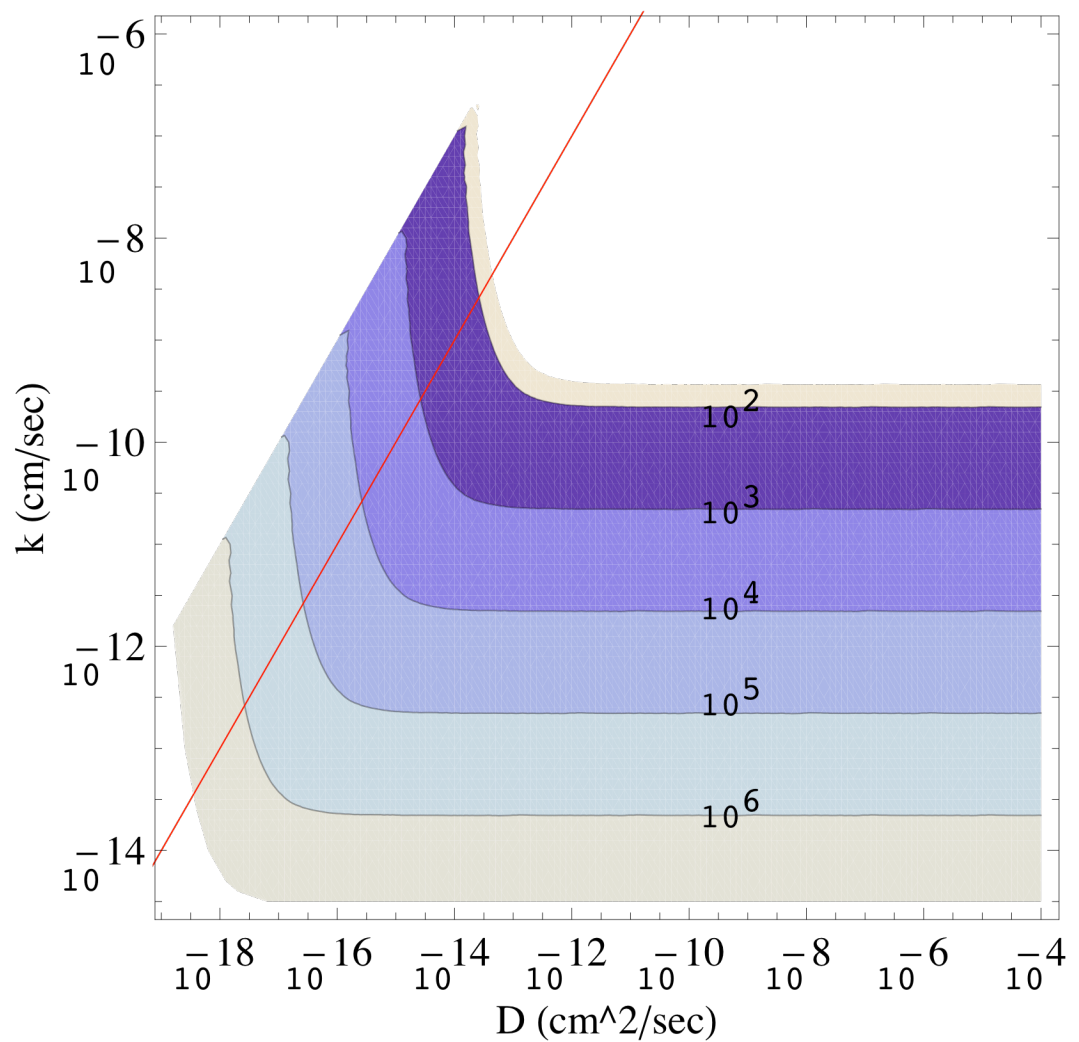


Figure A.8: Contour plot of the minimum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 10 nm thick film.

The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile.

An L value of 1 is marked with a red line.

