

# IN-SITU SEAL INTEGRITY SENSING FOR SOLID OXIDE FUEL CELLS

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## **Abstract**

Solid oxide fuel cells (SOFC) involve structures composed of multiple ceramic layers, or interleaved layers of ceramic membranes and metal interconnects. To eliminate premature mixing of fuel and air gases or leaking of these gases from interior regions of the structure, the interfaces of adjacent layers are sealed with a glass or ceramic seal. These seals must withstand the high-temperature environment of the SOFC over its lifetime. Therefore these materials must be thermally matched with the adjacent layers to minimize transient stress risers and eliminate the potential for consequent seal failure.

The conventional approach used when designing and manufacturing seals for high-temperature applications is to develop mathematical models for calculating the seal stresses that are likely to arise during device operation, and thereby attempt to predict operational regions of safety or failure. This method always requires correlation to the modeled effects for clarity in the design process. It is inherently difficult to monitor seal integrity once a SOFC has been fabricated. Further, failures are typically catastrophic and destroy the evidence of the cause. Any attempt to disassemble a failed device may also destroy the evidence for failure.

In-situ stress sensing methods relating real time results would permit operational performance stresses to be correlated to input variables thereby permitting the creation of a safe operational zone. Direct feedback to a closed-loop control system can then constrain the device within the safe zone. An in-situ seal integrity sensing design and methodology has been demonstrated by ENrG Inc. and JHUAPL.

## **High Temperature Issues**

Typical planar Solid Oxide Fuel Cell (SOFC) stacks are composed of various ceramic materials that exhibit a range of high thermal expansion coefficients, low thermal shock resistance, low fracture toughness, and poor mechanical strength characteristics. Stacks are layered structures composed of interleaved cells and either metal or ceramic interconnects. The interconnects are perimeter sealed to the cells to eliminate the possibility of air and fuel prematurely mixing around the cell instead of through the ceramic membrane of the cell component. Various ceramics are used to produce the cell component, which is a thin membrane of an ionic conductor with an anode and cathode on either side. All of these functional layers are either ceramic or cermet materials

capable of handling reducing conditions on the anode side and oxidizing conditions on the cathode side. At temperatures greater than 500°C, oxygen ions readily conduct from the cathode side of the ceramic membrane to the anode side where they combine with hydrogen ions creating water, heat and electricity. As long as fuel and air are flowing to the stack, it will become thermally self-sustaining.

For SOFC systems operating at high temperatures (>650°C), the thermal expansion coefficients of the cell components, interconnect structures, and hardware materials must be carefully matched to prevent the development of severe thermal stresses resulting in cell or seal failure during various operational modes. Although mathematical models have been used to calculate the generated stresses in the stack and attempt to predict operational regions of safety or failure, the complexity of a fuel cell stack makes it very difficult to quantify stresses that develop during operation, until of course a catastrophic failure occurs. Unfortunately with thin membrane ceramics or seals, these failures can be so catastrophic that if the failure itself does not destroy the ability to evaluate the very reason for the failure, the disassembly of the stack may result in the loss of the data. Therefore, other in-situ evaluation and ultimately control methodologies are necessary to further the development, commercialization, and reliability of SOFC based energy systems.

### **TDR and FR**

Ultimately, coupling high temperature in-situ evaluation techniques with correlation to stress models and predictive equations can result in the ability to produce a closed-loop in-situ control system that is cell and seal sensitive and permits safe stack operation in all modes while minimizing the resultant stress modes. To achieve such a control system requires the incorporation of seal structures which can be electronically tested using Time Domain Reflectometry (TDR) and Frequency Response (FR). These methods can appraise the integrity of the cell membrane and perimeter seal through analysis of the structure's electronic "signature" in response to pulsed and microwave signals. The incorporation of multilayer signal structures in the cell membrane and ceramic/glass seal tied to a signal generator and analyzer yields structural radar type images showing changes in cross-section, build up or relaxation of stress, existence of discontinuities, or ultimately failure of the ceramic medium.

