

ABSTRACT

Title of Thesis: RELIABILITY OF CERAMIC ELECTRODES
OF SOLID OXIDE FUEL CELLS

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Solid oxide fuel cells (SOFCs) are highly efficient chemical to electrical energy conversion devices that have potential in a global energy strategy. The wide adoption of SOFCs is currently limited by cell durability and manufacturing cost. Ceramic anodes show promise for improved durability and are prominent candidate for electrodes of SOFCs. Ishikawa diagram was developed and a comprehensive failure modes, mechanisms, effects, and criticality analysis (FMMECA) methodology is applied to ceramic anodes of SOFCs to understand possible causes of failure. Despite high conductivity and better performance of conventional ceramic electrodes i.e. strontium-based perovskite electrodes, there is a concern that humidity, especially high humidity and high temperature, during storage can affect the properties prior to installation. Degradation mechanisms which can manifest themselves during storage was found and empirical degradation model was developed to determine the storage specification for strontium-based perovskite electrodes of SOFCs.

RELIABILITY OF CERAMIC ELECTRODES OF SOLID OXIDE FUEL CELLS

by

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Chapter 1: Introduction of Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are expected to play a major role in a sustainable energy future given their high potential energy conversion efficiency. SOFCs convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. Fuel cells take advantage of the fact that, like heat engines, as long as fuel is available, they can produce power. Unlike heat engines, there is no mechanical motion in fuel cells, and hence they provide maximum efficiency [1].

One can understand fuel cell as an open energy conversion system unlike battery which is a close energy storage system. As long as fuel is supplied, the fuel cell will generate a voltage whereas a battery makes electricity from the energy it has stored inside the battery. This provide fuel cells an inherent advantage over battery by eliminating the capacity requirement.

A fuel cell consists of two electrodes that conduct electrons—the anode and the cathode. The electrodes are separated by an electrolyte that conducts ions. In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment. The oxidation reaction takes place at the anode and involves the liberation of electrons. These electrons travel around the external circuit providing electrical energy and arrive at the cathode where they participate in the reduction reaction.

1. Historical Background of Fuel Cells

William Grove, who was the first to perform reverse electrolysis of water, introduced the concept of fuel cells in 1839. However, fuel cells were largely unexplored until they were used in the National Aeronautics Space Program (NASA) Apollo space program [2] in the 1960s. In addition to satisfying the requirements for power, efficiency, weight, life, reliability, safety, mission flexibility, and development maturity, fuel cells were chosen for Apollo missions because of their unique ability to supply potable water (the product of electrochemical reaction) for crew consumption and cabin air humidification [3]. What emerged as a result of the NASA selection of the fuel cell was an almost explosive growth in fuel cell research and development in industries, in universities, and in government laboratories.

Combustion of fossil fuels is the most utilized power generation method in use today which causes significant environmental pollution [4]. Various alternative technologies have been put forward to reduce the carbon emissions, however many of these still suffer from high cost, low efficiency and low reliability [5, 6]. Interest in fuel cells for use in energy production is attributed to the fact that they are inherently much more energy efficient along with low carbon emissions as compared to other power

generation techniques [7]. The development of different kinds of fuel cells since their introduction is shown in Figure 1 [8, 9].

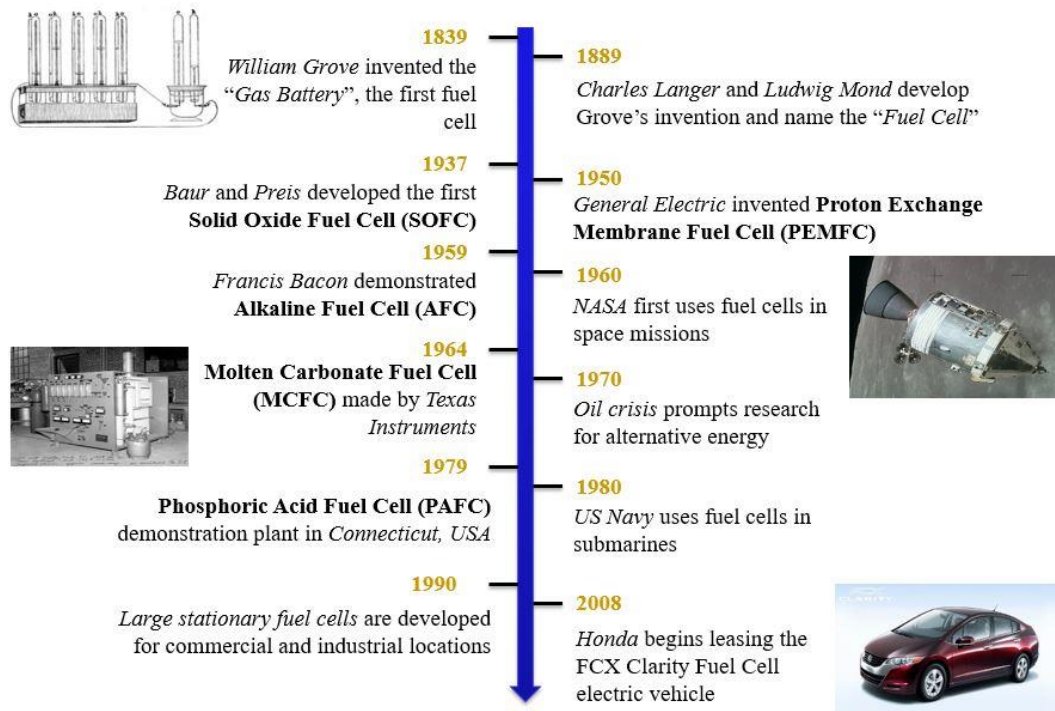


Figure 1. Historical timeline of fuel cell technology

2. Fuel Cell Types

The types of fuel cells under active development are summarized in Figure 2 [10, 11]. The basic design consists of an electronically insulating, ion-conducting membrane separating two electrodes, connected through an external circuit. The reaction products are formed at the anode for alkaline fuel cells (AFCs), molten-carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs), and at the cathode for polymeric-electrolyte-membrane fuel cells (PEMFCs) and phosphoric-acid fuel cells (PAFCs). The AFC, PEMFC, and PAFC stacks essentially require a supply of relatively pure hydrogen to the anode. Accordingly, the use of hydrocarbon or alcohol fuels requires an external fuel processor to be incorporated into the system. This external reforming process of hydrocarbon fuels increases the complexity and cost of

the system. In contrast, MCFCs and SOFCs operating at higher temperatures have the advantage that both CO and H₂ can be electrochemically oxidized at the anode, hence, eliminating the need of an external fuel processor.

