Microstructure and electrical properties of platinum thick film electrodes

Steven D. Toteda
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MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF PLATINUM THICK FILM ELECTRODES

by

Steven D. Toteda

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Abstract

The microstructure of the platinum electrodes used in zirconia oxygen sensors defines the resulting electrical response. At low firing temperatures, the platinum is highly porous and resembles an agglomeration of fine particles. Since the platinum acts as a catalyst, dissociating oxygen at the surface, the oxygen must diffuse along the platinum surface to reach the zirconia substrate. The platinum particles sinter together as the firing temperatures are increased. As the firing temperatures are raised even further, the surface of the platinum becomes smoother and begins to facet due to surface energy anisotropy. A computer program written for calculating the fractal dimension from a digitized portion of the micrograph allows a roughness parameter of the platinum electrode to be measured and thus correlated to the impedance data. The use of the fractal dimension to correlate the impedance response to the microstructure shows an inverse relationship. As the surface roughness is decreased, the value for α in the impedance equation increases. The experimental data for the overall response fits a theoretical treatment predicting such behavior.
Chapter 1

Introduction

Zirconia oxygen sensors are used to monitor the concentration of oxygen in a gas stream due to the selective transport of oxygen ions in yttria stabilized zirconia. Automobile engines require such devices to monitor and control the air-to-fuel ratio (A/F) to reduce engine emissions and fuel consumption. The A/F is defined as the ratio of the mass of air to the mass of fuel just before combustion. The stoichiometric A/F is that which contains just enough oxygen to convert all the hydrocarbons in the fuel to CO$\text{}_2$ and water. Precise control of this parameter is important since a fuel-rich mixture results in the emission of CO and H$_2$ as well as the unburned hydrocarbons. Fuel-lean ratios result in excess oxygen which, when combined with the nitrogen in the air at high temperatures, produces oxides of nitrogen (NO$\text{x}$). Thus, the primary use of this device in automobiles is to control the air/fuel mixture for pollution control.

In such applications as power plants and automobiles, these sensors generally use platinum electrodes for both electrical contact and the catalytic reaction to dissociate oxygen at the surface. The platinum electrode must be porous enough to allow the oxygen to reach the zirconia surface while still remaining electrically continuous. The microstructure of this film at the surface can be dramatically altered by changing the
sintering conditions, which affects the electrical response of the sensor. The modeling of such sensors generally leads to lumped resistance and capacitance terms, which are macroscopic equivalents and tend to lose a physical meaning at the molecular level [1]. Microscopic changes in the surface of the platinum due to various sintering temperatures, and the resulting changes in electrical response, reveal the physical nature of the limiting mechanisms of the platinum electrodes.

The microstructure of the electrode defines the resulting impedance response. At low firing temperatures, the platinum is highly porous and resembles an agglomeration of fine particles. Since the platinum acts as an oxygen dissociation catalyst, the oxygen must then diffuse along the platinum surface to reach the zirconia substrate. The platinum particles sinter together as the firing temperatures are increased. As the firing temperatures are raised even further, the surface of the platinum begins to facet due to surface energy anisotropy.

The reaction at the electrode surface can be correlated to the overall resistance and capacitance determined by impedance measurements. The capacitance information is dependent upon the geometric constraints placed on the film by processing. The resistance is linked to thermally activated processes, such as surface diffusion and the electron transfer step. By monitoring the changes in the impedance response, the changes in the microstructure can be quantified. A zirconia oxygen sensor with these parameters optimized, should perform well under service conditions.
Chapter 2

Background

2.1 Oxygen Sensor Structure and Operation

The device generally used to sense oxygen at the present time is an oxygen concentration cell consisting of yttria-stabilized zirconia electrolyte between two platinum electrodes [2]. The interest in zirconia stems from the ability of this material to selectively transport oxygen. By doping it with metal oxides of the form $M_2O_3$, a fluorite structure with a high equilibrium concentration of vacancies is produced. In this case, yttrium, $Y^{3+}$, will substitute on the zirconium, $Zr^{4+}$, site. The substitution reaction is shown here in Kroger-Vink notation:

$$Y_2O_3 \leftrightarrow 2Y^{3+} + V^{2-}_O + 3O_2$$  \hspace{1cm} (2.1)

The structure is very important in understanding the diffusion mechanisms. In the fluorite structure, $Zr^{4+}$ ions are arranged in face-centered cubic form with the oxygen anions arranged in a simple cubic packing in the four tetrahedral interstices. A typical lattice is shown in Figure 2.1. The zirconia electrolyte is of a class of materials known as fast ion transport solid electrolytes which allow ions (in this case
O\textsuperscript{2-}) to be conducted at high rates through zirconia [3]. The oxygen vacancies allow the oxygen ions to diffuse through the lattice by jumping to these highly favorable sites. The activation energy for such a jump will be rather low due to the favorable surroundings for the oxygen and the ionic conduction should be measurable. In reality, the resistance to current flow is very low above 500\textdegree{} or 600\textdegree{}C. With such favorable diffusion conditions, the mechanisms for diffusion as well as the diffusion coefficients have been carefully observed in these systems [4, 5, 6, 7, 8].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fluorite_structure.png}
\caption{Unit cell of the fluorite structure.}
\end{figure}

The typical ZrO\textsubscript{2} sensor is in the shape of a thimble with platinum electrodes deposited on both the inner and outer surfaces. A diagram is provided in Figure 2.2.
The outer electrode facing the gas to be measured is generally protected from erosion by a porous oxide layer that also restricts the amount of gas reaching the electrode. The internal surface of the thimble is exposed to a reference environment of ambient air. The difference in oxygen partial pressure between the inside, $P_2$, and the outside, $P_1$, drives the ion transport, causing an electromotive force (emf) to be developed between the electrodes according to the Nernst equation [9]:

$$emf = \frac{RT \log \left( \frac{P_2}{P_1} \right)}{4F}$$

(2.2)

Where constants $R$, $T$, and $F$, are the gas constant, the temperature, and the Faraday constant, respectively. This voltage is created through an electrochemical reaction with the platinum electrode, the doped zirconia, and the gas phase containing the oxygen. The three phases will be present at what will be termed the triple point. This dissociation reaction is written as:

$$O_2 + 4e^- \rightarrow 2O^{2^-}$$

(2.3)

The temperature range for an automobile oxygen sensor, for example, would be roughly 500° to 900°C. At these temperatures, the electrodes applied to the surface (mostly platinum) limit the performance of the sensor [10]. The effectiveness of the sensor will be reduced if there is a slow response time to a change in oxygen partial pressure. A low response voltage will also reduce the effectiveness of the sensor.

Since oxygen will not readily diffuse through the platinum lattice, surface diffusion of the dissociated oxygen ions will be the important mechanism for oxygen transport to the triple point, where it will enter the zirconia. The diffusion coefficient measurements for this process are few and inaccurate because of the difficulty in controlling the microstructure of the diffusion surface [11].
Figure 2.2: Schematic of a typical ZrO₂ sensor.
However, it is not enough for the ZrO₂ sensor to just detect oxygen. For automotive applications, the device must detect oxygen under severe thermal and chemical conditions that change rapidly as the engine warms and as acceleration varies. Detection performance of the sensor is favored by porous platinum electrodes that have a high surface area to provide good gas transport and high catalytic activity at the platinum electrode surface. The magnitude of the step-like change (see Figure 2.3) in the emf versus A/F ratio relationship of the sensor increases with the catalytic activity of the electrode, which should improve with increased platinum surface area [12]. But the need for durability of the device under adverse engine operating conditions demands that the electrode be thick enough to be mechanically stable. In addition, the same high temperatures (600-900 degrees Celsius) that allow rapid diffusion of oxygen through the zirconia also will tend to cause changes in performance due to electrode aging [13]. Thus, while it is clear that the microstructure of the platinum-zirconia interface plays a major role in the performance of the sensor, the open literature does not suggest that this microstructural aspect has been fully characterized and related to sensor performance. This microstructural characterization is now possible with advanced electron optical instruments and characterization techniques.

2.2 Complex Impedance Response

The microstructure of the sensor electrodes can be studied using a small amplitude (< 50mV) ac signal applied across the inner and outer electrodes. The resulting output can be measured and is termed the impedance response. This will be discussed in detail. The usefulness of this technique stems from the ability to monitor very small changes in the microstructure as well as supplementary information about the reactive mechanisms at the electrode [14]. Simple measurements, like cell resistance, can be
Figure 2.3: Emf versus air-to-fuel (A/F) ratio for typical ZrO₂ sensor.
made with this technique [12]. In the past, impedance measurements have been used successfully to determine the conductivity contribution of the electrolyte grain and grain boundary. More importantly, the presence of second phases at the grain boundary, such as alumina or other insulating phases, is easily determined [15]. The electrode resistance can also be measured quite easily. Such increases in electrolyte and electrode resistance due to microstructural changes are detrimental to the overall performance of an oxygen sensor. High resistances will make the sensor prone to electrical noise [13].