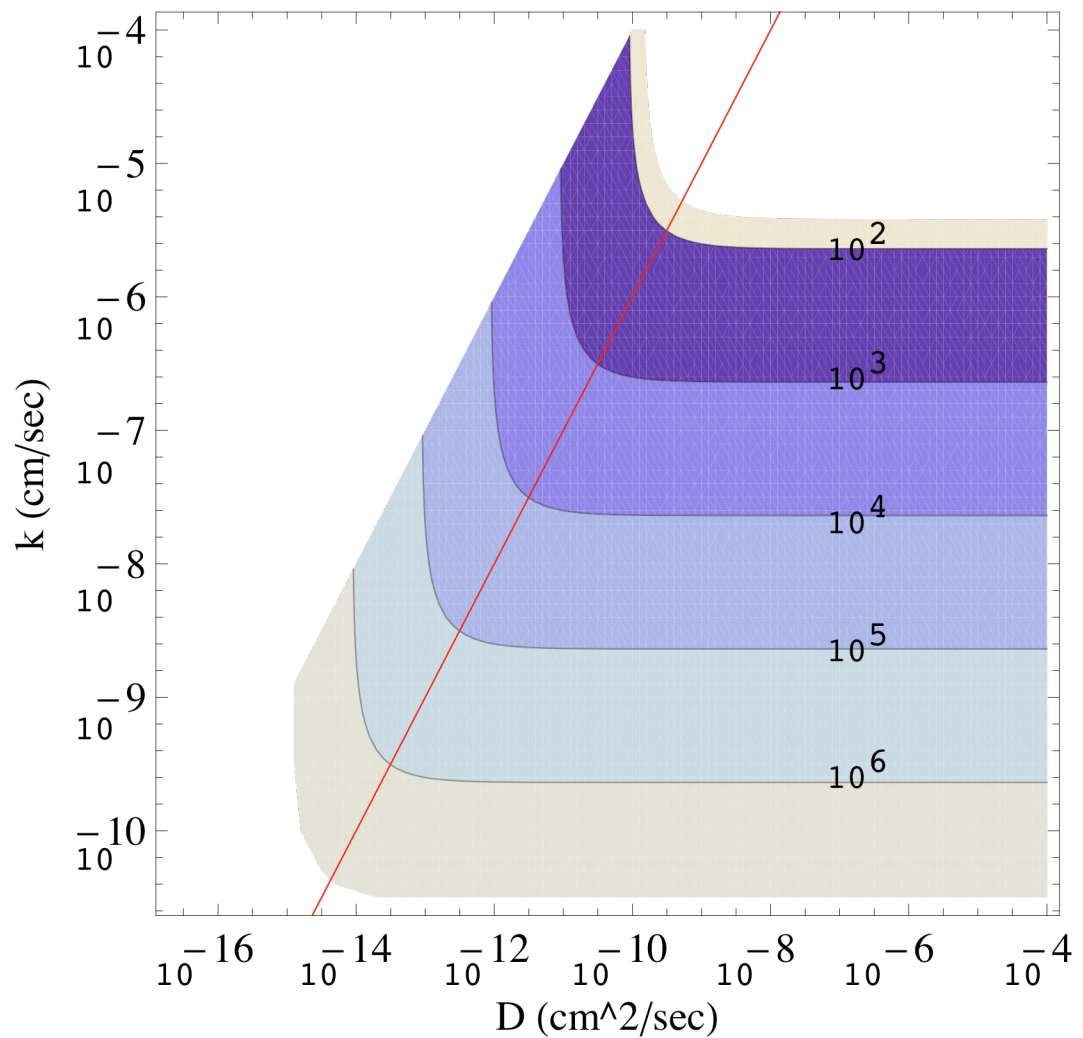


Figure A.9: Contour plot of the maximum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 1 micron thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

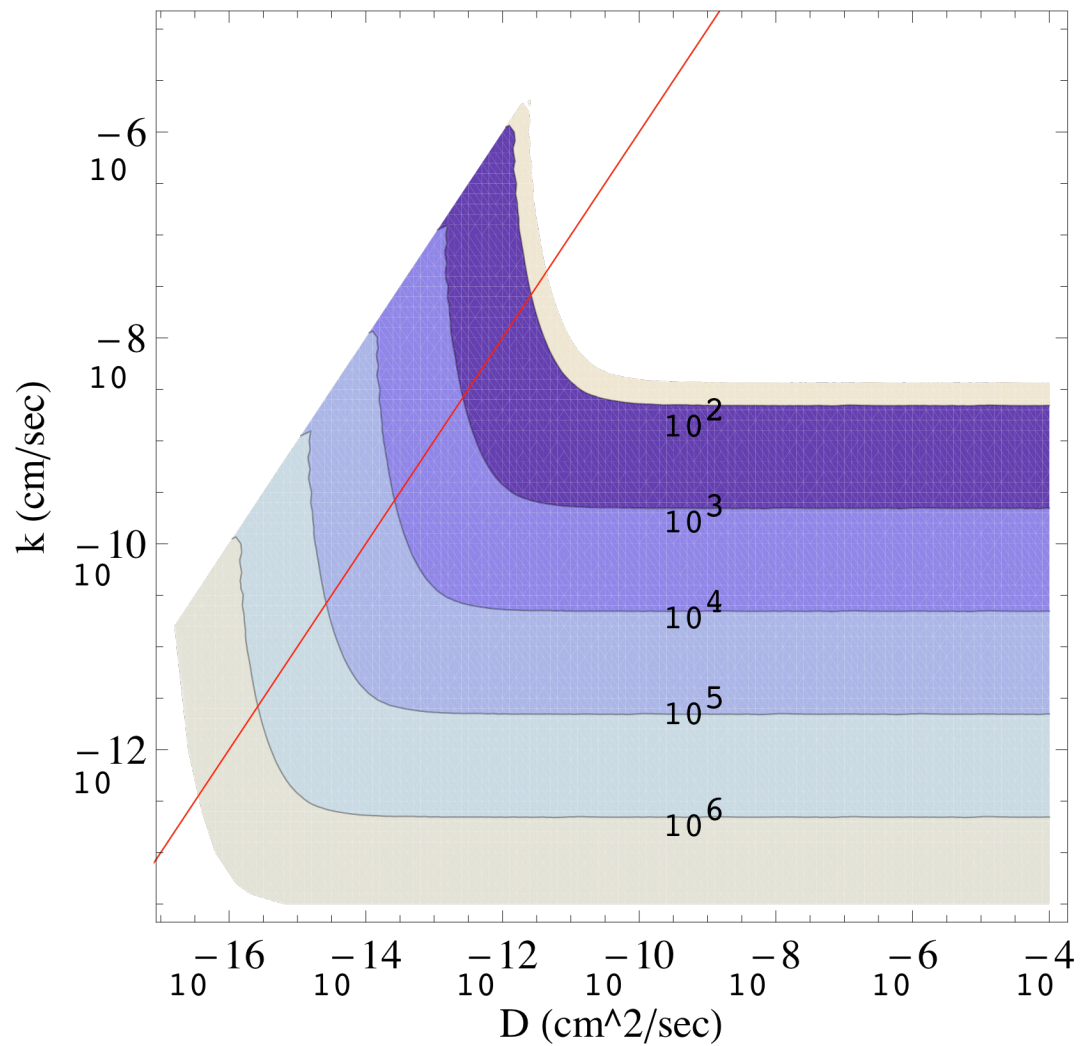


Figure A.10: Contour plot of the minimum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 1 micron thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