	Fuel at Anode	Anode	Electrolyte	Cathode	Fuel at Cathode
H ₂ O, CO ₂	Natural gas (internal reforming)	$\begin{aligned} &\text{H}_2 + \text{O}^{2-} \gg \gg \text{H}_2\text{O} + 2\text{e}^- \\ &\text{CO} + \text{O}^{2-} \gg \gg \text{CO}_2 + 2\text{e}^- \end{aligned}$	SOFC (500 - 1000°C) ← 2O ²⁻	$\begin{aligned} &\text{O}_2 + 4\text{e}^- \gg \gg 2\text{O}^{2-} \end{aligned}$	O ₂ (Air)
H ₂ O, CO ₂	Natural gas (internal reforming)	$\begin{aligned} &\text{H}_2 + \text{CO}_3^{2-} \gg \gg \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \end{aligned}$	MCFC (650°C) ← CO ₃ ²⁻	$\begin{aligned} &\text{CO}_2 + \frac{1}{2} \text{O}_2 + 2\text{e}^- \gg \gg \text{CO}_3^{2-} \end{aligned}$	O ₂ (Air) CO ₂
External reforming of natural gas	H ₂ , CO ₂	$\begin{aligned} &2\text{H}_2 \gg \gg 4\text{H}^+ + 4\text{e}^- \end{aligned}$	PAFC (200°C) 4H ⁺ →	$\begin{aligned} &\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \gg \gg 2\text{H}_2\text{O} \end{aligned}$	O ₂ (Air) H ₂ O
	H ₂ , CO ₂ (CO removal)	$\begin{aligned} &2\text{H}_2 \gg \gg 4\text{H}^+ + 4\text{e}^- \end{aligned}$	PEMFC (80°C) 4H ⁺ →	$\begin{aligned} &\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \gg \gg 2\text{H}_2\text{O} \end{aligned}$	O ₂ (Air) H ₂ O
H ₂ O	H ₂	$\begin{aligned} &2\text{H}_2 + 4\text{OH}^- \gg \gg 4\text{H}_2\text{O} + 4\text{e}^- \end{aligned}$	AFC (70°C) ← 4OH ⁻	$\begin{aligned} &\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \gg \gg 4\text{OH}^- \end{aligned}$	O ₂ (Air) (CO ₂ removal)

Figure 2. Summary of fuel cell types along with electrochemical reactions

However, to maintain the composition of electrolyte in the MCFC system, CO₂ has to be recirculated from the anode exhaust to the cathode input, which complicates the system [10]. Therefore, SOFCs are considered as one of the most promising technologies for high-efficiency electric generation from natural gas, both in simple fuel cell plants and in integrated gas turbine/steam turbine–fuel cell systems [11, 12].

3. Working Mechanisms of SOFCs

SOFC is an electrochemical device that converts chemical energy into electric power with high efficiency. A schematic representation of an SOFC is depicted in Figure 3. The reduction reaction takes place at the cathode, which produces the oxygen ion. The dense structure of the electrolyte does not allow the passage of cathodic gas

through it. The high ionic conductivity and high electrical resistance allow only O^{2-} ions to migrate from cathode to anode. At the anode, O^{2-} ions oxidize hydrogen and produce water and electricity. When pure hydrogen is used as fuel, SOFCs are an exceptionally clean form of energy. However, the use of natural gas as fuel results in production of water and CO_2 at the anode outlet.

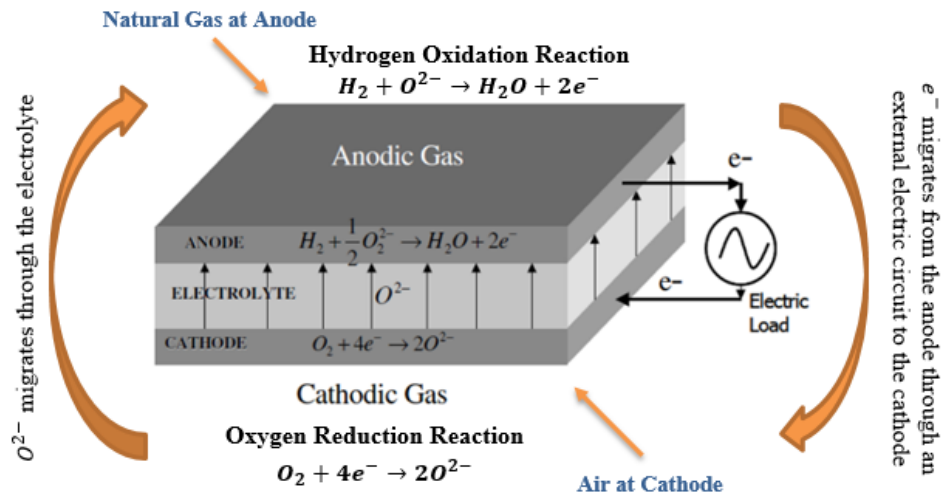
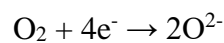
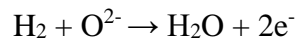


Figure 3. Schematic representation of an SOFC

At the cathode reduction of oxygen occurs via



These oxide ions travel through the ion-conducting electrolyte and react with hydrogen in oxidation reaction at the anode producing water:



As oxidation reaction occurs at the anode, electrons are released at the anode and migrate from the cathode through an external circuit, thus generating an electric current.

4. Advantages of SOFCs

Looking to the wide potential in SOFC based distributed power generation, the comparative study of different generation systems based on their percentage efficiency, capacity range, and capital and maintenance cost has been done [13]. Table 1 shows a comparison of different generation systems. It is observed that the efficiency of fuel cells is always higher as compared with conventional and other distributed generation systems. While comparing the fuel cell with other distributed generation technologies, it offers more advantages, like high energy conversion efficiency, zero emission, modularity, scalability, quick installation and good opportunities for cogeneration operations [14].