The use of TDR and FR signal methods to extract an electronic "signature" from fiber optic cables, printed circuit boards, moisture in soils measurements are well known. These techniques have yet to be applied to the field of energy production and specifically to SOFC stacks. Both techniques are classic methods for diagnosing failures along interconnects of the "controlled impedance" variety, such as high speed digital circuit boards, and to recognize small changes in performance in light of minor physical changes, such as those found in RF assemblies. TDR and FR techniques have been used in multiple cases to discern thermal stress anomalies in ceramics. Anderson<sup>1</sup> used TDR

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<sup>1</sup> Anderson, Paul M., Lindner, A.W., Chau, P.M., and Smith, A.D, "High Temperature Superconducting Multilayer Multichip Module: Fabrication and High Speed Characterization," Manuscript on work supported by Navy SBIR Contract #N61331-96-C-0017 at

<http://www.st.northropgrumman.com/whoweare/SiteFiles/docs/stratedgepaper.pdf>.

on difficult to fabricate high temperature Superconducting multilayers. Anderson was able to fabricate a simple circuit structure in the multilayer leading to the full characterization of the high-speed digital waveform and pulse integrity. Additionally, Anderson performed thermal cycling on the structures to identify if any thermal expansion mismatches occurred. Swaminathan<sup>2</sup> used high-speed analysis techniques to analyze process defects in embedded passive components such as capacitors and resistors in ceramic multilayers.

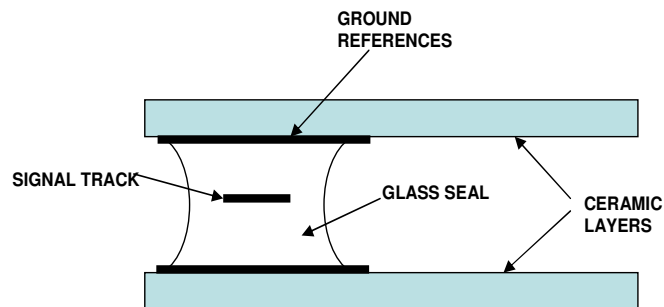
Demonstration of the creation of multilayer line structures in the seal will result in the collection of physical measurement data on the change in seal features during heat up, steady state operation, transients, or on cool down. A radar type image of the signal characteristics will show build up or relaxation of stresses, discontinuities in seal structure including porosity, delamination of the seal from either the cell or interconnect, and ultimately the catastrophic failure of the seal. Additionally with the ability to use a metal interconnect as one of the plane references coupled with a trace on the oxide coating on the interconnect, electrical conductivity and structural integrity of the thin oxide film on the metal interconnect can be determined within the vicinity of the trace.

### Seal Design

The seal design includes an electrical transmission line embedded within dielectric material sealing an interface between adjacent structures. A signal injection port is provided for exciting the transmission line with a signal source and a second port allows for sampling the transmission line while the excitation signal is present.

The sample ports were adapted for connection to test and measurement apparatus which are used to analyze signal samples for indications of seal integrity problems. Using time domain reflectometry or frequency response analysis, the transmission line was monitored for changes in characteristic impedance due to variation in seal dielectric constant and/or disruption of the transmission line. Such an evaluation provided useful information for making determinations about seal integrity in a manner that permitted safe seal operation and minimization of resultant stress modes.

Creating a seal in the image of a passive electronic component may be accomplished by building up the seal in a multilayered approach as shown in Figures 1 and 2. The perfect seal maintains a consistent and expected signal response over temperature. Anomalous



**Figure 1. Construction of a seal that also functions as a transmission line interconnect.**

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<sup>2</sup> Swaminathan, M. and Pannala, S., "Mixed Signal Portable Wireless Packaging Design and Test Challenges," Proceedings of the IEEE Computer Society Workshop on VLSI '98, pp. 89-94, Orlando, Florida, Apr. 1998.