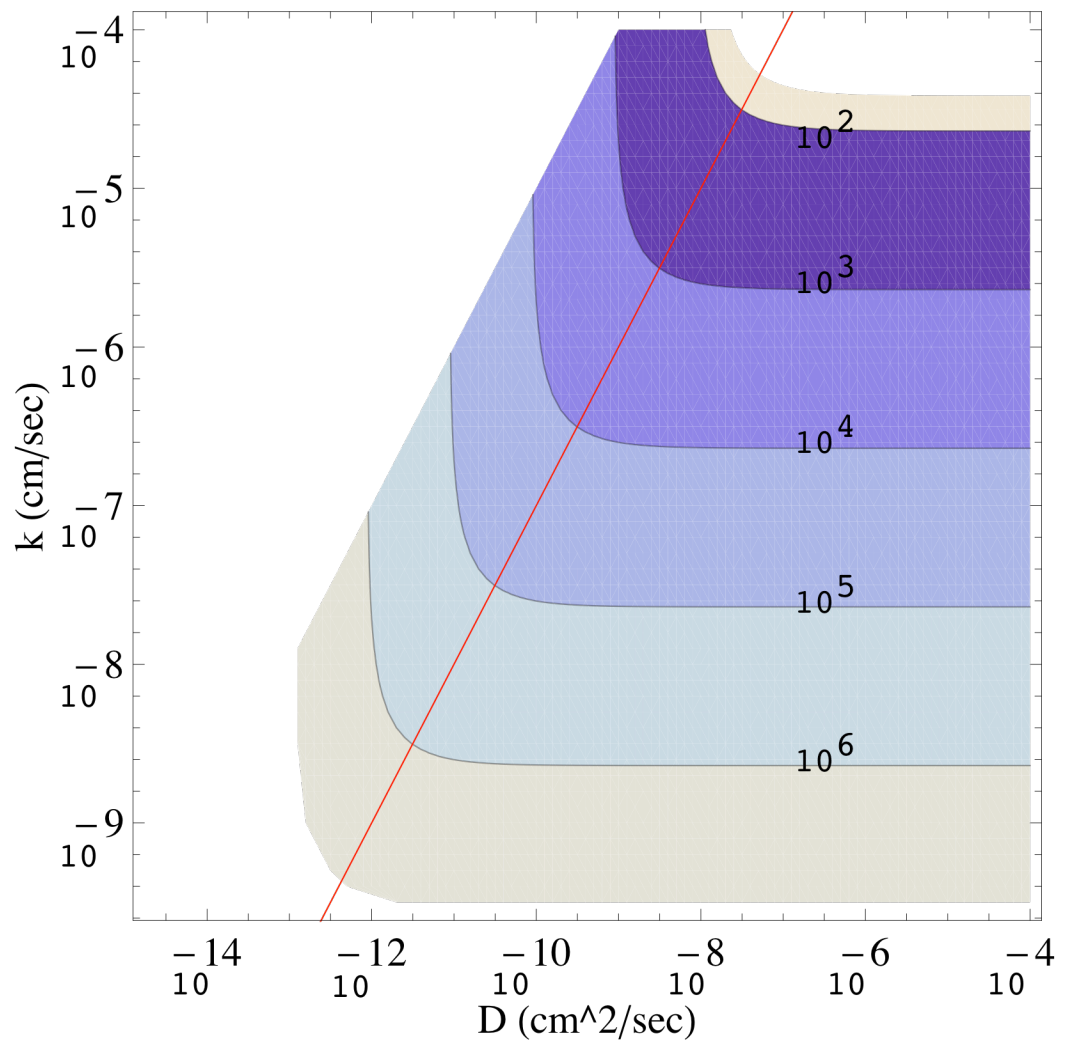


Figure A.11: Contour plot of the maximum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 10 micron thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

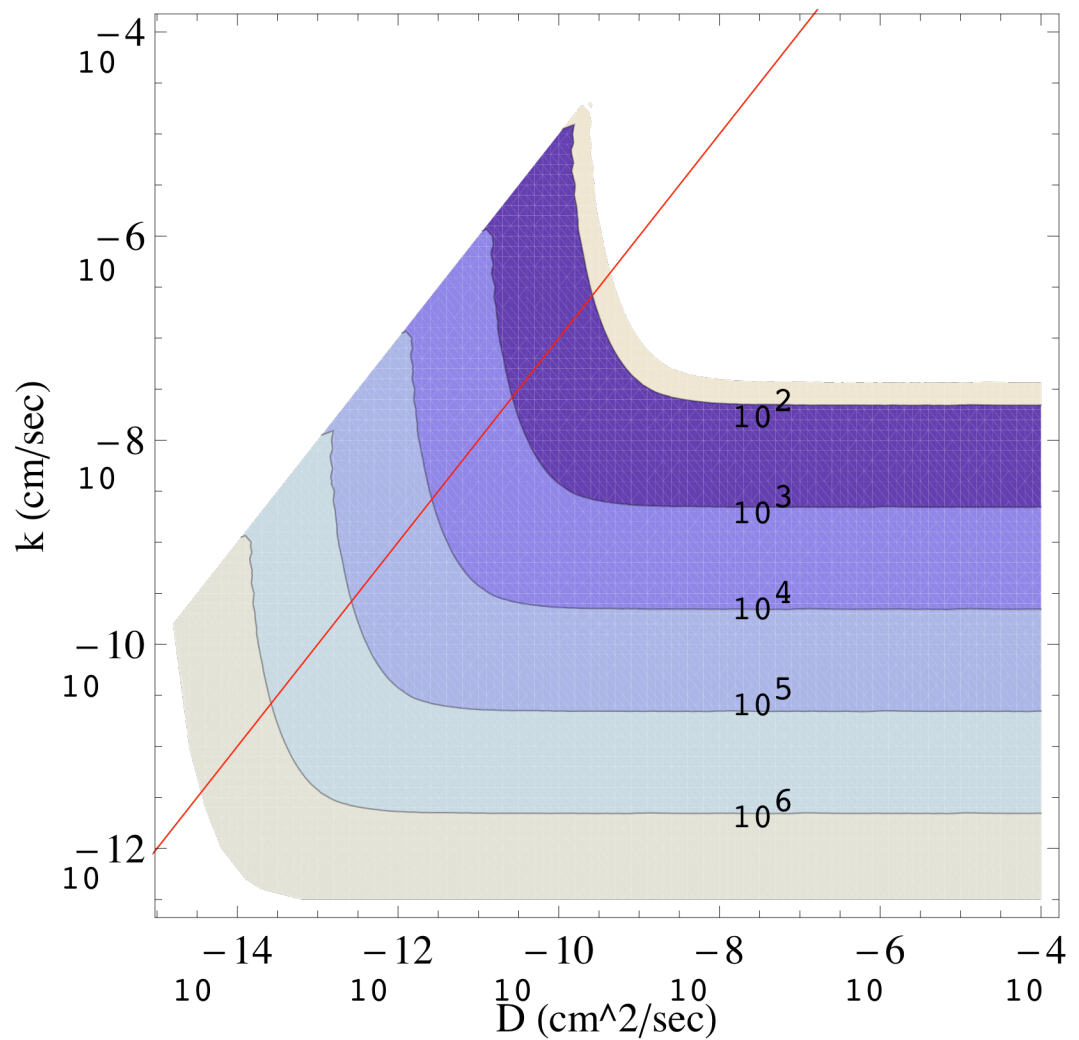


Figure A.12: Contour plot of the minimum exchange time required to measure k for a given surface exchange coefficient, k , and diffusivity, D , using a 10 micron thick film. The boundary conditions for the plane diffusion model are used. This contour plot is made for L values less than 100. L values greater than 100 require an increasingly large number of terms in the infinite sum to accurately determine the diffusion profile. An L value of 1 is marked with a red line.

Appendix B
MODELING PROGRAMS

Semi-infinite Diffusion Profiles

This program is designed to plot the diffusion profiles for specified surface exchange coefficient and bulk diffusion coefficient values using the semi-infinite diffusion model.

Constant Values

Clear all is used to remove any pre-assigned variables

```
ClearAll["Global`*"]
```

Here is the list of constants used in the plotting of the diffusion profiles. c_0 is the concentration of isotope in the exchange atmosphere. c_2 is the background level of isotope in the material. d is the bulk diffusion coefficient and k is the surface exchange coefficient used in the plotting. t is the exchange time in seconds.