The aging of the sensor electrodes can also be monitored through these techniques. A study of sensor lifetimes defines the useful “life” of a zirconia sensor with platinum electrodes as the operating time during which the sensor impedance increases by less than a factor of 3 [16]. It is interesting to note that the actual sensor output (in mV) in a lifetime test decreased by less than 3% when operated at 700°C for 2000 hours (3 fold increase in impedance).\(^1\) From this lifetime test, it is clear that the impedance test is very sensitive to a change in the microstructure.

By definition, impedance is the ratio of the voltage to the current in a system under an applied signal. Normally this signal would be an ac signal (sinusoidal) [17]. By applying a signal of a known frequency and amplitude, the overall response is determined, but in a “black box” fashion. The overall response can be broken up into basic elements and more can be learned about the electrical properties and elements of the electrical circuit, which can be correlated to physical processes.

Electrical circuits contain such things as resistors and capacitors of discrete values. Each will respond differently to a known electrical signal. A resistor, R, will essentially restrict the incoming current and a voltage will build up across the resistive element (see Equation 2.4). A capacitor, C, will respond by differentiating the voltage with

\(^1\)Figure 5 in [16]
respects to time (Equation 2.5). By using an example of a voltage, $v$, or current, $i$, the mathematical description of the component and the output for each element, when an input signal of $A \cos \omega t$ is applied, is given in Equation 2.4 and Equation 2.5. The value of $v$ in the first part of Equation 2.4 is replaced by $A \cos \omega t$ and scaled by $R$ to give the response. Replacing $v$ in Equation 2.5 with $A \cos \omega t$, then differentiating, gives the response of a capacitor. Replacing $-\sin \omega t$ in Equation 2.5 with $\cos \omega t + 90^\circ$, shows the phase lag due to the capacitor. This is also illustrated graphically in Figure 2.4.

\begin{align*}
v_R &= Ri \quad v_R = RA \cos \omega t \quad (2.4) \\
i_C &= C \frac{dv}{dt} \quad i_C = C A (-\sin \omega t) \quad (2.5)
\end{align*}

![Diagram](image)

**Figure 2.4**: Applied signal superimposed on measured output signal for a resistor and capacitor in series.

A material, like an electrical circuit, can be thought of as being made up of many discrete components, all combining to give rise to an overall response. Generally, this
overall response, or complex impedance, is given as \( Z(\omega) = R(\omega) - jX(\omega) \).\(^2\) The value of \( R \) is the ac resistance measured in ohms. The value of \( X \) is the capacitive reactance, \( X = -1/\omega C \), also in ohms \(^{17}\). The zirconia oxygen sensor would show similar behavior. Complex impedance measurements across the interface can be plotted to yield two characteristic arcs. One arc corresponds to the electrode structure and the other to the electrolyte. Work done by Bauerle et al.\(^{18}\) illustrates the ability to isolate such electrical parameters as resistance and capacitance for the electrode and electrolyte separately. This is illustrated in Figure 2.5a as a typical equivalent circuit for a \( \text{ZrO}_2 \) sensor. Figure 2.4b is essentially one of the arcs in Figure 2.5a, replotted to show how the values for \( R \) and \( r \) can be determined. Figure 2.5c illustrates what is meant by Constant Phase Angle (CPA) response, whereby the angle, \( \theta \), remains constant through a range of frequencies, \( \omega \). The value \( k \) is a constant. The impedance equations for the last two are given in the figure \(^{18}\). The most important consideration is to directly relate the cell impedance to the microstructure of the electrode.

Older literature contains references of the inability to model certain electrochemical systems with simple circuit elements. Some early work was fairly successful in treating a porous electrode as a transmission line \(^{19}\). However, it soon became clear that the surface roughness of an electrode could not be modeled in the same fashion. The mathematical description of even a single scratch requires at least a two dimensional approach \(^{20}\). The geometric assumptions required for such a treatment become difficult, if not impossible, for a typical electrode. Empirical models were often used to describe the frequency dependence of such systems.

The porous platinum-zirconia interface in the oxygen sensor is one of the difficult cases to model because of the surface roughness of the electrode. Results from Pizzini

\(^2\)In keeping with engineering notation, \( j \) will be used to denote the value of \( \sqrt{-1} \), while \( i \) is reserved for current.
Figure 2.5: a. Overall equivalent circuit, b. Portion of a. showing how values are determined, c. Constant Phase Angle (CPA) behavior.
[21] indicate that oxygen chemisorption and surface diffusion are the rate determining steps when porous platinum electrodes are used. A general impedance model to describe this type of behavior would be the Constant Phase Angle (CPA) element, where the phase angle is independent of the frequency (Figure 2.5c). Again, \( Z_\omega = k(j\omega)^{-\alpha} \), where the exponent has been shown to be 1/2 for a specific surface diffusion case called the Warburg impedance [22]. However, the value for \( \alpha \) will vary for individual systems and has been used to empirically fit experimental results. Some theories developed recently have been proposed to treat the electrode as a fractal object, linking it to the CPA element.

### 2.3 Electrodes as Fractal Objects

If one considers the history of algebra and calculus, the concept of fractals is fairly new. In the late 1970's, Mandelbrot introduced the term fractal and popularized the idea of using mathematics to describe a complicated geometric surface [23]. The intricate and colorful computer images containing fractals that can be created using a few lines of computer code are really quite amazing [24]. The more serious side of fractals allows many complicated shapes to be efficiently characterized with a fractal dimension, from Brownian motion to the structure of tree bark [25]. These concepts are directly applicable to the problem of electrode response.

Before diving into the electrode response, it is useful to briefly illustrate the concept of a fractal dimension, \( D_f \).\(^3\) To construct a fractal, a simple set of rules is employed. The process is repeated indefinitely and the construction appears to be almost totally random. The construction, however, is not totally random but made

\(^3\)To eliminate confusion with diffusion coefficients, \( D_f \) will be used for the fractal dimension. Sometimes \( D_H \) is used to denote the fractal dimension (Hausdorff-Besicovitch Dimension) in specific cases [23].
up of segments of the original piece differing only in scale. Such self-similarity allows complex geometric shapes to be simply described.

A basic shape such as a triangle can be used as a starting template in constructing a theoretical fractal figure. It may be useful to glance at Figure 2.6. The length of one side of this triangle would be set to $l = 1$. The perimeter of this triangle is clearly $N(l) = 3$. By demagnifying the original triangle by a factor of three, the length will become $\frac{1}{3}$ and by arranging these around the original triangle (smaller triangles around the perimeter of the big one), the second iteration is accomplished. The perimeter is now $N(l) = 12$. A third time will yield an $l$ value of $\frac{1}{9}$, with the perimeter, $N(l) = 48$. Continuing this process ad infinitum yields the theoretical Koch curve.

\[ l = 1, \ N(l) = 3 \quad l = 1/3, \ N(l) = 12 \quad l = 1/9, \ N(l) = 48 \]

Figure 2.6: Example of a Koch construction.

Calculating the fractal dimension of such an object is straight forward and requires the ratio of one iteration to the next iteration. Since $N(l) \propto l^{-D_f}$, the formula for $D_f$ is given below:
The fractal dimension for Figure 2.6 is calculated as 1.2619. The fractal approach to electrode reactions in electrochemical cells has been studied in depth over the last few years. There are several proposed models in the literature that use a fractal dimension to explain the frequency behavior commonly called CPA behavior [26, 27, 28, 29, 30].

Using the Sierpinski carpet as a fractal model, a theoretical relationship is made of the electrode structure to the CPA impedance element [26]. The electrochemical reaction taking place on a fractal electrode will proceed with a dependence upon the fractal dimension, $D_f$. The value of $\alpha$ is found from the relationship:

$$\alpha = 3 - D_f$$  \hspace{1cm} (2.7)

Using a modified Sierpinski electrode (because the original has an unrealistic infinite surface area) gives a fractal dimension in the plane, $D_p$, of $\log 5/\log 3$, and fractal dimension $D_f = 1 + D_p$ [27]. The results of this model and choice of fractal construction may not be entirely correct, however, and it was shown that the Sierpinski type electrode may not show CPA behavior if the surface of the electrode is in fact smooth [31]. Thus, the most important consideration would be the roughness of the electrode surface in determining the CPA type behavior, and Equation 2.7 cannot be used universally.