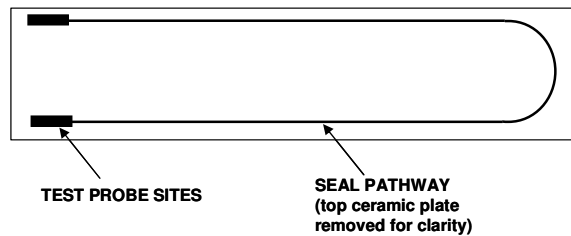
behavior would give a characteristic signal response. Anomalies of particular interest are breaks in the seal, effacing of the seal wall and changes in seal dimension due to thermal stress.

Inserting a pulse (TDR) that rises to final value within picosecond durations and listening to the “return” pulse is similar in principle to a radar or sonar system. The method can detect anomalies and their location along the line, but may not have the resolution to detect the seal’s proximity to failure. In contrast, inserting a spectrum of sinusoids (FR) into the seal and measuring the energy that is transmitted through or reflected back at each frequency can detect minor changes in seal integrity and proximity to failure but not location of an anomaly along the line. In effect both techniques must be used in this phase of the program in order to validate the type and location of the seal anomaly with its corresponding “electronic signature”.

There are two risks associated with this approach: First, the ability to create a seal with the required dimensions of the signal track and associated dielectric constant of the glass to yield sufficiently high impedance (target 50 ohms) and second, that the anomalies have recognizable and reproducible signatures within the passable bandwidth of the interconnect.

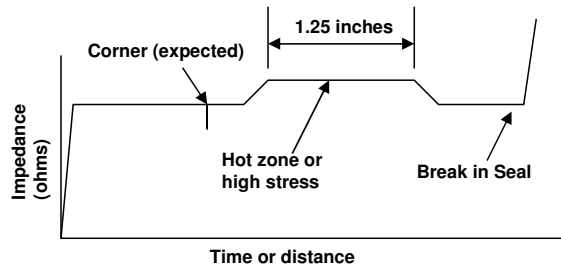
The TDR method measures the characteristic impedance along a transmission line. To be effective, the transmission line must be contiguous along the length of the seal and may turn corners. Ideally the seal must be accessible at both ends. Figure 2 illustrates a longitudinal cross section of a seal with an embedded transmission line and the instrumentation probe feature where the signal is inserted or observed.

The geometry of the signal insertion/probe point must be outside the cell seal area and is fabricated by the same screen printing process that creates the seal in a multilayer fashion. Figure 3 illustrates the plan view of a possible test sample (top ceramic layer removed for clarity).



**Figure 3. Plan view of a 2'' x 6'' seal test sample monitored using TDR & FR methods.**

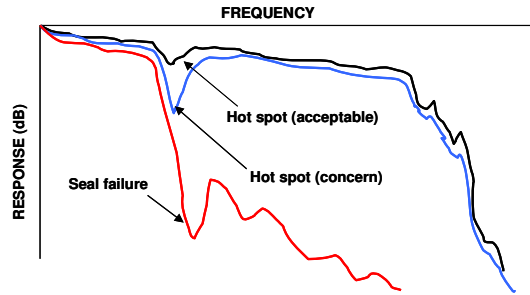
In operation the ideal response from the TDR signal will show a flat response at the impedance value of the line. Corners, breaks, deviations in impedance due to stress, and their distance from the signal source should all be recognizable features. Figure 4 illustrates a possible TDR response with several different kinds of seal anomalies.