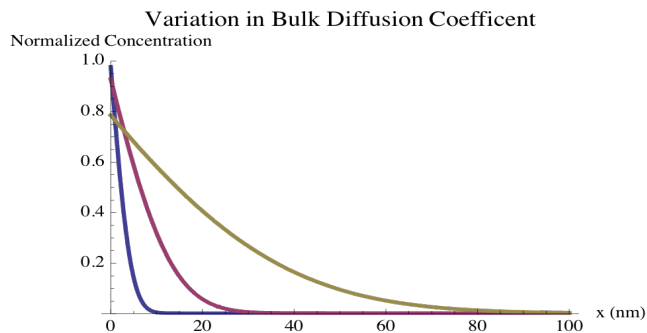
```
c0 = 1;  
c2 = 0.0022;  
d = {10^-15, 10^-14, 10^-13};  
k = 10^-7;  
t = 60;
```

The semi-infinite model of diffusion, si is the concentration as a function of x .

```
si = c2 + (c0 - c2) * (Erfc[x * (10^-7) / (2 * Sqrt[d * t])] - Exp[(k / d) * x * (10^-7) + (k / d)^2 * d * t] *  
Erfc[x * (10^-7) / (2 * Sqrt[d * t]) + (k / d) * Sqrt[d * t]]);
```

Plotting the diffusion profile for the specified range of x . The range showed below is $0 \leq x \leq 100$. Plot style details are entered below

```
Plot[si, {x, 0, 100}, PlotRange -> {0, 1}, PlotRange -> All,  
PlotStyle -> {Thick}, PlotLabel -> "Variation in Bulk Diffusion Coefficient",  
AxesLabel -> {"x (nm)", "Normalized Concentration"}]
```



Here the L values are found for the k and d values plotted

```
L = 10^-5 * k / d
```

Plane Diffusion Profile

This program is designed to plot diffusion profiles for a specified values of surface exchange coefficient, bulk diffusion coefficient and time using the plane diffusion model.

Constant Values

Clear all is used to remove any pre-assigned variables

```
ClearAll["Global`*"]
```

The variables of the diffusion equation are assigned. c_0 is the concentration of isotope/total oxygen in the exchange atmosphere. c_2 is the background concentration of ^{18}O /total oxygen. l is the thickness of the film. t is the exchange time. k is the surface exchange coefficient and d is the bulk diffusion coefficient.

```
c0 = 1;  
c2 = 0.0022;  
l = 1 * 10^-5;  
t = 60;  
k = 1 * 10^-8;  
d = 1 * 10^-12;
```

6 beta values are found based on the l , k , and d values assigned above. 6 points are used in the infinite sum

```
 $\beta_1 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{1\}\}];$   
 $\beta_2 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{3\}\}];$   
 $\beta_3 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{6\}\}];$   
 $\beta_4 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{9\}\}];$   
 $\beta_5 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{12\}\}];$   
 $\beta_6 = \beta /. \text{FindRoot}[\beta * \text{Tan}[\beta] == l * k / d, \{\beta, \{15\}\}];$ 
```

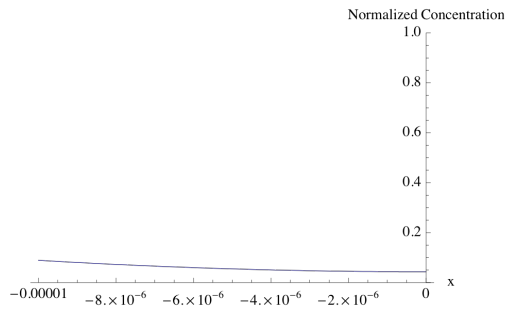
Diffusion profile plot

The diffusion profile is plotted using the plane diffusion model. The surface of the film is at the left of the plot and the substrate, with the zero flux boundary condition, is at $x=0$

```

Plot[{c2 + (c0 - c2) *
  (1 - ((2 * (1 * k / d) * Cos[β1 * x / l] * Exp[-((β1)^2 * d * t / l^2)]) / ((β1^2 + (1 * k / d)^2 +
    (1 * k / d)) * Cos[β1])) + ((2 * (1 * k / d) * Cos[β2 * x / l] * Exp[-((β2)^2 * d * t / l^2)]) /
    ((β2^2 + (1 * k / d)^2 + (1 * k / d)) * Cos[β2])) + ((2 * (1 * k / d) * Cos[β3 * x / l] *
    Exp[-((β3)^2 * d * t / l^2)]) / ((β3^2 + (1 * k / d)^2 + (1 * k / d)) * Cos[β3])) +
    ((2 * (1 * k / d) * Cos[β4 * x / l] * Exp[-((β4)^2 * d * t / l^2)]) /
    ((β4^2 + (1 * k / d)^2 + (1 * k / d)) * Cos[β4])) +
    ((2 * (1 * k / d) * Cos[β5 * x / l] * Exp[-((β5)^2 * d * t / l^2)]) /
    ((β5^2 + (1 * k / d)^2 + (1 * k / d)) * Cos[β5])) +
    ((2 * (1 * k / d) * Cos[β6 * x / l] * Exp[-((β6)^2 * d * t / l^2)]) /
    ((β6^2 + (1 * k / d)^2 + (1 * k / d)) * Cos[β6]))}],
{x, 0, -1 * 10^-5}, PlotRange -> {0, 1}, AxesLabel ->
{"x",
 "Normalized Concentration"},
LabelStyle -> {"larger"}]

```



L is calculated to ensure the system is a surface exchange limited system

$$L = 1 * k / d$$

$$\frac{1}{10}$$

Semi-infinite Contour Plots

This program is designed to make contour plots of the measurable surface exchange coefficients from thin film isotope exchange depth profiling using the semi-infinite diffusion model

Constant Values

Clear all is used to remove any pre-assigned variables

Here is the list of constant values used in this program. c_0 is the concentration of ^{18}O /total oxygen in the atmosphere found by exchanging a sample to saturation. c_2 is the concentration of ^{18}O /total oxygen present in air. x is the location where the specified concentration is measured. thicknessmin and thicknessmax are the minimum and maximum diffusion length. They are specified at $1/4$ th the minimum and maximum film thickness.

```
c0 = 1;
c2 = 0.0022;
x = 0;
thicknessmin = (1 / 4) * (7.5 * 10^-7);
thicknessmax = (1 / 4) * (10 * 10^-4);
```

t is the range of exchange times used to make a grid of points. the grid of points will be used to evaluate the diffusion equation

```
t = {3 * 30 * 24 * 3600, 30 * 24 * 3600, 7 * 24 * 3600, 24 * 3600, 3600, 5 * 60};
```

minD and maxD are the minimum and maximum bulk diffusion coefficients derived from the diffusion length

```
minD = thicknessmin^2. / t;
maxD = thicknessmax^2. / t;
```