While the physics regarding the problem may be fairly simple, the geometry involved is very complex. Attempts have been made to solve the mathematical Kirchoff circuit equations as a "brute force" approach [32]. This requires considerable computer time for even a very simple approximation of electrode surface. The numerical result also hides general conclusions relating the specific geometry to other electrodes.
An elegant and sound theory due to Nyikos and Pajkossy treats the case of an unknown two terminal RC network [30]. An unknown RC network lumps all the resistances into an R term and all the capacitances into a C term. The two terminal designation means that only one path in and one path out is considered. The assumption for this case is that the electrode is strictly capacitive. This is not the case with the platinum electrodes used for the zirconia oxygen sensor, but the authors were developing a general case only. The Nyikos and Pajkossy model consists of parallel combinations of a capacitor and resistor in series. The impedance of a series capacitor and resistor is written as:

\[
Z_i = R_i + \frac{1}{j\omega C_i} = \frac{1 + j\omega R_i C_i}{j\omega C_i}
\]  

(2.8)

The summation over the number of parallel combinations gives the complete, although simplistic, impedance equation. The final result gives the CPA impedance model where the phase angle is independent of frequency. The simplified terms match the empirical CPA impedance element:

\[
Z \propto (j\omega)^{-\alpha}
\]  

(2.9)

The value of \(\alpha\) is related to the fractal dimension by a simple relation:

\[
\alpha = \frac{1}{(D_f - 1)}
\]  

(2.10)

The mathematical steps and the important assumptions leading to this result are included in Appendix A.1. It is this model which forms the theoretical base for the research conducted in this thesis. The extension of this model to include a surface diffusion component is also included in Appendix A.2 [20].
2.4 Surface Diffusion

This section is included as an aside to the above arguments. The zirconia sensor clearly has a surface diffusion process which must be included in any definitive model of the performance. The incorporation of surface diffusion into the above arguments can be made in theory but the diffusion coefficient measurements for this process are few and inaccurate. As in a typical diffusion experiment, one could imagine setting up a diffusion couple and measuring the diffusion profile. This however is a very difficult, if not impossible, thing to do when dealing with a polycrystalline surface [11]. The experimental techniques to probe surface behavior are only now developing a modest base of data [33, 34].

The study of diffusion on a fractal lattice has been a subject of interest and computer simulations of random walks on such lattices provide a simplistic view [35, 36]. The actual displacement of a diffusing species can be defined as the root mean square displacement $< R^2(t) >$. In Euclidean space the random walker advances one step in unit time $t$. In a self-similar system, a series of small steps do not simply scale as one large step. Thus after $N$ steps, the random walker on a fractal lattice finds the root mean square displacement to be a function of the fractal dimension [37]. The fractal dimension describes the convoluted path taken by a diffusing species:

$$< R_N^2(t) > = (\alpha t)^{\frac{D_f}{2}}$$

(2.11)

Where $\alpha$ is a constant (not the frequency parameter introduced for the CPA element). The variables $t$ and $D_f$, are time and fractal dimension.

The oriented platinum field emitter allows the diffusion of oxygen to be studied on specific crystallographic planes. In the temperature range of 450-500°K, the diffusion is observed to occur with a sharp moving boundary. Plotting $1/T$ versus time for the
boundary to advance a fixed distance, yields an activation energy of roughly 27 kcal [34].

The most important conclusion from this work is the nature in which crystallographic orientation determines the diffusion over a specific plane. Diffusion is most rapid on the (111) planes. This result is expected in that this is the densest packing plane in the FCC platinum. A surprising result may be that the (100) planes actually act as traps for the diffusing oxygen. At temperatures of roughly 600 to 700°K, the interaction of adsorbed oxygen with platinum seems confined to a monolayer. Above 700°K, surface oxides of both platinum and of impurities are produced [34].
Chapter 3

Experimental Procedure

3.1 Sensor Body

Zirconia powder doped with 8 mole percent yttria was pressed and sintered to form the ceramic body of the oxygen sensor. This powder was obtained from the Toyo Soda Manufacturing Company. Table 3.1 gives the specific details as to the exact composition of the batch used. For each pellet, 1.25 grams of powder was used. This amount of powder before pressing was chosen because it yielded a 2mm thick disk, resulting in electrolyte resistances of 150 to 200Ω at 600°C.

<table>
<thead>
<tr>
<th>Contents</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>86.574</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>13.370</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.005</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.002</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.002</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.047</td>
</tr>
</tbody>
</table>

*Crystallite size is roughly 219Å.

*Lot Number Z805125

Table 3.1: Zirconia powder TZ-8Y, composition information.
The powder was mechanically pressed into a pellet using a stainless steel die with an inner bore diameter of 15mm. Figure 3.1 shows the dimensions of the die. The die was machined at Lehigh University from 316 type stainless steel. Before each pressing, the die was cleaned in an ultrasonic bath of acetone. The goal was to minimize contamination of the zirconia. Machinability and cost were factors in the decision to use the austenitic stainless steel for the die instead of a harder martensitic stainless steel. The die was used in a Carver hydraulic press rated for 10 metric tons. The load on the die was 0.9 metric ton, which corresponded to a uniaxial pressure of 50MPa for each sample. The samples were then vacuum-packed in Penrose drains (large surgical tubing) and isostatically pressed to 350MPa in a Fluitron press.

![Die Dimensions](image)

Figure 3.1: Die used to uniaxially press the zirconia powder (Type 316 stainless steel).

The green disks were placed in a zirconia boat covered in zirconia powder and calcined at 800°C for three hours prior to firing. The disks were then sintered in a Lindberg box oven at a temperature of 1200°C. Different sintering times were tried to determine the time needed to obtain roughly 97% of theoretical density, and 14 hours was found to give acceptable results. Figure 3.2 illustrates this with substrate densities versus sintering times. A typical heating cycle incorporated heating rates of

---

1^Theoretical density is defined as 5.97g/cm³.
roughly 20°C per minute, holding at 800° for three hours, heating to 1200° at roughly the same heating rate, sintering at 1200° for 14 hours, followed by very slow cooling to prevent thermal shock.

![Plot of zirconia densities versus sintering time.](image)

Figure 3.2: Plot of zirconia densities versus sintering time.

Experiments showed that a rough surface interfered with the impedance measurements. Thus, the fired disks were polished before the platinum paste was applied. This step also removed surface impurities. The disks were mounted to a steel block in groups of five by using a hotplate and a heat setting glue. The surface was ground with 120 grit silicon carbide paper (3M Company) to produce parallel sides, then the polishing schedule outlined in Table 3.2 was followed. The disks were polished down to Buehler 1/4μm diamond paste on a polishing cloth with Hypez W lubricant.
Grind/Polish media | Time
---|---
120 grit | to a flat surface
240 grit | 2-3 minutes
320 grit | 2-3 minutes
400 grit | 2-3 minutes
600 grit | 2-3 minutes
6µm diamond | 4-5 minutes
1µm diamond | 4-5 minutes
½µm diamond | 4-5 minutes

Table 3.2: Polishing schedule for the zirconia disks.

### 3.2 Electrodes

Platinum paste was used to form the electrodes (Engelhard product #6082 - lot M22674). The exact composition of the paste was not given, but each component was listed on the right-to-know label. The paste was made up of platinum metal, terpineol, rosin, turpentine oil, and bismuth subnitrate. Rectified turpentine was used as a thinner and cleaning agent for the paste. A high quality artist brush was used to apply the paste. Each side of the polished disk was painted with circular electrodes and allowed to air dry before firing. The sintering of the electrodes was accomplished in the same box oven as before, using temperatures of 600, 700, 800, 900, and 1000°C. The firing time for each sample was five hours at the selected temperature. With this schedule of temperatures and time, the microstructure of the electrode could be controlled to develop various microstructures and resulting impedance behavior.

### 3.3 Microscopy and Sample Preparation

The microstructure of the as fired electrode was characterized with a JEOL 6300F scanning electron microscope (SEM). The field-emission electron source used in this
instrument provides sufficient current in a fine probe size to produce 10-20nm resolution at low accelerating voltages (2-3kV). Thus, this low kV performance is orders of magnitude better than a conventional tungsten source. A high magnification was desirable because the initial particle size in the platinum paste was very small (less than 100nm). A low accelerating voltage was employed to lower the interaction volume with the platinum, which also favored improved resolution. The underlying zirconia, being an insulator, also benefited from low-kV operation because it did not charge under the electron beam. Since platinum is of a fairly high atomic number, the interaction volume is already smaller than that of a lower atomic number material. Thus, true surface perturbations should be imaged with the use of very low accelerating voltages, especially for platinum surfaces not coated with the traditional metal or carbon coating.