Table 1. Comparison of power generation systems

	Reciprocating Engine: Diesel	Turbine Generator	Photovoltaic	Wind Turbine	Solid Oxide Fuel Cells
Capacity Range	500 kW to 5 MW	500 kW to 25 MW	1 kW to 1 MW	10 kW to 1 MW	200 kW to 2 MW
Operating Temperature	90 - 105°C	1200 to 1400°C	25°C	-20 to 40°C	500 - 1000°C
Efficiency	35%	29–42%	6–19%	25%	40–80%
Capital Cost (\$/kW)	200–350	450–870	6600	1000	1500–3000
Operation and Maintenance Cost (\$/kW)	0.005–0.015	0.005–0.0065	0.001–0.004	0.01	0.0019–0.0153

Because of their high efficiency as compared to other power generation techniques, SOFCs are one of the most efficient and effective solutions to environmental problems that we face today. The high efficiency of SOFCs results in less fuel being consumed to produce a given amount of electricity, which corresponds to a lower emission of

carbon dioxide (CO₂). SOFCs generally provide the lowest emissions of any non-renewable power generation method, such as traditional thermal power plants, as shown in Table 2. This is very important with regard to energy related environment concerns.

Table 2. Typical SOFC air emission as compared to fossil fuel plants

Air emissions (per 1650 MWh)	SO_x (Kgs)	NO_x (Kgs)	CO (Kgs)	Particles (Kgs)	Organic compounds (Kgs)	CO₂ (Kgs)
Fossil fueled plant	12740	18850	12797	228	213	1840020
SOFC system	0	0	32	0	0	846300

5. Electrodes of SOFCs

Study of electrodes of an SOFC is critically important because of the three-major functions of the electrodes: (1) Allowing access to reacting gases. (2) Allowing transport of electrons as well as ions. (3) Providing active catalytic sites. To accommodate these functions, the anode and cathode requires porosity of 30-40% [15]. Significant reduction in porosity with each redox cycle has been observed in traditional Ni-based anodes [15]. Traditional SOFCs (composition shown in Table 3 [16]) have disadvantages, such as low-electrochemical performance ($\leq 350 \text{ mW cm}^{-2}$), redox cycling instability, higher operating temperatures (above 700°C), and chromium-based expensive alloys for interconnect.

Table 3. Traditional SOFC composition

Component	Composition	Conductivity depends upon
Anode	Ni/YSZ cermet (Nickel/Yttria stabilized zirconia)	Particle size ratio, Nickel content
Cathode	LSM (Strontium doped Lanthanum Manganite)	Cathode, Porosity, and Sr content
Electrolyte	YSZ (Yttria stabilized zirconia)	Electrolyte density

Long-term stability is an important requirement for the commercial application of the SOFC technology. For stationary applications, the commercial lifetime requirement is generally more than 40,000h. In comparison, up to a 20,000h lifetime with more frequent thermal cycles is required for auxiliary power units in transportation application. However, these lifetime requirements are difficult to achieve with traditional electrode materials. Operating conditions of SOFCs lead to a variety of degradation mechanisms and represent a significant challenge in meeting lifetime requirements. For stationary applications, the chemical instability at the interfaces is one of the key issues. Thermomechanical instability is important in transportation because of frequent thermal cycles [17]. Additionally, it has been reported for Ni based anodes that each reduction-oxidation (redox) cycle causes degradation at the rate of 0.3% per cycle [18]. In order to solve these problems and make this technology cost effective, ceramic anodes have been developed.

Chapter 2: Degradation Mechanisms for Ceramic Anodes of SOFCs

Degradation is usually defined as the performance degradation as well as mechanical failure such as crack formation and propagation. To predict the lifetime of a stack, it is essential to understand the physical and chemical (physicochemical) reasons for respective degradations. Physicochemical features should be clarified in relation to the electrochemical mechanism. Furthermore, degradation may occur as a result of many related deteriorations which take place sequentially. These deterioration-chain phenomena are currently not well recognized for ceramic-anode-supported SOFC [19, 20, 21, 22].

1. Anode Composition and Requirements

The anode of SOFCs not only functions as a site for electrochemical oxidation of the fuel, but also transfers charge to a conducting contact. Therefore, both the catalytic and electronic conductivity of the anode are critical. In addition, the anode materials must be compatible (chemical and thermal compatibility) with other components (the electrolyte and interconnects) [23]. Design of anode materials should also consider the operating temperatures of SOFCs which is usually above 500 °C [24]. This requires materials which do not degrade or alter at high temperatures and should be non-reactive with electrolyte. Coefficient of thermal expansion of anode materials should be close to electrolyte and cathode materials in order to prevent interfacial delamination and cracking at high-temperature operations. Ceramic-metallic (cermet) anodes, especially nickel-based anodes, can produce a combination of these required properties and hence, have been used as traditional anode materials for SOFCs [25]. However, traditional

nickel-based anode material for SOFCs have disadvantages, such as volumetric changes during the initial reduction of NiO to Ni resulting in stress in the cell and susceptibility to catastrophic mechanical failure in the event fuel is unintentionally lost during operation with consequent oxidation of the Ni to NiO. Ceramic anodes have been developed to solve these problems and make this technology cost-effective.

Since, it is very difficult to devise oxide-based anodes with high electronic and ionic conductivity, and good chemical compatibility with electrolytes, it has been proposed to decouple the anodes into substrate and functional layers [19]. The substrate layer forms the thicker portion of the anode. It serves as a mechanical support and a current collector in the cell, but it does not play a role in the electrochemical reaction that takes place at the anode end. The thickness of the substrate is around 500–1500 μm [26]. The functional layer provides the site for the electrochemical reaction to take place. The thickness of this layer is generally around 10–15 μm [26]. It is possible to decouple these two layers because of functional differences between them by using different materials for each component based on the desired chemical, thermal, and physical characteristics [27]. For instance, the substrate material should have a high electronic conductivity to reduce Ohmic losses, whereas ionic conductivity is not essential. In the case of the functional layer, a high ionic conductivity is required, whereas the electronic conductivity may be lower than the substrate. Thus, using materials that have different properties allows anodes to be more flexible. The desirable properties of both these components are tabulated in Table 4 [26].