A range of d values is created from the minimum to the maximum diffusion coefficient values with three points for each order of magnitude

```
d = {minD, minD * 10 * (1 / 3), minD * 10 * (2 / 3), minD * 10,
minD * 10^2 * (1 / 3), minD * 10^2 * (2 / 3), minD * 10^2, minD * 10^3 * (1 / 3),
minD * 10^3 * (2 / 3), minD * 10^3, minD * 10^4 * (1 / 3), minD * 10^4 * (2 / 3), minD * 10^4,
minD * 10^5 * (1 / 3), minD * 10^5 * (2 / 3), minD * 10^5, maxD / 3, maxD * 2 / 3, maxD};
```

Initiate lists for the k values corresponding to the solutions of the minimum and maximum concentrations of ^{18}O /total oxygen allowed

```
kmin = {};
kmax = {};
```

Solution to the semi-infinite diffusion equation

This iteratively evaluates the semi-infinite diffusion equation for each combination of time and bulk diffusion coefficient from the lists above to solve for surface exchange coefficient. Lists are created with column 1 being the bulk diffusion coefficient, column 2 being the exchange time and column 3 being the surface exchange coefficient.

```

Do[Do[k = k /. FindRoot[
  0.44 == c2 + (c0 - c2) * (Erfc[x / (2 * Sqrt[d * t[[n]]]]) - Exp[(k / d) * x + (k / d) ^ 2 * d * t[[n]]] *
  Erfc[x / (2 * Sqrt[d * t[[n]]]) + (k / d) * Sqrt[d * t[[n]]]], {k, 10^-13}];
  AppendTo[kmin, {d, t[[n]], k}];, {d, d[[All, n]]}], {n, 1, 6}];
Do[Do[k = k /. FindRoot[.9 == c2 + (c0 - c2) * (Erfc[x / (2 * Sqrt[d * t[[n]]]]) - Exp[(k / d) * x +
  (k / d) ^ 2 * d * t[[n]]] * Erfc[x / (2 * Sqrt[d * t[[n]]]) + (k / d) * Sqrt[d * t[[n]]]],
  {k, 10^-13}]; AppendTo[kmax, {d, t[[n]], k}];, {d, d[[All, n]]}], {n, 1, 6}];

```

Contour Plots

The log of the kmin and kmax lists is taken so that the values can be plotted on a log scale contour plot

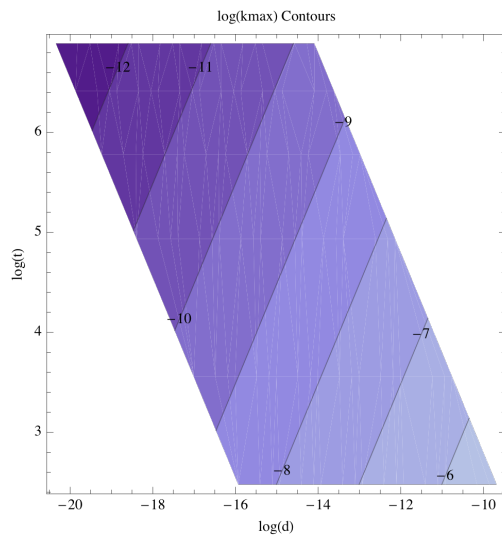
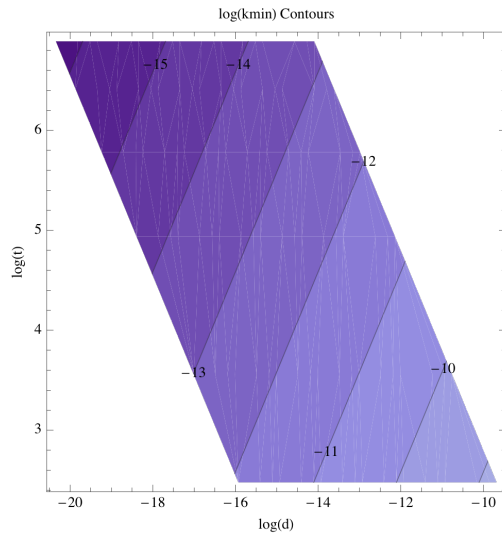
```

kminlog = Log10[kmin];
kmaxlog = Log10[kmax];

```

Contour plots are made from the list of kmin and kmax

```
ListContourPlot[{kminlog}, ContourLabels → All,
  FrameLabel → {"log(d)", "log(t)", "log(kmin) Contours"}]
ListContourPlot[{kmaxlog}, ContourLabels → All,
  FrameLabel → {"log(d)", "log(t)", "log(kmax) Contours"}]
```



Labels are prepended to the lists

```
kmin = Prepend[kmin, {"d", "t", "k"}];
kmax = Prepend[kmax, {"d", "t", "k"}];
```

Lists are exported to excel files


```
Export["kmin.xls", kmin];  
Export["kmax.xls", kmax];
```

Thin Film IEDP Capabilities

In this program we show viable combinations of k, D and t values that are accurate solutions to the diffusion equation for a plane sheet with surface evaporation.

Assigning Variables

Clear all assigned variables

```
ClearAll["Global`*"]
```

Assign variables, create blank lists and define the range of exponents of k and D (n,m) . In this code d is used for D because D is protected

```
c0 = 100;  
c2 = 0.22;  
x = .5 * 1;  
n = Range[4, 17, .1];  
m = Range[4, 17, .1];  
kmin = {}; kmax = {}; LValues = {};  
tmin = 10;  
tmax = 3 * 30 * 24 * 3600;  
Cmax = .9 * 100;  
Cmin = 2 * .44;  
l = 10 * 10^-5;
```

Creating lists of k, D, L, and beta values

Form a list of k and D using the n and m range defined above

```
k = Flatten[{10^-n}];  
d = Flatten[{10^-m}];
```

Create a list of L values which range from the largest k over the smallest D to the smallest k over the largest D

```
LValues = 10^Range[Log10[1 * Last[k] / First[d]], Log10[1 * First[k] / Last[d]], 0.1];
```

Export the list of L values to the matlab folder so that the matlab code can be used to create a table of every beta value needed for this range. For this program the first 6 beta values are used to ensure accuracy

```
Export["MATLAB/LValues.xls", LValues]  
  
MATLAB/LValues.xls
```