**Figure 4. Notional TDR response of a seal with anomalies**

## Frequency Response Applied to Seal Integrity

The TDR method sends a “step function” (containing a broad spectrum of signals) down the seal and observes the response in the time domain. In contrast, the frequency response method sends a narrower spectrum of sinusoids down the seal and observes the response in the frequency domain by comparing the signal energy



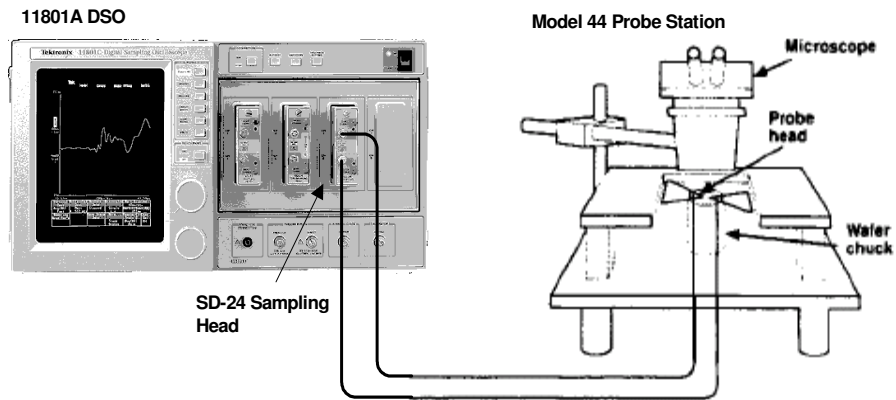
**Figure 5. Notional  $S_{21}$  responses superimposed of a seal with a hot spot identified, growth in severity and final failure.**

sent at each frequency with the energy making it through the line ( $S_{21}$  or forward gain), and that reflected at the source ( $S_{11}$  or return loss). Figure 5 is an illustration of a notional  $S_{21}$  response of a hot spot growing in severity until failure. It is envisioned that the FR technique could be used to recognize anomalies and their severity. The FR method views the seal as a network made up of passive components (such as a capacitors, resistor, or inductors), which have a unique response “signature”. Changes in seal integrity, as mentioned above, will all be observed as characteristic differences at unique frequency or band of frequencies. Although the location of the anomaly cannot be determined, the resolution and awareness of the proximity to failure should be superior to the TDR method. Both techniques are necessary, however, to establish and validate a link between a particular anomaly and its impact on the FR signature.

## Evaluation Testing

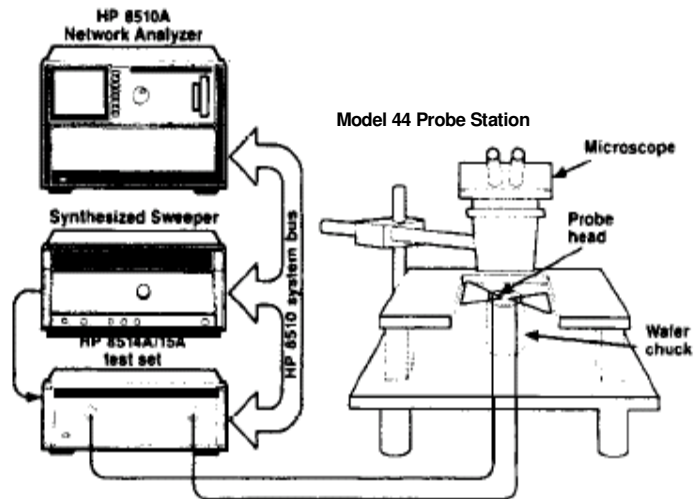
It was apparent that voids were created in the top/bottom of the dielectric seal during processing of the samples that contained the Microstrip transmission line. For this reason, a majority of the testing was performed on samples containing the Coplanar transmission line.

The fuel cell seal samples were tested using the Microtech Model 44 Probe Station. A block diagram of the TDR measurement system is shown in Figure 61. The sample is mounted on the wafer chuck, and both ends of the transmission line embedded in the sample are connected to the TDR sampling head.



**Figure 61 - Block Diagram of TDR Measurement Setup**

A block diagram of the Network Analysis measurement system is shown in Figure 7.