Table 4. Desirable properties of the anode substrate and functional layer materials

Property	Anode Substrate	Anode Functional Layer	Comments
Electronic conductivity (at 800 °C)	>10 S/cm	>1 S/cm	Basic properties required for functioning
Ionic conductivity (at 800 °C)	Not required	>0.02 S/cm or comparable to that of YSZ (electrolyte)	
Good electro-catalytic activity for H ₂ /CO oxidation	Not required	Required	
Chemical stability in anode atmosphere (H ₂ , CO, CO ₂ , H ₂ O, CH ₄)	Required	Required	Compatibility with working environment
Thermal expansion coefficient	10.5–13 ppm/K	10.5–13 ppm/K	
No detrimental effect solid-state reaction with electrolyte (e.g., YSZ)	Not required but preferred	Required	
Linear expansion or shrinkage upon redox cycling	<0.2%	<1%	Important for the reliability of anode supported cells
Tolerance to dry hydrocarbons (no carbon buildup)	Required	Required	Further simplification of fuel pre-processing
Tolerance to sulfur poisoning	Required	Required	

2. Ceramic Anodes for SOFCs

While ceramic-metallic (cermet) anodes have been used in the past because of their high performance in syngas (a mixture of CO and H₂ formed by hydrocarbon reforming); these cermets are sensitive to presence of sulfur in the fuel [28, 29], they cannot tolerate re-oxidation during shut-down and start-up cycles, and tend to form

carbon in presence of dry hydrocarbons [30]. In order to improve reliability, ceramic materials for the anodes of SOFCs have been investigated extensively because of their tolerance to reduction-oxidation (red-ox) cycling and excellent thermal stability [31, 32, 33]. To this end, ceramic anodes should have: (1) negligible dimensional changes during red-ox cycles (less than 0.1 to 0.2% of linear expansion), (2) electrical conductivities higher than 10 S/cm, (3) stability in reducing atmospheres and air and compatibility with the electrolytes, (4) thermal expansion coefficients close to that of the electrolyte, and (5) good catalytic activities for H₂ and CH₄ oxidation. Ionic conductivities should be >0.02 S/cm [34].

However, the performance of ceramic anode has been modest as compared to cermet because of their low oxide ion conductivity and poor catalytic activity for hydrogen oxidation and their requirement of operating temperatures of more than 900 °C to achieve the comparable performance which can be achieved at 700 °C using Ni-based cermet [35, 36]. Several types of ceramic anodes have been investigated because of their tolerance to coking and sulfur poisoning [37]. Much of the effort has focused on perovskite materials because they provide: (1) mixed ionic electronic conductivity, (2) structurally stable chemistries throughout a wide range of oxygen partial pressure and temperatures, and (3) no reactivity with other components [31, 38, 39]. Vanadium-doped perovskite, Sr_{1-x/2}V_xTi_{1-x}O₃ (SVT) and Sr_{0.2}Na_{0.8}Nb_{1-x}V_xO₃ (SNNV) achieved high conductivities and performance as high as 500 mWcm⁻² as compared to 350 mWcm⁻² for conventional SOFCs. Gadolinium-doped ceria (GDC) electrolyte supported cell was fabricated with Sr_{0.2}Na_{0.8}Nb_{0.9}V_{0.1}O₃. Performance was measured in hydrogen and methane, respectively. Due to vanadium's intrinsic

problems, such as long-term stability problems associated with the liquid phase sintering [40], the vanadium-doped anode-supported cell has not been commercialized.

In 2013, symmetric solid oxide fuel cells (SSFCs) with the configuration of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM)/LSGM/SFM, in which SFM was proposed as a promising electrode [41, 42, 43], reached 835 and 230 mWcm^{-2} in wet H_2 and CH_4 , respectively. In order to improve the further catalytic activity and electrochemical performance of SSFCs, modified SFM by cobalt-substitution was developed [44]. The presence of cobalt is beneficial to the hydrogen oxidation reaction (HOR) and contributes to low polarization loss. The cobalt as dopant not only affects the catalytic activity of anodes but also improves oxygen ionic conductivity. Sivaprakash et al. [45] presented a new A-site layered double perovskite-manganese oxide which exhibit superior SOFC anode performance and fuel flexibility. Recently, iron-doped double perovskite $\text{Sr}_2\text{CoMoO}_6$ (SFCM) has been developed as a promising anode [46], through which the conductivity was improved over one order of magnitude and performance reached 2 Wcm^{-2} .

3. Operating Conditions for Ceramic Anodes of SOFCs

A basic organization of operating conditions of the SOFC is shown in Figure 4. The anodes of SOFCs can operate in steady state mode (constant stress conditions) and transient mode. Typically, the transient mode is more deleterious and can cause sudden failure of SOFCs because of interfacial delamination or cracking of anodes due to thermal cycles, load cycles, or red-ox cycles. Degradation is usually defined as performance degradation as well as mechanical failure such as crack formation and propagation. Systematic investigations of such degradation phenomena can be done with several tests: durability tests, thermal-cycling tests, red-ox stability tests, and accelerated aging tests. To predict the lifetime of a stack, it is essential to understand the physicochemical reasons for respective degradations. Furthermore, degradation may occur as a result of related deteriorations that take place sequentially.

To investigate the degradation in anodes of SOFCs, experiments shown in Table 5 can be performed. These test plans are based on reviewed literature and the final test