Import the beta values and create tables for each beta value where the first column is the L value and the second column is the corresponding beta value

```
b = Flatten[Import["Desktop/betavalues.xls"], 1];  
b1 = Table[{LValues[[p]], b[[p, 1]]}, {p, 1, Length[LValues]}];  
b2 = Table[{LValues[[p]], b[[p, 2]]}, {p, 1, Length[LValues]}];  
b3 = Table[{LValues[[p]], b[[p, 3]]}, {p, 1, Length[LValues]}];  
b4 = Table[{LValues[[p]], b[[p, 4]]}, {p, 1, Length[LValues]}];  
b5 = Table[{LValues[[p]], b[[p, 5]]}, {p, 1, Length[LValues]}];  
b6 = Table[{LValues[[p]], b[[p, 6]]}, {p, 1, Length[LValues]}];
```

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Interpolating functions are used so that the beta values can be read from the list and imputed into the function. Interpolating functions are made for each beta value

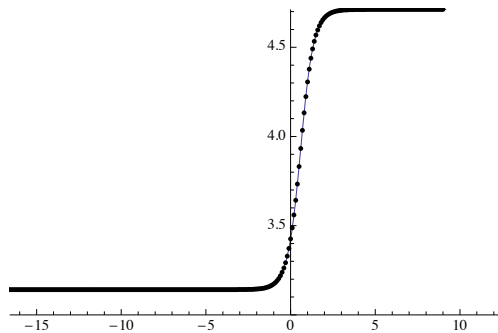
```

 $\beta_1$  = Interpolation[b1];
 $\beta_2$  = Interpolation[b2];
 $\beta_3$  = Interpolation[b3];
 $\beta_4$  = Interpolation[b4];
 $\beta_5$  = Interpolation[b5];
 $\beta_6$  = Interpolation[b6];

b2[All, 1] = Log10[b2[All, 1]];

Plot[ $\beta_2[10^L]$ , {L, -16, 12}, PlotRange  $\rightarrow$  {3,  $3\pi/2$ }, Epilog  $\rightarrow$  Map[Point, b2]]

```



Solving Diffusion Model For t

Here the solutions are found for each combination of k and D . This is done by finding time t for specified k and D values, then looping the k and D values for every value in the range. The values of D , t and k are appended to a list. For this solution the concentration at the midpoint is 90% of the atmosphere concentration which is the upper bound of concentration

```

Do[Do[L = 1 * k[[n]] / d[[m]];
  t = t /. FindRoot[{Cmax == c2 + (c0 - c2) * (1 - ((2 * (L) * Cos[β1[L] * x / 1) *
    Exp[-((β1[L])^2 * d[[m]) * t / 1^2]]) / (((β1[L])^2 + (L)^2 + (L)) * Cos[β1[L]])) +
    ((2 * (L) * Cos[β2[L] * x / 1) * Exp[-((β2[L])^2 * d[[m]) * t / 1^2]]) /
    (((β2[L])^2 + (L)^2 + (L)) * Cos[β2[L]]) + ((2 * (L) * Cos[β3[L] * x / 1) *
    Exp[-((β3[L])^2 * d[[m]) * t / 1^2]]) / (((β3[L])^2 + (L)^2 + (L)) * Cos[β3[L]]) +
    ((2 * (L) * Cos[β4[L] * x / 1) * Exp[-((β4[L])^2 * d[[m]) * t / 1^2]]) /
    (((β4[L])^2 + (L)^2 + (L)) * Cos[β4[L]]) + ((2 * (L) * Cos[β5[L] * x / 1) *
    Exp[-((β5[L])^2 * d[[m]) * t / 1^2]]) / (((β5[L])^2 + (L)^2 + (L)) * Cos[β5[L]]) +
    ((2 * (L) * Cos[β6[L] * x / 1) * Exp[-((β6[L])^2 * d[[m]) * t / 1^2]]) /
    (((β6[L])^2 + (L)^2 + (L)) * Cos[β6[L]]))}],
  {t, 1}, Method → "Secant"]; If[L ≤ 100 000 000, If[tmax >
  t,
  tmin,
  AppendTo[
    kmax,
    {Log10[d[[m]]],
    Log10[t],
    Log10[k[[n]]}]]],
{n, 1, Length[k]}, {m, 1, Length[
d]}]

```

Here the solution is found as above with the concentration at the midpoint being 2 times background concentration (0.44)

```

Do[Do[L = 1 * k[[n]] / d[[m]];
  t = t /. FindRoot[
    {Cmin == c2 + (c0 - c2) * (1 - ((2 * (L) * Cos[β1[L] * x / 1] * Exp[-((β1[L])^2 * d[[m]] * t / 1^2)) /
      ((β1[L])^2 + (L)^2 + (L) * Cos[β1[L]])) + ((2 * (L) * Cos[β2[L] * x / 1] *
      Exp[-((β2[L])^2 * d[[m]] * t / 1^2)) / ((β2[L])^2 + (L)^2 + (L) * Cos[β2[L]])) +
      ((2 * (L) * Cos[β3[L] * x / 1] * Exp[-((β3[L])^2 * d[[m]] * t / 1^2)) /
      ((β3[L])^2 + (L)^2 + (L) * Cos[β3[L]])) + ((2 * (L) * Cos[β4[L] * x / 1] *
      Exp[-((β4[L])^2 * d[[m]] * t / 1^2)) / ((β4[L])^2 + (L)^2 + (L) * Cos[β4[L]])) +
      ((2 * (L) * Cos[β5[L] * x / 1] * Exp[-((β5[L])^2 * d[[m]] * t / 1^2)) /
      ((β5[L])^2 + (L)^2 + (L) * Cos[β5[L]])) + ((2 * (L) * Cos[β6[L] * x / 1] * Exp[
      -((β6[L])^2 * d[[m]] * t / 1^2)) / ((β6[L])^2 + (L)^2 + (L) * Cos[β6[L]]))}],
    {t, 1}, Method -> "Secant"]; If[L ≤ 1 000 000 000, If[tmax >
  t >
  tmin,
AppendTo[
  kmin,
  {Log10[d[[m]]],
  Log10[t],
  Log10[k[[n]]]}],
{n, 1, Length[k]}], {m, 1, Length[
d]}]