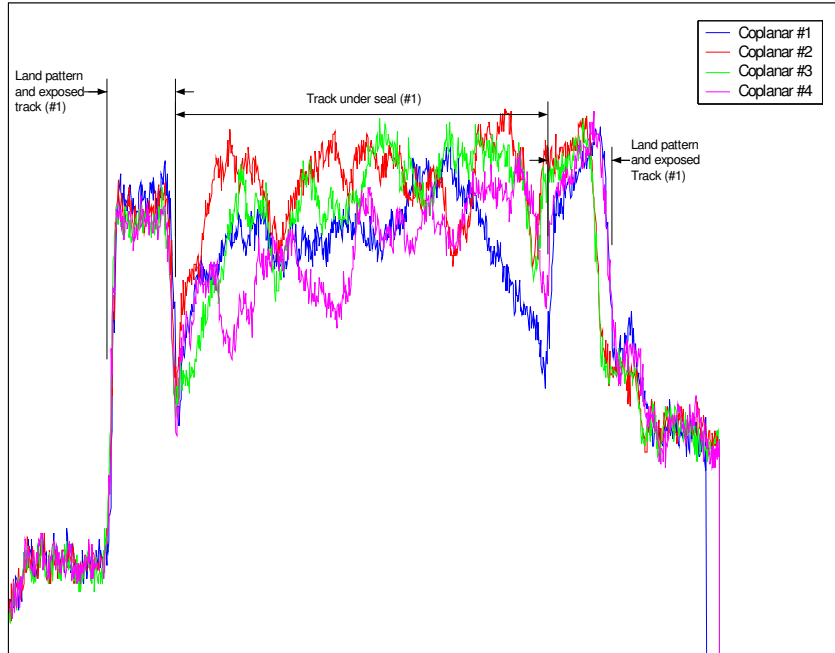


**Figure 7 - Block Diagram of Network Analyzer Test Setup**

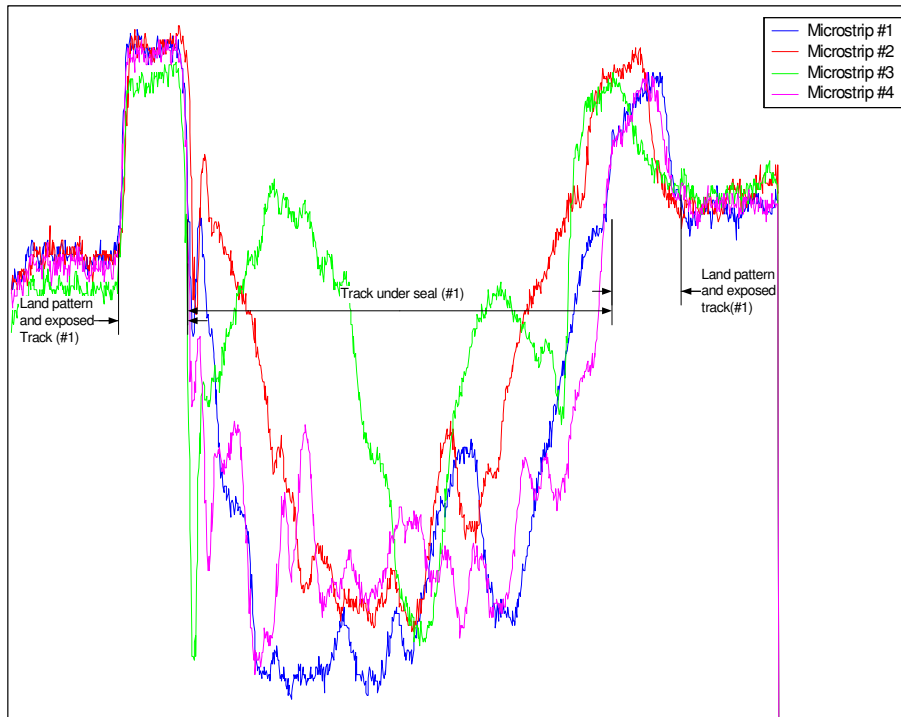
A propane torch was used to heat selected samples. The samples were cooled using compressed air.