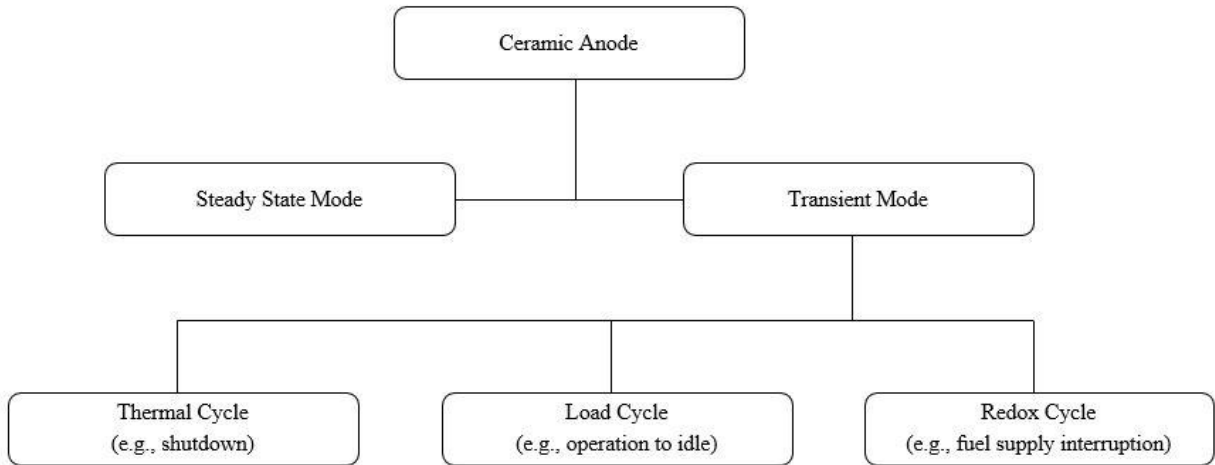


Figure 4. Operating conditions for ceramic anodes of SOFCs

conditions will be determined based on specific operating conditions based on the

electrodes used in SOFCs [47] [48] [49] [50] [51] [52] [53] [54] [55] [56]. These tests have not been performed at CALCE, University of Maryland, however, one can use this guideline to develop accelerated testing plans for electrodes of SOFCs.

Table 5. Tests reported in literature to determine degradation mechanisms of anodes of SOFCs

Tests	Description
1. Isothermal (steady state) ageing	By raising the stacks to desired operating temperature (between room temperature and peak temperature).
2. Thermal cycling	By rapidly alternating between peak temperatures and room temperatures.
3. Redox cycling	By changing the fuel flow between maximum and no-flow.
4. Thermal shock	By heating the stack to the shock temperature and then abruptly cooling to ambient temperature.
5. Electrical shock	By passing current through the anode while the cell is held at peak temperature.
6. Contamination	By introducing impurities at elevated levels.

4. Failure Modes in Metal-Ceramic (Cermet) Anodes and Ceramic Anodes

Different failure mechanisms for ceramic – metallic anodes have been studied extensively [57, 58, 59, 60]. However, the organization and prioritization of failure mechanisms along with effect of these mechanisms on different anode materials is required to assess and improve reliability of SOFCs. Red-ox instability, which refers to the chemo-mechanical instability of the SOFC anode and support under oxygen partial pressure variation during reduction and oxidation at high temperature (500 – 1000 °C), is one of the main limitation for cermet anodes [61]. Besides that, cermet anodes are prone to carbon deposition, sulfur poisoning, and reduction in porosity upon prolonged use. The ceramic anodes appear promising because of their high red-ox stability, high sulfur tolerance, and resistance to coking [24]. However, ceramic anodes suffer from low electronic conductivity in reducing atmosphere, and reduction in

catalytic activity because of phase decomposition in presence of high humidity [19, 24]. The different failure modes for cermet anodes and ceramic anodes on the basis of possibility of occurrence are shown in Table 6.

Table 6. Failure modes for ceramic-metallic anodes and all-ceramic anodes

Failure modes	Possibility of occurrence in ceramic-metallic anodes	Possibility of occurrence in all-ceramic anodes
Interfacial delamination or cracks due to red-ox instability	High	Low
Coke deposition	High	Low
Sulfur adsorption onto metal catalyst	High	Low
Reduction in porosity	High	Low
Corrosion of anode	Low	High
Reduction in catalytic activity	High	High

5. Ceramic Anode Degradation Mechanisms

The kinetics of most of the anode degradation mechanisms are influenced by the operating conditions of the SOFC. The key operating parameters for anode degradation in the steady-state mode are temperature [62], gas composition (especially the partial pressure of water), and current density (i.e., the working potential) [63]. In contrast, the number of red-ox and thermal cycles is the most critical parameter in the transient mode [64]. Electrolyte cracking is a major threat to the anode-supported cell under redox cycling conditions. Varying operating conditions of SOFCs can lead to the following degradation mechanisms: thermomechanical, chemo-mechanical, material transport, and deactivation and passivation.

5.1. Thermomechanical Mechanisms

Thermomechanical mechanisms pertain to variation in the mechanical properties of anode material with temperature. An SOFC's typical operating temperature is $>500^{\circ}\text{C}$, which leads to severe thermal stresses caused by the differences in mechanical properties during thermal cycling [65, 66]. For anode-supported SOFCs, the stress field in the anode may arise due to thermal expansion mismatch between the anode and other components, residual stresses, and stresses resulting from thermal cycles. These stresses can cause delamination and micro-cracking in the anode/electrolyte interface and lead to performance degradation and eventual failure [67]. Another factor leading to degradation is the generation of thermal gradients due to uneven thermodynamic reactions that occur in the triple-phase boundary of the cells [15]. The release of large amounts of thermal energy in different sections of the anode is likely to accumulate thermal stresses that are capable of weakening the bonds between materials.

5.2. Chemo-mechanical Mechanisms

As discussed above, chemo-mechanical mechanisms involve both chemical and mechanical action and can lead to catastrophic failures of the SOFC. The effect of the red-ox cycle on the performance of SOFCs has been widely studied [68]. It has been found that red-ox cycling is the most damaging because it primarily affects the SOFC anodes, unlike thermal cycling where there is bulk volume displacement in the whole SOFC due to changes in temperature. The bulk strain induced by the oxidation of the ceramic anode has been shown to lead to high tensile stresses in the thin electrolyte layer [68]. The ceramic anode cannot expand freely and remains constrained by the

dense electrolyte substrate, leading to strain accumulation and delamination or bulk degradation of the anode layer.

Ceramic anodes are typically mixed-ionic electronic conducting single-phase materials. Researchers have shown that during operation, changes in oxygen partial pressure result in significant departures from stoichiometry in mixed ionic and electronic conducting oxides [69]. This large change in oxygen vacancies often leads to significant dilation of the lattice known as chemical expansion, which results in large stresses and ultimately leads to mechanical failure. However, the strain associated with chemo-mechanical expansion of non-stoichiometric anodes is still much less than the strain associated with, e.g., oxidation of Ni to NiO, a completely different phase.