```

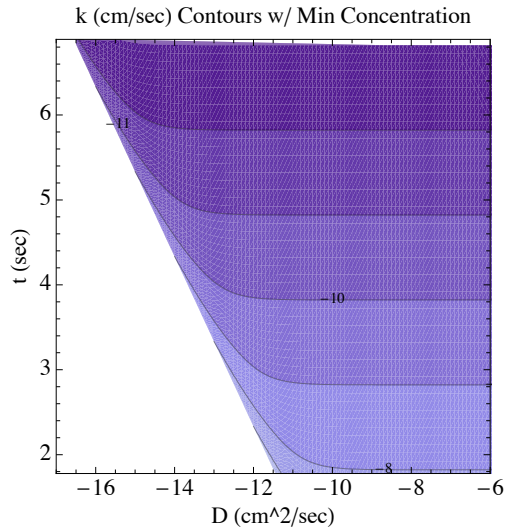
Contour Plots

Contours are created using the solutions above. Contours of k are plotted with D on the x axis and time on the y axis. Log scale is used

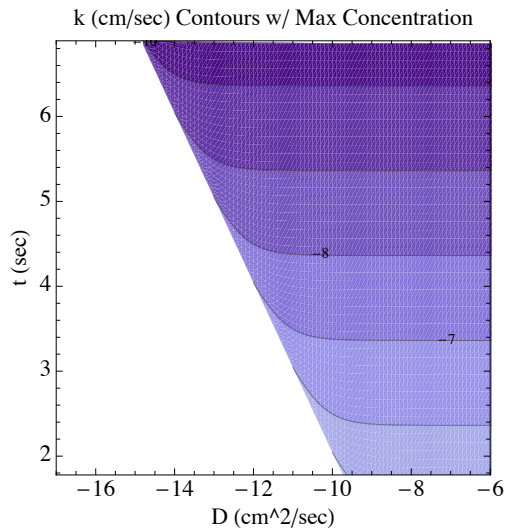
```

ListContourPlot[{kmin}, PlotRange -> {{-17, -6}, {Log10[60], Log10[3 * 30 * 24 * 3600]}},
PlotRangeClipping -> True, ContourLabels -> All,
FrameLabel -> {"D (cm^2/sec)", "t (sec)", "k (cm/sec) Contours w/ Min Concentration"},
LabelStyle -> Directive[Larger]]

```



```
ListContourPlot[{kmax},
  PlotRange -> {{-17, -6}, {Log10[60], Log10[3 * 30 * 24 * 3600]}}, ContourLabels -> All,
  FrameLabel -> {"D (cm^2/sec)", "t (sec)", "k (cm/sec) Contours w/ Max Concentration"},
  LabelStyle -> Directive[Larger]]
```

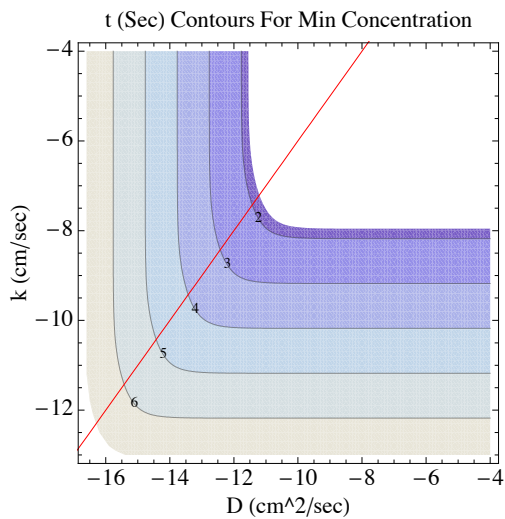
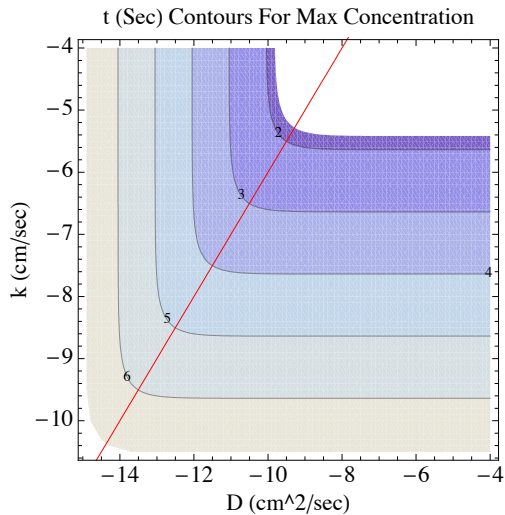


Here the order of the lists are changed. now column 1 is D, column 2 is k, and Column 3 is t

```
tmax = Table[{kmax[[n, 1]], kmax[[n, 3]], kmax[[n, 2]]}, {n, 1, Length[kmax]}];
tmin = Table[{kmin[[n, 1]], kmin[[n, 3]], kmin[[n, 2]]}, {n, 1, Length[kmin]}];
```

Contour Plots are created for contours of time. D is on the x axis and k is on the y axis. The red lines shown are for L values of 10, 1, and 0.1

```
Show[ListContourPlot[{tmax},
  PlotRange -> {Log10[60], Log10[3 * 30 * 24 * 3600]}, ContourLabels -> All,
  FrameLabel -> {"D (cm^2/sec)", "k (cm/sec)", "t (Sec) Contours For Max Concentration"},
  LabelStyle -> Directive[Larger]], Plot[Log10[1 * 10^d / 1], {d, -17, -6}, PlotStyle -> Red]]
Show[ListContourPlot[{tmin}, PlotRange -> {Log10[60], Log10[3 * 30 * 24 * 3600]}, ContourLabels ->
  All, FrameLabel -> {"D (cm^2/sec)", "k (cm/sec)", "t (Sec) Contours For Min Concentration"},
  LabelStyle -> Directive[Larger]], Plot[Log10[1 * 10^d / 1], {d, -17, -6}, PlotStyle -> Red]]
```



Export the data to excel files

```
Export["tmin10000nm.xls", tmin];
Export["tmax10000nm.xls", tmax];
```

```

Lval=[];
LValues=xlsread('LValues');
LValues=LValues';
for n=1:length(LValues)
L=diffbeta(LValues(n));
Lval=[Lval;L];
end
xlswrite('betavalues.xls',Lval)

```

```

function y = diffbeta(L)
%DiffBeta Zeroes of the Crank thin plane diffusion 'Beta function'.
% Y = DiffBeta(L) computes the zeroes of
% B*tan(B)=L
%
% Given that the zeroes can be estimated at:
% n*pi, for L<1e-10
% (2n+1)*pi/2, for L>1e10
% and between these two intervals for 1e-10<L<1e10

if L<1e-30
y=[0:5]*pi;
elseif L>1e10
y=(2*[0:5]+1)*(pi/2);
else
for n=0:5
y(n+1)=fzero(@(x) (x*tan(x))-L, [(n*pi), (2*n+1)*(pi/2)-
1e5*eps]);
end
end
end

```

Thin Film Data Fitting

This program is made to fit SIMS data for a thin film 18O exchange. Data to be provided in .xls form