The microscope conditions were generally similar for all images and all magnifications for fractal dimension determination were 10,000x. The working distance was as short as possible to enhance the resolution of the platinum electrode coating and the underlying zirconia. The stage height was set for 8mm, but the actual working distance varied from 10 to 12mm, because a modified 5 mount sample holder was used [38]. The microscope was carefully aligned at the beginning of each session. The accelerating voltage seemed to be optimum at around 2.7kV with a probe current of $2 \times 10^{-11}$ amps (estimated from manufacturer's data). Images were recorded with Polaroid type P/N 55 film, which contained both a positive and a negative.

Sample preparation consisted of carefully centering a sensor on a thoroughly cleaned aluminum SEM stub. The sample was glued in place with carbon dag at three points. The carbon dag serving the dual purpose of a conductive path to ground as well as a mechanical bond to the stub. The samples were then kept in a
vacuum desiccator to prevent any sample deterioration due to the laboratory environment. Figure 3.3 shows the typical sample mounted on an SEM stub, along with the orientation of the sample to the electron beam inside the microscope.

Figure 3.3: Typical SEM sample and electron beam orientation.

3.4 Fractal Dimension Determination

A Dosanto digitizing table, Mirco Plan II - DIGI PAD #5, was used to digitize the outline of the microstructures obtained from the SEM. The Dosanto table used a mouse-type device with a set of cross hairs indicating where the coordinates were to be taken from. The table was linked to a personal computer, IBM PC-XT, which allowed areas and perimeters to be calculated. The computer also allowed the pad to be used in a stream mode, where x-y coordinates were recorded automatically as the cross hair is moved by hand across the micrograph. The table had a resolution of 0.25mm point to point. A discrete set of points can be saved to a floppy disk in ASCII form. This data also included various scale and endpoint data. This extra data was later stripped and only the raw x-y data of the microstructure was used.

The computer file contained a profile of the 2-dimensional microstructures traced from a micrograph. The micrograph was taped to the digitizing table and a profile of the microstructure was chosen. The profile generally chosen ran lengthwise across
the micrograph and contained roughly 500 x-y data pairs. These coordinates were saved to a floppy disk and transferred to a computer program to determine the fractal dimension.

The relation used to determine the fractal dimension is developed in Mandelbrot's insightful text [23]. In this method, the fractal curve is covered with line segments of increasing length, \( r \). This value for \( r \), or the ruler length, is scaled to smaller and smaller values in successive measurements of the data set. As this is done, the total number of rulers, \( N(r) \), needed to cover the curve increases exponentially. This exponent is the fractal dimension, \( D_f \), as shown below:

\[
N(r) \propto r^{-D_f} \quad (r \to 0)
\] (3.1)

The value for \( D_f \) can be found experimentally by plotting various values of \( \log N(r) \) versus \( \log r \), using various values for the ruler length, \( r \). The slope of this line, ideally a straight line, will then be the value \(-D_f\). To experimentally vary the ruler for each profile, a computer program was written to automatically increment the ruler size after a run through the digitized file. The program was written at Lehigh using Borland's TurboBasic computer language. A listing of the program is provided in Appendix B. This program used the x-y pairs created by the digitizing pad after stripping out the unnecessary data. This left x-y coordinates with a 0.25 unit resolution (0.25mm) between points. The ruler length initially used was 1 unit. This was incremented by 0.5 to a final value of 10.

To verify the ability of the program to determine a fractal dimension from a profile, two theoretical constructions were digitized. One construction was a line, which has a fractal dimension, \( D_f = 1 \). The line was created with a steel ruler taped to the digitizing pad. From Figure 3.4, the value of \( D_f \) is determined 0.99999989. This value is very close to 1. The other was a Koch construction photocopied from Mandelbrot's
text [23]. Here, the theoretical value for $D_f$ is 1.2619, while the measured value using the above method gave $D_f = 1.23$. The photocopied Koch curve was not a true fractal construction because it was only iterated two or three times (Plate 44 [23]). This may explain why the data seems to plateau for several values of $r$ (Figure 3.5), causing a lower than predicted fractal dimension.

![Graph showing fractal dimension](image)

**Figure 3.4:** Fractal dimension of a line (1.00).

### 3.5 Impedance Measurements

An apparatus to test the finished oxygen sensors at the test temperature of 600°C was fashioned from a 50mm inner diameter quartz tube fitted into a Marshall tube furnace. The one end of the quartz tube was necked and fitted with a small opening suitable for a valved connection. The other end was fitted to a Pyrex 55/50 end cap. The sample holder was fabricated at Lehigh using the Pyrex 55/50 end cap with a
Teflon inner sleeve to support the ceramic tubes inside the furnace. Since the end cap was not in the furnace, a cooling fan was used to keep temperatures below 100°C. The Teflon sleeve was machined to accept two 6.35mm alumina tubes, one for two platinum probes and one for a K-type thermocouple (nickel-chromium vs. nickel-aluminum). A larger hole was machined to fit a 19.05mm closed end zirconia tube for the actual sample holder. The zirconia tube end was partially cut away to form a sample cradle and another 6.35mm alumina tube was fitted inside the bore and pressed the probes to the sensor with a spring loaded clamp. Figure 3.6 illustrates this sample holder.

As mentioned before, a Marshall tube furnace with a three inch diameter bore provided the heat. The furnace was rated for 1200°C, but it was only necessary to use it at 600°C for the electrical tests. The temperature was controlled with an Athena proportional temperture controller and a Potter and Brumfield solid state
Figure 3.6: Diagram of sample holder.
relay. Since the Athena controller was not powerful enough to drive the furnace, the actual power to the heating elements was direct from an autotransformer, with the live side passing through the P&B relay. The Athena controller output was connected across two 800Ω power resistors in parallel, \( R_{P1} \) and \( R_{P2} \), and the input to the relay. This was necessary because the relay in the temperature controller would only work properly with a load at the output (the resistors provided a 50 watt load). The autotransformer was routinely set for 90% power. In this fashion, the temperature was held very stable (to within one degree Celsius) over the hour or so needed to make the electrical measurements. The electrical circuit for this is given in Figure 3.7.

![Electrical schematic of furnace wiring.](image)

The actual electrical measurements were made by applying an ac signal of 50mV across the sample in series with a current limiting 100Ω resistor, \( R_L \). The frequency of the ac signal could be manually adjusted with an Interstate Electronics Co. model F55 function generator, using 1Hz to 10kHz as the frequencies of interest. The frequencies were calibrated with an oscilloscope and periodically checked. A Tektronix model 564
storage oscilloscope (affectionately known as “The Scopemobile”) provided two input
channels, Type 3A1 (vertical) and 3A6 (horizontal) modules. The dual trace feature
allowed the phase and amplitude information from the sample to be measured from
the ellipse formed on the screen due to the phase lag and attenuation across the
sample. The circuit used to set up the two channel input along with the sample
probes is given in Figure 3.8.

![Oscilloscope and sample probe circuit](image)

Figure 3.8: Oscilloscope and sample probe circuit.

The ellipse formed on the oscilloscope was used to measure two voltage ratios
[22]. As shown in Figure 3.9, the ratios of $a/b$ and $c/a$ are obtained as magnitude
and phase in polar form and substituted into Equation 3.2. The value of $R_L$ is a
100Ω series resistor. The resultant impedance, as a function of frequency, is $Z_{cell}(\omega)$. The data is obtained point by point in this fashion as the frequency is swept through
the range of interest. The real and imaginary portions can be extracted in Cartesian
form to simplify the plotting of the data [39]. Equation 3.3 shows the real portion,
$Z' = M \cos \theta$, and the imaginary part, $Z'' = -M \sin \theta$, where $M = (a/b)R_L$. This
will be plotted as $Z''$ versus $Z'$.

$$Z_{cell}(\omega) = \frac{a}{b} R_L \exp^{-j(\arcsin \frac{a}{b})}$$  \hspace{1cm} (3.2)
\[ M \exp^{-j\theta} = M \cos \theta - jM \sin \theta \] (3.3)

Figure 3.9: Example of oscilloscope screen and general shape of the ellipse formed due to the sample impedance.