## Results

The variation in the impedance of the microstrip transmission line samples was approximately 150% greater than that of the samples that employed the Coplanar type transmission line. Figure 8 shows a composite of the coplanar waveforms while figure 9 shows a composite of the microstrip waveforms.



**Figure 8 - Composite of TDR waveforms from four coplanar waveguide samples**

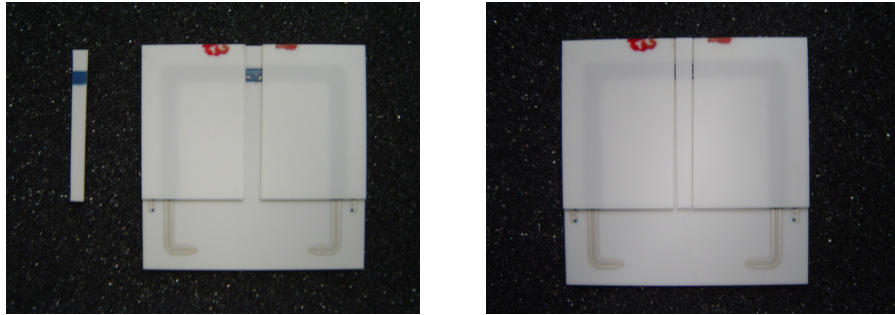


**Figure 9- Composite of TDR waveforms from four microstrip samples**

TDR measurements of a sample subjected to localized heating and cooling showed a variation of approximately 5% from a recorded baseline measurement of the reflected signal in the region at which the temperature source was applied.

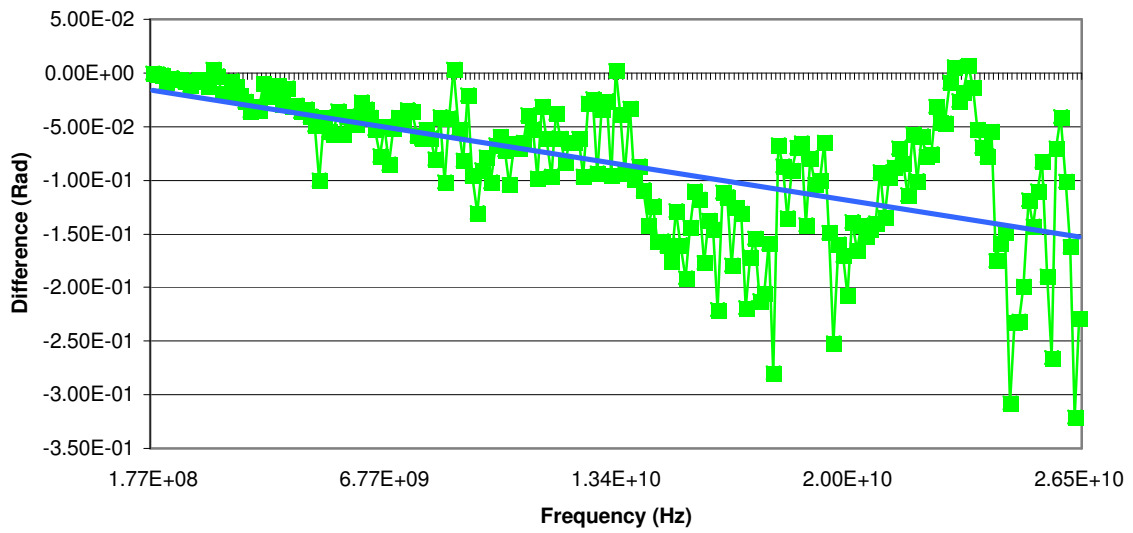
Baseline TDR measurements were made for two samples in their entirety and then the two samples were ablated. In one case a laser was used to make a cut perpendicular to the direction of the track formed by the dielectric seal material. In the second sample, a dicing saw was used to cut through the top plate of the sample and remove a portion of the dielectric seal. After the samples were ablated, a second set of TDR measurements were made for comparison with the baseline. In both cases, there were no visible differences between the baseline and the second measurement.