Constant Values

Clear all is used to remove any pre-assigned variables

```
ClearAll["Global`*"]
```

Here is the list of constants used in this data fitting. c0 is the concentration of 18O/total oxygen in the atmosphere found by exchanging a sample to saturation. c2 is the concentration of 18O/total oxygen present in air. l is the thickness of the material. n and m are lists of exponents for k and d. the range is taken to be wide so that the data can be fit any values of k and d in the region. LValues is a list to be made shortly.

```
c0 = 76.5 / 100;  
c2 = 0.22 / 100;  
l = 1.02 * 10^-5;  
n = Range[6, 15, .1];  
m = Range[6, 17, .1];  
LValues = {};
```

list of possible k and d values are made using the exponents decided above. These lists are used to make beta values.

```
k = Flatten[{10^-n}];  
d = Flatten[{10^-m}];
```

A list of L values is made using the values from the list of k and d

```
LValues = 10^Range[Log10[1*Last[k] / First[d]], Log10[1*First[k] / Last[d]], 0.1];
```

The L values list is exported to a MATLAB folder to have a MATLAB program create a list of every possible beta value for all the combinations of L. The file is exported as a .xls file.

```
Export["MATLAB/LValues.xls", LValues]
```

```
MATLAB/LValues.xls
```

From here the user should open MATLAB and create the list of beta values for the data. This must be done before continuing on to the next section.

β values

The list of beta values are imported from MATLAB and made into a list of L values, beta values

```
b = Flatten[Import["Desktop/betavalues.xls"], 1];  
b1 = Table[{LValues[[p]], b[[p, 1]]}, {p, 1, Length[LValues]}];  
b2 = Table[{LValues[[p]], b[[p, 2]]}, {p, 1, Length[LValues]}];  
b3 = Table[{LValues[[p]], b[[p, 3]]}, {p, 1, Length[LValues]}];  
b4 = Table[{LValues[[p]], b[[p, 4]]}, {p, 1, Length[LValues]}];  
b5 = Table[{LValues[[p]], b[[p, 5]]}, {p, 1, Length[LValues]}];  
b6 = Table[{LValues[[p]], b[[p, 6]]}, {p, 1, Length[LValues]}];
```

An interpolation function is used to give beta values for the entire range of L values.


```

 $\beta 1 = \text{Interpolation}[b1];$ 
 $\beta 2 = \text{Interpolation}[b2];$ 
 $\beta 3 = \text{Interpolation}[b3];$ 
 $\beta 4 = \text{Interpolation}[b4];$ 
 $\beta 5 = \text{Interpolation}[b5];$ 
 $\beta 6 = \text{Interpolation}[b6];$ 

```

Fitting the data

The data is imported from an .xls file and made into a list called data. It is flattened to prevent extra brackets from interfering with the data fitting. The data must be entered in this form, column 1 is x values, column 2 is 18O/total oxygen

```
data = Flatten[Import["Desktop/SrCoO3_400C_60min.xls"], 1];
```

k and d values are cleared so that they can be variables to be fitted

```
Clear[k, d];
```

The fitting model is described below. This model is Cranks Plane diffusion model with surface evaporation. 6 roots of beta are used in the infinite sum.

```

model = c2 + (c0 - c2) *
  (1 - ((2 * (L) * Cos[beta1[L] * x / 1] * Exp[-((beta1[L])^2 * d * t / 1^2)]) / ((beta1[L]^2 + (L)^2 + (L)) *
    Cos[beta1[L]])) + ((2 * (L) * Cos[beta2[L] * x / 1] * Exp[-((beta2[L])^2 * d * t / 1^2)]) /
    ((beta2[L]^2 + (L)^2 + (L)) * Cos[beta2[L]])) + ((2 * (L) * Cos[beta3[L] * x / 1] *
    Exp[-((beta3[L])^2 * d * t / 1^2)]) / ((beta3[L]^2 + (L)^2 + (L)) * Cos[beta3[L]])) +
  ((2 * (L) * Cos[beta4[L] * x / 1] * Exp[-((beta4[L])^2 * d * t / 1^2)]) /
    ((beta4[L]^2 + (L)^2 + (L)) * Cos[beta4[L]])) +
  ((2 * (L) * Cos[beta5[L] * x / 1] * Exp[-((beta5[L])^2 * d * t / 1^2)]) /
    ((beta5[L]^2 + (L)^2 + (L)) * Cos[beta5[L]])) +
  ((2 * (L) * Cos[beta6[L] * x / 1] * Exp[-((beta6[L])^2 * d * t / 1^2)]) /
    ((beta6[L]^2 + (L)^2 + (L)) * Cos[beta6[L]]));

```

L and t are decided so that beta values can be pulled based on their corresponding L values and t is constant.

```

L = 1 * k / d;
t = 3600;

```

Initial guesses are needed to fit the model. The solution does not vary depending on initial guess as long as the guess is not many orders of magnitude off. Some issues can arise for if guesses of k and d values are far off involving overflow and underflow where the numbers become smaller or larger than machine precision. This is fixed with better initial guesses

```

kguess = 10^-9;
dguess = 10^-14;

```

NonlinearModelFit is used to fit the data to the model described above.

```
fit = NonlinearModelFit[data, model, {{k, kguess}, {d, dguess}}, x, MaxIterations -> 100]
```

```
FittedModel[0.0022 + 0.7628 (1 - <<19>> Cos[<<1>>] + <<6>> + 7.83561 × 10-131 Cos[1.54155 × 106 x])]
```

Parameter table shows the best fit values for k and d with their standard error. ParameterConfidenceInterval shows a 95% confidence region for k and d.

```
fit["ParameterTable"]
fit["ParameterConfidenceIntervals"]
```

	Estimate	Standard Error	t-Statistic	P-Value
k	9.89094×10^{-10}	6.31494×10^{-12}	156.628	$3.128908642138 \times 10^{-715}$
d	3.43121×10^{-14}	1.80658×10^{-15}	18.9928	4.2444×10^{-69}
	$\{\{9.76702 \times 10^{-10}, 1.00149 \times 10^{-9}\}, \{3.0767 \times 10^{-14}, 3.78571 \times 10^{-14}\}\}$			

This plot shows the data and the fit together. 0 on the x-axis corresponds to the substrate and the oxygen is diffused from left to right

```
Show[ListPlot[data, PlotRange -> {0, 1}, AxesLabel -> {"x (cm)", "18O / Total Oxygen"},
LabelStyle -> Directive[Bold, Larger]], Plot[fit[x], {x, -1, 0}, PlotStyle -> {Red}]]
```