The data obtained by the previous methods was plotted as real versus imaginary parts. To derive the frequency parameter, \( \alpha \), from this data, the capacitive reactance is converted to capacitance and the log \( \omega \) versus the log \( \omega C \) is plotted. The slope of this line is the value of \( \alpha \). When the data plots as a straight line, the \( \alpha \) is due to CPA behavior. Since the capacitive values are directly determined from the impedance data, a quantitative relation of \( \alpha \) to the fractal dimension is possible.
Chapter 4

Results and Discussion

The relevant experimental data will be presented and discussed in this section. Significant changes in the ac impedance were observed as the microstructure of the platinum was altered. The value of $D_f$ serves to quantify the microstructural changes. The microstructure of the zirconia substrate was kept uniform to avoid introducing new experimental parameters. This microstructure will be briefly discussed. The electrical measurements are presented by showing typical impedance plots. This was used to obtain the $\alpha$ parameter which was correlated to the fractal dimension. The data is then presented in a final plot of $\alpha$ versus $D_f$. This result is compared to a model that attempts to correlate the fractal dimension to the value of $\alpha$ using a surface scaling argument [30]. A modified model, which accounts for the surface diffusion component, is also presented [20]. It is not the goal of this work to absolutely agree or refute this modified model, but to present experimental data supporting the correlation of frequency independent electrical response with the microstructural changes (fractal dimension) of the electrode.
4.1 Microstructure

4.1.1 Zirconia Substrate

The zirconia disks posed no problems in preparation or polishing. A micrograph (Figure 4.1) of the polished zirconia surface (thermally etched for imaging) shows a typical substrate with very little porosity and no major polishing artifacts (such as scratches or grain pullout). Each sample set was prepared to a similar surface and verified by microscopic inspection. The main concern was a smooth substrate for platinum deposition. Since these samples were prepared at relatively low temperatures for typical sintering of zirconia (1300° - 1600°C), liquid phase transport most likely played a role in densification during sintering [4, 40].

Figure 4.1: SEM micrograph of the polished and thermally etched (3 hours at 800°C) zirconia substrate.
4.1.2 Platinum Electrode

The electrode surface was observed in a planar orientation. Since the surface was not disturbed by destructive sample preparation, such as mounting in epoxy or by diamond wafering, there was no concern about a difference in sample versus bulk properties associated with some sample preparation techniques.

The set of sensors with the platinum electrodes sintered at 600°C did not show a significant change in microstructure over what one would expect from the dried paste. The particle size was roughly uniform and very small, on the order of 10nm in diameter. The resulting film was very porous with a sponge-like appearance. Figure 4.2 is an SEM micrograph of the platinum electrode sintered at 600°C. The microstructures resulting from the full series of sintering temperatures are shown in Figure 4.2 through Figure 4.6. Each image represents a typical area of the electrode at the indicated temperature photographed at a magnification of 10,000x. This series shows the gradual change in the microstructure of the film as the sintering temperature is increased. It was suggested by Engelhard that this paste should be fired at a minimum of 800°C to insure a proper coverage on the zirconia. Note that at 1000°C, the film appears markedly different from the film sintered at 600°C.

It is clear from the following images that the grain size of the platinum changes as the sintering temperature is increased. Measuring grain sizes from the film would be difficult to do for such a porous microstructure. Although the kinetics are similar, the grain growth for a very porous compact of alumina is quite different from normal coalescence and grain growth of a dense compact [41]. The growth involves the filling of the contact region between adjacent grains. This necking is accomplished by vapor-phase and surface diffusion during sintering of the porous compact, and the grain boundary will sweep through the smaller particle [42]. This type of behavior is seen in the early stages in Figure 4.3. The bimodal microstructure shows the small particles
being accommodated into the larger particles. These lower activation energy processes serve to reduce the specific surface area \((m^2/g)\). However, densification occurs only when matter is transported to the surface of the pores through volume and grain boundary diffusion rates [42]. The platinum grains are expected to follow similar behavior due to the low volume and grain boundary diffusion at these experimental temperatures. The electrodes shown here are also constrained in two dimensions by the zirconia substrate. The reduction of specific surface area is analogous to a reduction of the fractal dimension. By measuring the fractal dimension of the electrode, this process can be quantified quite well. However, as the grains become larger, it is not known entirely how different grain sizes affect the impedance response.

The grain size would have an effect upon the bulk electrical properties of the platinum since there will be an electron current in the bulk. This current flow will not be measurable at the frequencies used in this study, and grain size effects on this parameter must be ignored. The question of grain size effects on the measurement of the fractal dimension cannot be ignored. As a thought experiment, if the average platinum grain size is increased and the sintering time modified in proportion to the sintering kinetics, one would expect to generate similar microstructures. As long as the scale of observation encompassed a significant portion of the microstructure, one would expect the fractal dimension to remain the same with the larger grain size. However, this would require altering the scale of observation when using the techniques presented here. The digital profiling would fail if only a portion of a single grain filled the micrograph, likewise, a micrograph at 10x would appear as a uniform film. With electrodes sintered at the same temperatures, yet of very different grain sizes, for example, 600°C, with a few different films of initial particle sizes ranging from 100nm to 1µm, the impedance response could be measured and compared. It would then be possible to separate the fractal dimension from grain size as microstructural
variables contributing to the overall film impedance. Perhaps future work could address this issue.

Figure 4.2: SEM micrograph of the top surface of a platinum electrode sintered at 600°C.
Figure 4.3: SEM micrograph of the top surface of a platinum electrode sintered at 700°C.

Figure 4.4: SEM micrograph of the top surface of a platinum electrode sintered at 800°C.
Figure 4.5: SEM micrograph of the top surface of a platinum electrode sintered at 900°C.

Figure 4.6: SEM micrograph of the top surface of a platinum electrode sintered at 1000°C.
Higher magnification images of the electrode fired at 600 and 1000°C are included to highlight the development of surface structure (Figure 4.7 and Figure 4.8). At the higher sintering temperature, the platinum grains appear to coarsen by a ledge growth mechanism. This is further supported by the fact that surface diffusion appears to be the dominant transport mechanism for the platinum sintering [42]. Surface faceting occurs, whereby the planes with lower crystallographic index, but more importantly, lower surface energy, are larger in extent. The second figure provides a striking example of the crystallography of such platinum grains. The symmetry elements associated with various planes can be picked out. What is assumed to be the (111) is marked on this figure. From Chapter 2, regarding diffusion of oxygen on platinum, this plane will provide the fastest diffusion path along the surface of the platinum.

Figure 4.7: Higher magnification image of the platinum film sintered at 600°C.
4.1.3 Fractal determination

The fractal dimensions of the electrodes were measured from micrographs similar to those in the previous section and the results are listed in Table 4.1. The use of a fractal dimension to describe the surface of an electrode assumes the roughness is in fact self-similar. The definition of self-similar must be relaxed for this case because the surface is sintered from a paste with a finite size distribution. The importance lies in the electrode pores and perturbations being characterized regardless of the specific geometries.

In the experimental section the accuracy of the fractal determination was tested with two theoretical constructions, a line and a Koch curve. The program determined the fractal dimension correctly. However, when dealing with an experimental surface such as these electrodes, it is difficult to verify a "true" value of $D_f$. For this reason,
Temperature | $D_f$ ($\bar{x}$) | $s$
---|---|---
600° | 2.230 | 0.062
700° | 2.150 |
800° | 2.043 | 0.015
900° | 2.013 | 0.006
1000° | 2.005 | 0.003

Table 4.1: Table of electrode fractal dimension versus sintering temperature.

multiple regions were recorded and a dimension determined from each micrograph. A sample mean and deviation for these values are recorded in Table 4.1. A table with all the experimental values is included in Appendix C.

A commercial sensor was used to provide a reference for the platinum electrodes. The detailed commercial fabrication process is not known, but a qualitative comparison of Figure 4.5 with Figure 4.9 shows the similarities between the experimental films sintered at 900°C and a commercial oxygen sensor (AC Spark Plug #AFS 20, sintering temperature unknown). The measured fractal dimension is roughly the same for the 900°C experimental electrodes ($D_f = 2.013$) and the commercial sensor ($D_f = 2.010$).

### 4.2 Electrical Response

#### 4.2.1 Impedance plots

Examples of typical impedance response for these sensors are depicted Figure 4.10 through Figure 4.18. For brevity, only two tests are shown at each sintering temperature (there was only one sensor at 700°C). Within each of the figures, the sensor response shows the typical linear behavior in the left hand part of the plot, which is CPA behavior. Essentially, as the frequency is increased, the microstructure presents
different scale pores and perturbations to oxygen ions, appearing self-similar. The frequency range of this behavior is roughly 100Hz to 1000Hz for all the samples. Polarization and charge transfer corresponding to frequencies such as these, would be associated with the oxygen molecule or ion interacting with the surface of the platinum.
Figure 4.10: Impedance response of platinum film sintered at 600°C (4pt600).

Figure 4.11: Impedance response of platinum film sintered at 600°C (5pt600).
Figure 4.12: Impedance response of platinum film sintered at 700°C (3pt700).
Figure 4.13: Impedance response of platinum film sintered at 800°C (4pt800).

Figure 4.14: Impedance response of platinum film sintered at 800°C (5pt800).
Figure 4.15: Impedance response of platinum film sintered at 900°C (6pt900).

Figure 4.16: Impedance response of platinum film sintered at 900°C (8pt900).
Figure 4.17: Impedance response of platinum film sintered at 1000°C (1pt1000).