5.3. Material Transport Mechanisms

Typically, the ceramic anode will have a metal catalyst added to it to increase electrochemical performance. The material transport mechanism is driven by two key phenomena: changes in the metal catalyst surface morphology and an increase in the metal catalyst particle size [70]. Both of these phenomena are driven by the tendency of the metal catalyst to reduce its surface free energy under the operating conditions of the SOFC. First, this mechanism causes a reduction in the available surface area of the metal catalyst, thereby reducing the number of active catalytic sites and ultimately increasing the polarization resistance. Second, the increased particle size causes a disconnection among the metal catalyst particles, thus decreasing the electrical conductivity [70, 71]. Material transport mechanisms can also occur during the storage of ceramic anodes. The exposure of ceramic anodes to high humidity and temperature

may lead to morphological and resistance changes which can affect the reliability of SOFCs.

5.4.Deactivation and Passivation Mechanisms

Deactivation and passivation mechanisms primarily include sulfur poisoning and coking of the anode. Sulfur poisoning mainly occurs when there are sulfide impurities in the fuel used in the SOFC [72, 29]. The performance degradation is attributed to the surface adsorption on the exposed metal catalyst in the anode, e.g., Ni, which blocks H₂ dissociation from taking place. However, these short-term effects were reversible for conventional Ni-based anodes, and the cells eventually regained their performance. Permanent damage to the cell was observed on prolonged exposure (on the order of tens of hours) to H₂S [72].

Coking is of concern when hydrocarbon-based fuels are used in the SOFC. Hydrocarbons such as CH₄, when used along with Ni-impregnated ceramic anodes, lead to carbon deposition over the metal catalyst surface and thus deactivation of the anode [73, 74, 75]. In order to prevent carbon deposition, either steam reformation or dry reformation (using CO₂) is used, causing water-gas shift reactions (like $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) and thereby converting the carbon into CO or CO₂ and preventing its deposition. However, the addition of CO₂ or steam along with the fuel decreases the fuel concentration and in turn significantly reduces fuel utilization as well as the electrical performance of the cell [76, 77]. These mechanisms mainly apply to Ni catalysts; whereas, the impact on other catalyst needs to be studied.

Chapter 3: Root Cause Analysis for Ceramic Anodes of SOFCs

The fundamental issues associated with SOFC durability are still insufficiently characterized and identified [19, 20, 21, 22]. Most review papers focus on a small number of specific degradation mechanisms. Since SOFCs can take many different paths toward failure, a methodology to illustrate all causes of failure is desirable. Additionally, there has been less failure mode analysis on newly developed reduction-oxidation stable SOFCs using ceramic anodes, as compared to more conventional Ni-cermet anodes. In this study, an Ishikawa analysis is performed for ceramic anodes of SOFCs and a comprehensive failure modes, mechanisms, effects, and criticality analysis (FMMECA) methodology is applied to ceramic anodes to prioritize the failure mechanisms considering reliability and durability of SOFCs. The FMMECA highlights the potential failure mechanisms, root causes and failure modes, the likelihood of occurrence, severity and detection of the associated failure mechanisms. It is the aim of this study to assist future researchers in assessing the durability and reliability of the anodes of SOFC technologies.

1. Ishikawa Diagram for Ceramic Anode

An Ishikawa diagram, also known as a “fishbone” diagram or as a “cause and effect” diagram [78] has been developed (see Figure 5) for the ceramic anodes based on the discussion above. The causes for the anode failures have been categorized into

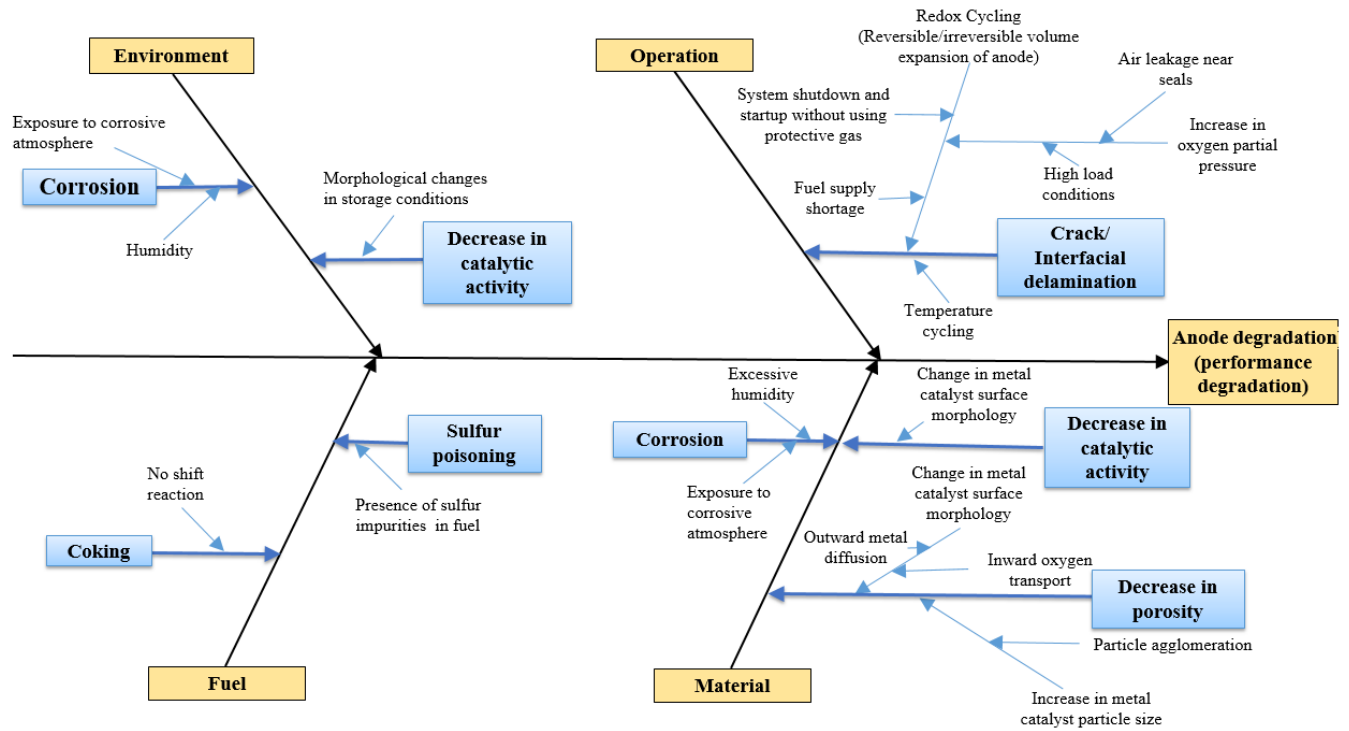


Figure 5. Ishikawa diagram for ceramic anodes

operation, material, environment, and fuel and the factors that can lead to degradation of anodes associated.