In a third sample, two dicing saw cuts were made perpendicular to the track direction and parallel to one another, as shown in Figure 10 allowing a section of the ceramic top plate and a print of the dielectric seal material to be removed. In this sample, TDR measurements comparing the same sample in cases both with the ceramic “lid” in place and with the lid removed showed a visible phase-shift in the time-domain signal.

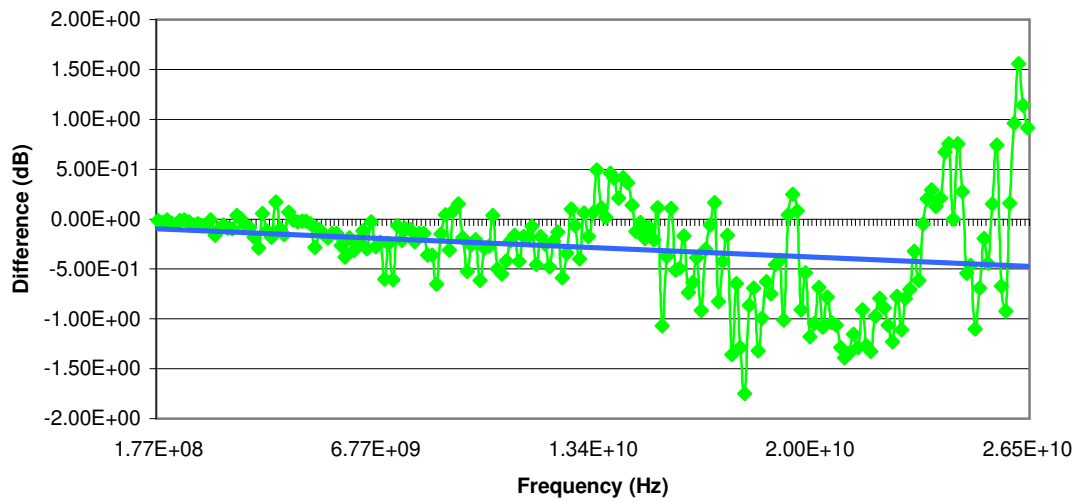


**Figure 10 – Coplanar Sample #5: Ceramic cutout shown removed from sample (Left) and placed on sample (Right)**

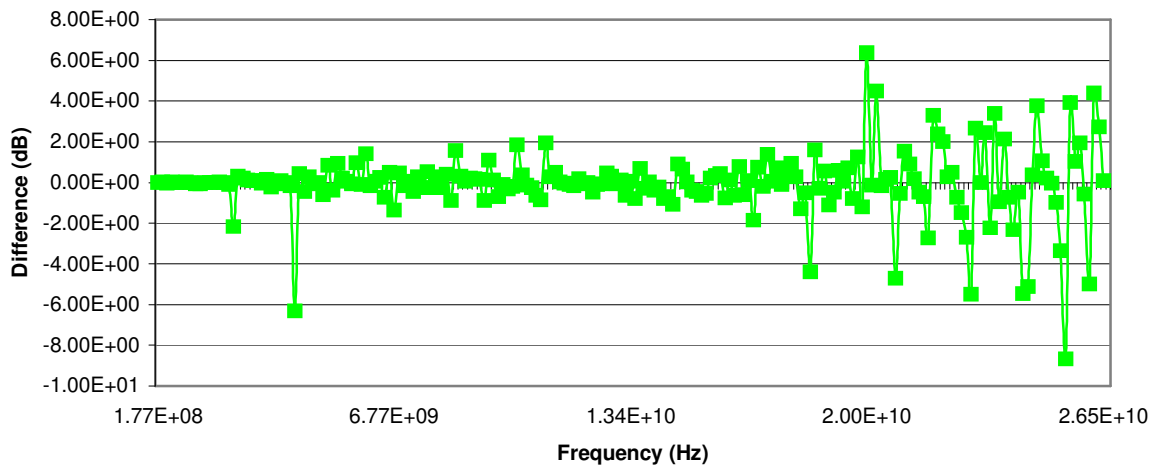
Network analyzer measurements showed very frequency-selective changes in reflected and transmitted power in response to localized changes in the dielectric constant or to heating of the sample. The measurements were made over the range between 45Mhz and 26.5GHz. In most cases, the largest changes occurred in the high end of this spectrum. These results are shown in Figures 11 through 14.