Figure 4.18: Impedance response of platinum film sintered at 1000°C (2pt1000).
4.2.2 Determination of the Alpha Parameter

The data in the previous figures illustrate the overall sensor response by plotting the frequency response as real versus imaginary components. Chapter 3 details how the general impedance data is manipulated to yield the value for $\alpha$. The experimental values for $\log \omega C$ versus $\log \omega$ plotted linearly, supporting the observed CPA behavior in the general impedance plot. Figure 4.19 is an example taken from a typical sample (1pt1000), showing how $\alpha$ is determined. The impedance data is given in Figure 4.17 for this sample. The plot of $\log \omega C$ vs. $\log \omega$ is shown to illustrate how the data will be linear for CPA behavior. For example, the slope of the regression fit to Figure 4.19 is 0.522.

![Graph](image)

Figure 4.19: Capacitive data showing how $\alpha$ is determined.

The increase in $\alpha$ as the fractal dimension goes down agrees with the simplified model of only capacitive response (Appendix A.1). Table 4.2 shows the values measured for $\alpha$ at each sintering temperature (see Appendix C for a complete list).
Temperature $\alpha (\bar{x})$ $s$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\alpha (\bar{x})$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.286</td>
<td>0.034</td>
</tr>
<tr>
<td>700</td>
<td>0.340</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.424</td>
<td>0.053</td>
</tr>
<tr>
<td>900</td>
<td>0.417</td>
<td>0.041</td>
</tr>
<tr>
<td>1000</td>
<td>0.511</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 4.2: Table of $\alpha$ versus temperature.

4.3 Correlation Between $D_f$ and the $\alpha$ Parameter

4.3.1 Observed Results

Since the capacitive values are determined from the impedance data, a quantitative relation of $\alpha$ to the microstructure is possible. The fractal dimension is directly measured from the SEM images of the microstructure, therefore the data presented for the fractal dimension of the film and the value for the $\alpha$ parameter can be plotted together to show the relation. Since it is assumed that the value of $\alpha$ is dependent upon the microstructure, it is plotted as $\alpha$ versus $D_f$. Error bars are rather large due to the limited number of samples available to test. Although firing conditions were uniform for each sample, the fact that each was handmade individually led to differences in the microstructure and electrical performance. The value of $\alpha$ is dependent upon the value of $D_f$ for each individual sample, leading to spread in the data. The plot in Figure 4.20 gives all the data recorded, using individual $\alpha$-$D_f$ pairs (Table C.1). Figure 4.21 is essentially a cleaned up version using the sample mean and deviation from Table 4.1 and Table 4.2. The calculated deviation was used to define the error bars at a value of one estimated standard deviation in both the $x$ and the $y$ direction.

These two figures clearly show that the value of the fractal dimension can be used
Figure 4.20: Plot of $\alpha$ versus $D_f$, raw data.

Figure 4.21: Plot of $\alpha$ versus $D_f$, mean value at each temperature.
to predict the value of $\alpha$. However, the predicted theoretical relation does not hold exactly. A very rough linear fit would lead to slope and intercept values of $-1.1$ and $0.7$, respectively. This relation, $\alpha = -1.1D_f + 0.7$, is not meant to replace the theoretically predicted response because it is only found through experimental data. Theoretical treatment predicts the relation given in Equation 3.9 and emphasized again [30]:

$$\alpha = \frac{1}{(D_f - 1)} \quad (4.1)$$

Figure 4.22 is a modified version of the Figure 4.21, plotting both experimental and theoretical on the same graph. It is clear that the two do not agree exactly, but the general trend is correct. This result is very encouraging.

![Graph of $\alpha$ versus $D_f$ for theoretical and experimental](image)

**Figure 4.22:** Plot of $\alpha$ versus $D_f$ for theoretical (Equation 4.1) and experimental.

The underlying result is that the impedance response of the platinum electrode
can be correlated to the fractal dimension. Since capacitance is proportional to area, the fractal dimension describes the change in surface area of the electrode as the fractal dimension is increased. In a flat plane, area changes as a squared relationship, $l^2$, where $l$ is a linear measurement. When the surface is considered to be a fractal surface, this relationship is no longer squared, but raised to the value of the fractal dimension, $l^{D_f}$ [23]. Therefore, the capacitive properties of the platinum electrode should be some function of the fractal dimension. The evidence indicates that this is the case, however, agreement with theory in Figure 4.22 is only good in terms of the slope of the curve.

It is very difficult to determine exactly why the theoretically predicted and the experimental plots do not superimpose upon one another. A close look at the capacitive model of Nyikos and Pajkossy (Appendix A.1) reveals the assumptions made for the resistance were that these values are of a bulk nature and should scale linearly, $r^{-1}$. It is possible that this is not the case with these platinum electrodes and the resistive values would scale with some other value. The $(D_f - 1)$ factor in Equation 4.1 could be modified to show this as $(D_f - A)$, where $A$ is some constant since -1 in the first expression is due to the -1 scaling. In actuality, assuming some values for $A$ still does not cause agreement with the experimental data. Another possibility is that the surface diffusion inherent in the oxygen sensor introduces new factors unaccounted for in this model.

### 4.3.2 Surface Diffusion

To account for surface diffusion in the electrochemical modeling of a fractal electrode, the charge transfer of the oxygen ions and the electrochemical activity at the electrodes must be incorporated into the capacitive model of Nyikos and Pajkossy [30]. Recent work by de Levie [20] attempts this with some success. Appendix A.2
gives the mathematical details of this model, a model built directly upon the original capacitive model (Appendix A.1).

Recalling the discussion of a random walker on a fractal lattice (section 2.4), a change in the fractal dimension will affect the diffusion of oxygen on the platinum electrode. Diffusion is a time dependent process, $\sqrt{Dt}$, where D is the diffusion coefficient. This time dependence corresponds to a frequency dependence of $\sqrt{D/\omega}$. Recent work has shown the diffusion limited current, $i_d$, on a fractal surface will obey the proportionality given in Equation 4.2 [43, 44, 45, 46].

$$i_d \propto t^{(1-D_f)/2}$$  \hspace{1cm} (4.2)

The impedance model by de Levie (Appendix A.2) predicts the general shape of an impedance curve depending upon the fractal dimension. Predictions assuming three parameters that include diffusional effects are shown in Figure 4.22. The equation used to plot this data is (A.8):

$$Z_{hc} = R_s + \frac{R^{\xi}_{ct}}{b} \left( \frac{1 + B'(j\omega)^{-1/2\xi}}{1 + j\omega R_{ct} C(1 + B'(j\omega)^{-1/2\xi})} \right)^{\xi}$$  \hspace{1cm} (4.3)

The exponent, $\xi$, is used instead of $\alpha$. Values for $\xi$ and $\alpha$ are not fully interchangeable here. The $\xi$ value related to the fractal dimension is inclusive of the diffusional processes at the electrode, while the argument for $\alpha$ only incorporates the capacitive properties of the electrode. In this section, $\xi$ is not calculated from experimental data. Equation 4.1 from Nyikos and Pajkossy can be used to estimate the fractal dimension from de Levie's values for $\xi$. The fractal dimensions would be: 3.00, 2.25, and 2.00, for $\xi$ values of 0.5, 0.8, and 1.0, respectively.

The individual parameters for each of the variables in Equation 4.3 can be estimated from the actual experimental data presented earlier. The values for the charge-transfer resistance, $R_{ct}$, can be estimated as the resistance of the film. The
Figure 4.23: Theoretical prediction of the impedance response for frequency parameters: $\xi = 0.5, 0.8, \text{and} 1.0$.

The impedance arc touches the x-axis at the low frequency end and the high frequency end. The difference in the real values of these two points will yield the overall film resistance. The value for $R_{ct}$ used in all three simulations of Figure 4.23 was $10\Omega$. Notice that for a $\xi$ value of 0.5, the apparent film resistance is $3.3\Omega$ instead of the specified $10\Omega$. For a $\xi$ value of 1.0 the apparent and specified film resistance are the same. This behavior is not understood, nor mentioned in de Levie's theoretical model. The capacitive value, $C$, can be estimated at the peak of the arc by $\omega RC = 1$.

The value for the solution resistance, $R_s$, would be the resistance of the solid electrolyte. This value is found at the high frequency end of the impedance spectrum, where the data converges to the real axis. Figure 4.24 is a copy of Figure 4.10, along with a computer simulation using the electrolyte resistance, $R_s$, of $170\Omega$ determined experimentally. Using an $R_{ct}$ value of $100\Omega$ did not produce a proper film resistance.
Using the observed behavior of Figure 4.23, $R_{ct}$ was chosen to be 1000Ω.