Temperature cycling and irreversible expansion of the anode due to redox cycling during **Operation** of SOFCs can lead to cracking of the anode and anode-electrolyte interfacial delamination. Temperature cycling mainly results in thermomechanical failure mechanisms. Irreversible expansion of the anode is mainly caused by redox cycling where re-oxidation of the anode causes a larger volume expansion in the metal catalyst particles and chemical expansion in anodes as compared to shrinkage during the reduction cycles (NiO particles shrink by about 40% volume on reduction, whereas on re-oxidation, Ni expands by about 66% volume [61]). Due to this uneven expansion and shrinkage, during redox cycling significant amount of residual mechanical stresses are developed which can ultimately cause interfacial delamination or cracking of the

anode. According to one study of Ni-based anodes, each reduction/oxidation (red-ox) cycle causes degradation at the rate of 0.3% per cycle, which makes the anodes of SOFCs a critical component [71]. Fuel shortage, system shutdown or startup without using protective gas, current overload, excessive fuel usage, and air leakage can cause the re-oxidation of the SOFCs.

The degradation causes that can ultimately lead to change in material morphology and material properties and result in failure of the anodes are classified in the **Material** category. Variation in material properties can affect the performance of SOFCs. The main degradation causes are decreased porosity of the anode catalyst material and decreased catalytic activity of the metal catalyst. Change in metal catalyst surface morphology can occur due to tendency of metal catalyst to diffuse outward and due to inward oxygen transport. Corrosion of anode is one other important failure cause under this category. This can occur due to exposure to excessive humidity or other corrosive atmospheres (e.g., Cl impurities in fuel from waste). Corrosion can severely deteriorate the structural integrity of the anode, thus hampering performance.

Environmental factors that can degrade the performance of anodes mainly include excessive humidity and corrosive atmospheres and are shown in the **Environment** category. Both of these factors can change material properties by corroding the top layer of ceramic anode, which will decrease the catalytic activity of the anode. The effect of environmental factors on the structural integrity of conventional Ni-based anodes has been studied [79], but the effects of these factors on the performance of new ceramic anode materials have not been studied.

Coking and sulfur poisoning are the degradation causes under the category of **Fuel**. Both of these mechanisms can affect the performance and reliability of fuel cells. Coking mainly occurs when hydrocarbon-based fuels are used directly, without any steam or dry reforming, which leads to no shift reaction and results in coke deposition [80]. Sulfur poisoning occurs when there are sulfide impurities in the fuel, which blocks hydrogen adsorption and hence reduces the performance of the SOFC. Zhangbo et al. [81] presented wet impregnation/infiltration techniques to improve carbon and sulfur tolerance of Ni-based anode materials. The impact of this degradation mechanism on all-ceramic anodes needs further research.

2. Failure Modes, Mechanisms, Effects, and Criticality Analysis for Ceramic Anodes

SOFCs consist of multiple components, each with its own failure mechanisms and criteria. The anode is believed to be one of the most sensitive components in SOFC degradation and is the focus of this study. This paper developed the FMMECA for ceramic anodes. The FMMECA will play a key role in the development of degradation and failure test plans for assessing SOFC reliability.

Failure modes, mechanisms, and effects analysis (FMMEA) is “a systematic methodology to identify potential failure mechanisms and models for all potential failure modes, and to prioritize failure mechanisms” [82] and is the cornerstone of the physics-of-failure (PoF) approach to reliability assessment of systems, subsystems, and components. When extended by criticality analysis (CA) procedures, FMMEA is known as failure modes, mechanisms, effects, and criticality analysis (FMMECA). Failure mechanisms are identified as the “processes by which physical, electrical,

chemical, and mechanical stresses induce failures” [83]. These mechanisms describe the fundamental manner in which a device or component can fail. Failure modes, on the other hand, are defined as the manner by which a failure is physically observed. The mode may not be easily observed in situ; however, a complete failure analysis would reveal the source of the failure. The failure cause is the driving force behind the failure mechanism and can be the result of either internal or external stresses. The failure effect is how the failure mechanism impacts the usability of the device or component. Finally, the criticality analysis ranks all failure modes and mechanisms in order of importance to help prioritize maintenance work [84].

It is necessary to understand which failures are the most severe and how reliability can be improved by mitigating the effects of those failures. One way to determine which failures to focus on is to rank the failure mechanisms from 1 to 10 with respect to likelihood of occurrence, degree of severity, and detectability. Scores are assigned for each of these three considerations, and the results are combined into an overall risk prioritization number (RPN). The RPN is the product of the severity rating, the occurrence rating, and the ease of detection (e.g., $1 \leq \text{RPN} = \text{Severity} * \text{Occurrence} * \text{Detection} \leq 10$) [85], with larger numbers meaning a greater risk. For example, a failure mechanism that has a high likelihood of occurrence, high severity, and is not easy to detect would be ranked above all other failure mechanisms. A failure mechanism that is easy to detect would not be ranked as high as other failure mechanisms. Additionally, the calculated RPN value is dependent on the application and the expected use conditions. Using Institute of Electrical and Electronics Engineers (IEEE) standardized RPN methodology and evaluation criteria [86], a criticality analysis for ceramic anodes

of SOFCs is shown in Table 7. The RPN technique can be used by industry groups to perform comprehensive criticality analysis in the presence of field data. For example, if customer is dissatisfied with the product because of the specific failure mechanism but still managed to execute the task and the degradation is within warranty then severity will get rating of 3. Occurrence will get rating of 3, when the degradation rate is low for specific failure cause but there is lack of understanding of responsible mechanisms, while with the clear understanding of responsible mechanisms for same failure cause will get occurrence rating of 2. Finally, detection will get rating of 3, when there are chances that failure cause will be identified and removed before it can cause the failure. It should be noted that a criticality analysis anticipates the future, so the numerical rating is a subjective value, not an objective one [87].