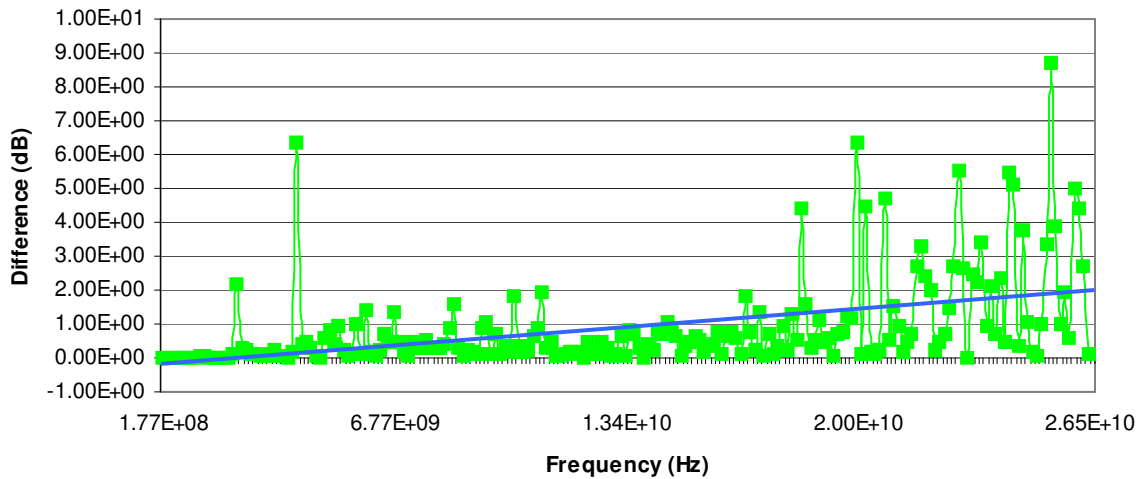
**Figure 11 – Plot of S21 phase difference. Difference calculated for two Sample #4 measurements at cold and hot temperatures (Blue line is first order trendline)**



**Figure 12 – Plot of S21 magnitude difference. Difference calculated for two Sample #4 measurements at cold and hot temperatures (Blue line is first order trendline)**



**Figure 13 – Plot of S22 magnitude difference. The difference calculated for two Sample #5 measurements with and without “lid”**



**Figure 14 – This plot shows the absolute value of the difference calculation in Figure 13, illustrating increasing variability in magnitude as frequency increases (Blue line is first order trendline).**

The test results suggest that the fuel cell seal variant which contains the coplanar waveguide structure is probably a better candidate than the microstrip variant for the goal of designing a seal that might be indicative of defects or precursors to seal failure, as the sample-to-sample variability is much greater in the microstrip variant.

## **Summary**

A comparison of the TDR and the frequency response methods for fault detection/measurement suggests that high-frequency measurement of transmitted/reflected power ( $S_{21}/S_{11}$ ) and phase using the frequency response method is the most effective means of detecting changes in the seal characteristics due either to temperature changes or to changes in the dielectric constant in and near the transmission line structure. When evaluated in its entirety, comparisons of the TDR signatures of a given sample do not appear to offer the same degree of sensitivity.