The comparison of these two curves show them to be very similar in both shape and actual values. This indicates that the model fits the experimental data very well. To mimic the skewed behavior of the experimental curve, the value of $\xi$ was chosen to be 0.5, suggesting a fractal dimension of 3.00. However, the measured fractal dimension was 2.23. Qualitatively, the theory and the experiments show a strong similarity, but the exact mathematical relationship between $\alpha$ and $D_f$ remains elusive. The overall model of de Levie incorporates the important parameters needed to describe the change in impedance response by microstructural changes, changes quantified by the change in fractal dimension.

Figure 4.24: Experimental impedance data (Figure 4.10 of electrode sintered at 600°C) along with the theoretical prediction of the impedance response from Equation 4.3 ($R_{ct} = 1000Ω, \xi = 0.5, C = 0.0001$ Farads.)
4.4 Sensor Performance

The main goal of this work was to use the fractal dimension as a tool to describe the microstructure of platinum electrodes on zirconia oxygen sensors. To this end, the work was successful. Issues relating to sensor timing and specific performance were not evaluated explicitly in this study. It is clear that more work must be done to determine the optimum microstructure, and hence the optimum processing parameters such as sintering time and temperature. The direction of future work should concern itself with the two competing events outlined here. The catalytic reaction requires as much specific surface area as possible, while the diffusion of oxygen would be ideally along (111) planes. Since the availability of such low energy planes occurs by sacrificing surface area, the optimum sensor would force a compromise between these two properties of the platinum electrode. The quantification of the electrode with a fractal dimension provides a very useful tool to help meet these goals.
Chapter 5

Conclusions

- The microstructures of the platinum electrode can be quantified by using a fractal dimension. A simple method allows the value for $D_f$ to be determined from an SEM image. Using $D_f$ determined for different processing parameters such as sintering temperature, the microstructure can be used to predict the overall film impedance.

- The impedance of the platinum electrode can be measured experimentally. From the experimental data, a value of $\alpha$ can be determined. The value of the frequency parameter, $\alpha$, is dependent upon the microstructure of the film. Since this value of $\alpha$ was shown to be dependent upon the surface roughness of the platinum, the value of this parameter can be used to define the microstructure.

- The ability to approach the microstructure-property relation from either $D_f$ or $\alpha$, suggests that the model of Nyikos and Pajkossy to predict this relationship is a valid one. While the experimental data and the theoretical predictions do not superimpose exactly, it was shown that the slopes between $D_f$ and $\alpha$ seemed to be correct when the two were plotted together. However, the intercept on the $\alpha$ axis differs by a factor of 0.5. The reason for this is not fully understood.
The incorporation of surface diffusion into the impedance model is necessary to begin to understand the processes occurring at the electrode. While the parameters chosen to predict the experimental data for a particular sample were slightly modified to cause the two impedance curves to agree, there is a great deal of hidden information in this. As the fractal dimension of the microstructure is increased the apparent film resistance is decreased. However, the value for the film resistance is maintained in the impedance simulation. This suggests that the true value for $R_{ct}$ in sample 4pt600 is in fact 1000Ω, instead of the apparent 250Ω. The experimental curves show agreement with the theoretical data, and serve to support the impedance model of de Levie [20].
References


[24] A computer program to generate fractal images is available from most public domain ftp sites. An ftp site like cica.cica.indiana.edu has a copy to run under Microsoft Windows 3.0.


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[38] J. D. French, D. Ackland, A joint project with the ceramics department and the EM Laboratory, Lehigh University (1991).


Appendix A

Impedance Model

A.1 Model Due to Nyikos and Pajkossy

The model of Nyikos and Pajkossy is outlined in this Appendix [30]. While the mathematics involved are quite simple and short, care should be taken to understand the assumptions involved in the model. The main assumption is that the electrode processes are capacitive only. In the case of the zirconia sensor, this assumption is not valid. The zirconia sensor will have a surface diffusion component. Later work by de Levie addresses this and incorporates semi-infinite planer diffusion on a fractal surface [20].

Beginning with a two terminal network, any combination of resistance and capacitance can be written as a lumped resistor and capacitor in series. This can then be summed to give the parallel combination of many such elements. The following equations are written as admittance, \( Y \). Impedance and admittance are simply inverses of each other, \( Y = 1/Z \).

\[
Y = \sum_{n} \frac{j\omega C_n}{1 + j\omega R_n C_n} \quad (A.1)
\]
Since the values of R and C are lumped, actual values are unknown and can be distributed, but the distribution is unknown. If the system is scaled by a factor, r, the elements will change by this factor, r. The resistance of the system will change linearly, \( R_n \rightarrow rR_n \), while the capacitance element, \( C_n \), will scale with area of the electrode (capacitance \( \propto \text{area} \)). Since the surface of the electrode is assumed to be of a fractal nature, the scaling factor will depend upon the fractal dimension, \( D_f \). These two terms are shown in Equation A.2.

\[
R_n(r \cdot l) = r^{-1} R_n(1) \tag{A.2}
\]

\[
C_n(r \cdot l) = r^{D_f} C_n(1) \tag{A.2}
\]

Replacing the lumped values in Equation A.1 with the scaled values, leads to the final form in Equation A.3.

\[
Y(r \cdot 1, \omega) = \sum_n \frac{j\omega C_n(r \cdot 1)}{1 + j\omega R_n(r \cdot 1)C_n(r \cdot 1)} \tag{A.3}
\]

\[
= \sum_n \frac{j\omega r^{D_f} C_n(1)}{1 + j\omega r^{-1} R_n(1)r^{D_f} C_n(1)}
\]

\[
= r \sum_n \frac{j\omega r^{D_f-1} C_n(1)}{1 + j\omega r^{D_f-1} R_n(1)C_n(1)}
\]

\[
= rY(1, \omega r^{D_f-1})
\]

Since the phase angle is independent of the frequency over the range of interest, the ratio of admittances at frequencies of \( \omega \) and \( k\omega \) will be a real constant.

\[
\frac{Y(k\omega)}{Y(\omega)} = k^\alpha \tag{A.4}
\]

Comparing the final expression of Equation A.3 to the expression of Equation A.4, the ratio of CPA behavior becomes:

\[
\frac{Y(1, \omega r^{D_f-1})}{Y(1, \omega)} = r \tag{A.5}
\]
The comparison of the two equations gives the relation between the fractal dimension and the value for $\alpha$:

$$r^{\alpha(D_f-1)} = r^1$$

$$\alpha = \frac{1}{D_f-1}$$  \hspace{1cm} (A.6)

### A.2 Extension to Include Surface Diffusion

The extension of the previous case to one with a diffusional component requires the consideration of diffusion along a fractal surface. The diffusion limited current on a fractal surface should obey similar scaling laws as the non-diffusional case [46]. The incorporation into the electrochemical model is based upon the assumption of semi-infinite planer diffusion. The incorporation requires a value for charge transfer resistance, $R_{ct}$, to be multiplied by a factor containing rate constants. Now the cell impedance is modified as in Equation A.7. Note that impedance is used instead of admittance. It does not matter for the end result, but for consistency with the work of the different authors, it was not altered to all admittance or all impedance.

$$Z_{hc} = R_s + \frac{R_{ct}^\xi}{b} \left( \frac{1 + B'(j\omega)^{(1-D_f)/2}}{1 + j\omega R_{ct} C (1 + B'(j\omega)^{(1-D_f)/2})} \right)^\xi$$  \hspace{1cm} (A.7)

The value of $\xi$ is similar to the value of $\alpha$. Since the exponent due to diffusion is also a function of the fractal dimension, they can be rewritten as a function of $\xi$. The equation then becomes:

$$Z_{hc} = R_s + \frac{R_{ct}^\xi}{b} \left( \frac{1 + B'(j\omega)^{-1/2\xi}}{1 + j\omega R_{ct} C (1 + B'(j\omega)^{-1/2\xi})} \right)^\xi$$  \hspace{1cm} (A.8)

It is this equation that is used to predict the impedance response of an electrochemical cell.
Appendix B

Program to Calculate Fractal Dimensions of Electrodes

The Turbo BASIC computer language from Borland was used because of the relatively simple command structure involved in transferring data from the digitizing pad. The digitizing pad was supported by the BASICA language and the output was an ASCII text file. The premise behind the method to calculate the fractal dimension was mentioned in the Experimental section, along with the basic mathematics behind the approach. To calculate the fractal dimension numerically, the same model was adapted to a computer program. The program is included below and has numerous comments to describe the different operations in detail. An outline of this program should familiarize the reader with the methods and reasoning for doing the calculations in this manner.

5 REM Program to calculate the dimension
10 REM using XY files from digitizing pad.
20 zz = .5      REM Sets up RULE to be 1 when adding 0.5.
30 TEST$ = "false"

90 zz = zz+.5    REM Sets RULE to 1.
100 REM Define the variables.
110 NRULE = 0    REM NRULE is the number of RULE lengths used.
120 PRST = 0     REM PRST is used for the first iteration.
130 F$ = "0"     REM F$ used for data input.
140 I$ = "0"     REM backs up F$.
145 NFILE$ = "0" REM the file name.
150 XF = 0: YF = 0 REM XF, YF are initial values of x and y.
160 XFRAC = 0: YFRAC = 0 REM Previous point of x and y.
170 XFMI = 0: YFMI = 0 REM Middle value between points.
180 XSUB = 0: YSUB = 0 REM Allows continuous iteration.
190 LEFTOVER = 0 REM Gives a leftover value at the end.
200 INTDIS = 0   REM Gives the intermediate distance.
210 PERCENT = 0  REM Expresses the intdis as a percent.

1000 REM Read in data points.
1010 GOSUB 2000   REM get a file name from operator.
1020 OPEN NFILE$ FOR INPUT AS 2     REM opens the xy file to get
1030 WHILE NOT EOF(2)            REM data saved by the pad.
1040 LINE INPUT #2, I$           REM
1050 F$ = I$
1055 REM check for carriage return (end).
1060 WHILE LEFT$(F$,1) = CHR$(10)$ OR LEFT$(F$,1) = CHR$(13)$

            : F$ = RIGHT$(F$, LEN(F$)-1) : WEND

1070 N$ = LEFT$(F$, 3)                        REM the line number of the data.
1080 IF VAL(N$) = 0 THEN 1210

1090 XF = VAL(MID$(F$, 7, 9))                REM takes the
1100 YF = VAL(MID$(F$, 20, 9))               REM value of the data
1110 LF = VAL(MID$(F$, 33, 9))               REM but not the scale factor.

1120 IF PRST = 0 THEN XFRAC = XF             REM to set initial
1125 IF PRST = 0 THEN YFRAC = YF             REM values.
1130 PRST = 1
1200 DIS = SQR((XF - XFRAC)^2 + (YF - YFRAC)^2) REM Triangle RULE.
1201 IF DIS - RULE > 0 THEN GOSUB 1500        REM Advance nRULE.
1202 REM This is essentially the drawing of circles on the outline of
1203 REM the image, with the radius as DIS and the changes in x and y
1204 REM a triangle inscribed in a circle.
1205 PRINT XF, YF
1206 XFMI = XF                                 REM Stores XF and YF for later use.
1207 YFMI = YF
1210 WEND
1220 CLOSE

1230 REM The leftover amount is treated as a fraction.
1240 LEFTOVER = SQR((XF-XFRAC)^2 + (YF-YFRAC)^2)/RULE
1245 REM. The following file name and drive letter can be
1246 REM changed to suit the user.
1250 FILE$ = "a:\data.me"
1260 OPEN FILE$ FOR APPEND AS #3 REM opens file "data.me".
            REM must clear this file for each
            REM separate block of runs.
1270 PRINT #3, RULE, "," NRULE, "," LEFTOVER, CHR$(13)
1275 REM Puts data in the file.
1280 CLOSE #3
1290 PRINT "RULEr"; RULE
1300 PRINT "nRULEr"; NRULE, LEFTOVER

1312 GOTO 9999 REM Restarts program advancing RULE by .5

1500 REM advance nRULE.
1510 NRULE = NRULE + 1
1520 REM start in the proper spot.
1530 REM INTDIS will be greater than DIS - RULE.
1540 REM (two points in XY files, XF-XFMI).
1550 INTDIS = SQR((XF - XFMI)^2 + (YF - YFMI)^2)
1560 PERCENT = (DIS - RULE) / INTDIS
1665 REM assign value for interim point.
1570 XSUB = (XF - XFMI) * PERCENT
1580 XFRAC = XF - XSUB
1590 YSUB = (YF - YFMI) * PERCENT
1600 YFRAC = YF - YSUB
REM Value for RULE.

Ends program when RULE = 11.

REM Get a file name.
GOSUB 3000 Nfile$ = "a:7pt601b.dat"
REM PRINT "Input a file name"
REM INPUT "Filename:"; NFILE$
REM Replace line 2015 with 2017 and 2020 to do each
REM iteration individually.
RULE = zz
REM Value for RULE.
IF RULE = 11 THEN 10000
REM Ends program when RULE = 11.
REM INPUT "RULEr: " ;RULE
REM Replace lines 2023 and 2024 with 2025 to do each iteration
REM separately, or change the values to suit the user. Care
REM should be taken when changing the values because the
REM resolution of the pad gives a low limit of roughly 1 and the
REM lack of sufficient points (roughly 500 is recommended) forms
REM a limit when the number of RULErs around equals the RULEr
REM length.
RETURN.

REM Clears screen.
LOCATE 1,1 : PRINT STRING$(40, &H20) ; LOCATE 1,1
CLS
RETURN

GOTO 90
The program is divided into subgroups beginning with the initial comments in line numbers 1 through 210. The variables are mentioned as to what they mean and set to zero to clear all the variable registers. Line 20 sets an initial value for the quantity called RULE. This quantity is the diameter of a circle used to cover a portion of the trace of the micrograph recorded of the platinum surface. The number of RULE that are needed to cover the entire trace is given as NRULE. Line 30 simply prevents the values from getting overwritten when the program is run.

The next section of the program opens up the file saved by the digitizing pad to input the x-y coordinates into the program. Each line is read in as a string, F$, and the coordinates are removed from this string to be used in later sections. Lines 1120 through 1220 take each value out of the x-y file in sequential order and compare the distance from the starting point to the current data point with the distance set by the quantity RULE. Since these two quantities are never exactly equal, due to the discrete nature of the points recorded by the digitizing pad, roughly equal is used to set the new starting point and increment the value of the quantity NRULE. This is done in lines 1500 to 1610.

The trace of the micrograph will invariably have a fraction left over which must be accounted for, especially when the value of RULE gets large. This fraction is calculated by geometry and then divided by the quantity RULE to give a fractional value, which is then added to the quantity NRULE. These values are then saved in a file and the process is repeated with the value of the RULE increased by 0.5.

Lines 2000 through 2040 allow the input files and output files to be defined. Also the values of the RULE can be input manually with a few changes in the program. These changes can be made quite easily and are highlighted in the program. The
viability of the method is not in question but initially the program had to be modified, adding the section for the fraction leftover, for example. The program was checked using two profiles of known dimension and this is given in the Results section.
Appendix C

Experimental Values for $\alpha$ and $D_f$

The experimental values for $\alpha$ and $D_f$ are included in Table C.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha$</th>
<th>$D_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4pt600</td>
<td>0.266</td>
<td>2.35, 2.23, 2.27</td>
</tr>
<tr>
<td>5pt600</td>
<td>0.262</td>
<td>2.23, 2.19</td>
</tr>
<tr>
<td>7pt600</td>
<td>0.34</td>
<td>2.20, 2.14</td>
</tr>
<tr>
<td>3pt700</td>
<td>0.34</td>
<td>2.15</td>
</tr>
<tr>
<td>1pt800</td>
<td>0.322</td>
<td>2.05, 2.08</td>
</tr>
<tr>
<td>2pt800</td>
<td>0.416</td>
<td>2.04, 2.06, 2.04, 2.03</td>
</tr>
<tr>
<td>3pt800</td>
<td>0.49</td>
<td>2.03</td>
</tr>
<tr>
<td>4pt800</td>
<td>0.445</td>
<td>2.03</td>
</tr>
<tr>
<td>5pt800</td>
<td>0.46</td>
<td>2.06, 2.04</td>
</tr>
<tr>
<td>6pt900</td>
<td>0.398</td>
<td>2.009, 2.011</td>
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<tr>
<td>7pt900</td>
<td>0.474</td>
<td>2.01, 2.013</td>
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<tr>
<td>10pt900</td>
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<td>2.01, 2.026</td>
</tr>
<tr>
<td>1pt1000</td>
<td>0.522</td>
<td>2.001, 2.005</td>
</tr>
<tr>
<td>2pt1000</td>
<td>0.483</td>
<td>2.01</td>
</tr>
<tr>
<td>3pt1000</td>
<td>0.515</td>
<td>2.003</td>
</tr>
</tbody>
</table>

Table C.1: Experimental values for $\alpha$ and $D_f$. 
Vita

Steven Toteda was born in New York City in July 1967. In May of 1985 he graduated from Haborfields High School and went on to obtain his Bachelor Degree in Electrical Engineering from Lehigh University in 1989. Prior to returning to graduate school, he worked for one year at Dent Manufacturing, where his responsibilities included specialized testing of manufactured parts and setup of computer-assisted manufacturing equipment. During his two years of graduate work in the Materials Science Department at Lehigh, Steven worked on porous platinum electrodes used for oxygen sensing equipment. In 1992, he was recognized as an EMSA Presidential Scholar for his work in this area.
END
OF
TITLE