Table 7. Criticality analysis for ceramic anodes

Rating	Degree of Severity	Likelihood of Occurrence	Ease of Detection
1	The adverse effect is insignificant	Remote	Certain that potential failure will be found or prevented
2	Customer will experience annoyance due to slight degradation of performance	Low failure rate with supporting documentation	Almost certain that the potential failure will be found
3	Customer dissatisfaction due to reduced performance	Low failure rate without supporting documentation	Low likelihood that potential failure will reach the customer
4	Customer is made uncomfortable due to continued degradation (degradation within annual goal)	Occasional failures	Controls may not detect or prevent the potential failure

Rating	Degree of Severity	Likelihood of Occurrence	Ease of Detection
5	Degradation beyond annual goal results in warranty repair	Moderate failure rate with supporting documentation	Moderate likelihood that potential failure will reach the customer
6	Violation of governmental regulation with less degradation in performance	Moderate failure rate without supporting documentation	Controls are unlikely to detect or prevent the potential failure
7	Shutdown of system due to component failure	High failure rate with supporting documentation	Poor likelihood that potential failure will be detected or prevented
8	Shutdown of system and violation of governmental regulations	High failure rate without supporting documentation	Very poor likelihood that potential failure will be detected or prevented
9	Customer endangered due to immediate shutdown without warning	Failure is almost certain based on warranty data	Controls probably will not even detect the potential failures
10	Customer endangered due to the adverse effect of operation results in fire in system	Assured of failure based on warranty data	Absolute certainty that the controls will not detect the potential failure

In the absence of field data, more generalized rating techniques (shown in Table 8) can be used to identify and prioritize the potential failure modes and mechanisms. The severity, occurrence, and detectability of failure depends on a combination of factors such as type of user, purpose of usage, and environmental conditions. The numerical rating of severity, occurrence, and detectability is a subjective value and will change from installation to installation. The author have generalized numerical ratings for criticality analysis into high, moderate, and low classes as shown in Table 8. Severity gets high ratings in the scenario where failure affects the users instantly and causes

immediate shutdown and safety issues. A moderate severity rating is assigned when the degradation meets or exceeds failure criteria but there are no sudden shutdown or associated safety issues. When the degradation is within the failure criteria then it gets a low severity rating. Occurrence of failures is also categorized into these three classes of high, moderate, and low. For specific failure cause, a high occurrence rating indicates the degradation is certain while moderate and low occurrence ratings indicate occasional failures and when the chances of failure are very low, respectively. Contrary to severity and occurrence ratings, the detection rating is assigned on the basis of ease of detection. Failure causes that are easy to detect and can be prevented get a low detection rating. Failure causes that are very unlikely to be detected and have a very poor likelihood of prevention get high detection ratings. Failure causes with moderate likelihood of prevention before reaching the end-user get a moderate detection rating.

Table 8. Severity, occurrence, and detection rating for SOFC power system

Rating	Degree of Severity	Likelihood of Occurrence	Ability to Detect
Low	Performance degradation within annual goal	Chances of failure is low	Easy to detect and can be prevented
Moderate	Performance degradation beyond annual goal	Occasional failures	Moderate likelihood that potential failure will be detected and prevented
High	Immediate shutdown, safety issues	Failure is almost certain	Very unlikely to detect and prevent the potential failure

The FMMECA in Table 9 was constructed for product development and qualification purposes, where one can physically observe degradation in situ. It is easier

to identify causes and mechanisms behind degradation when one has an FMMECA. This analysis will help manufacturers understand the root causes of failure, improve reliability, and perform corrective actions during repair. It provides a comprehensive list of the failure modes from the user's perspective, the potential causes that drive failure mechanisms, potential failure mechanisms, and whether the failure is brought on by abrupt overstress or by progressive degradation (wear out).

Criticality analysis can be conducted by assigning numerical ratings to different failure modes and mechanisms and by calculating RPNs according to their usage and requirements. Because RPNs are relative, mechanisms that are assigned higher RPNs are considered critical. The anode-electrolyte interfacial delamination is one of the critical failure mode which can cause failure of system instantaneously and is assigned high severity ratings, however, the occurrence of this failure mode has dramatically reduced with the development of ceramic anodes which results in low occurrence rating. The failure causes such as volume change in anode and mechanical stress responsible for the anode-electrolyte interfacial delamination is very unlikely to detect and prevent before actual failure, hence high detection rating has been provided. Redox cycling is one of the critical failure cause which can result in both overstress and wear out failure mechanisms shown in Table 9. Change in metal catalyst surface morphology and reduction in catalyst porosity are the failure modes which can occur due to redox cycling and can cause wear out degradation of anodes of SOFCs. With the development of ceramic anodes, severity of these failure modes have been reduced, hence moderate severity ratings have been provided. Since, these are wear out degradation mechanisms hence there are moderate likelihood that these failure modes can be detected and

prevented with gradual decrease in performance of SOFCs. Reductions in porosity are assigned higher occurrence ratings because it is more certain with each redox cycle even with the development of ceramic anodes and requires further research.

Crack can occur in the anodes of SOFCs due to any of three possible causes listed in Table 9 and can cause instantaneous failure of the system, hence high severity rating is provided. However, the failure causes responsible for crack failure mode such as air leakage, fluctuation in fuel supply and current overload can easily be detected and prevented before the failure of system, hence low detection rating is provided. The occurrence of crack failure mode is provided moderate rating because of occasional nature of failure cause. Corrosion of anode, sulfur poisoning, and coke deposition are failure modes which can occur due to humidity exposure or impurities in fuel. The severity of sulfur poisoning and coke deposition has been reduced with the development of ceramic anodes as compared to ceramic-metallic anodes where these were major critical failure modes. The occurrence of these failure modes have significantly reduced for ceramic anodes, hence low occurrence rating has been provided. Moreover, since deactivation and passivation failure mechanisms are wear out mechanisms which results in gradual performance degradation, moderate detection ratings have been provided.

It was found that the redox cycling and thermal cycling are the critical failure cause which can cause sudden failure of system and are also responsible for number of wear out degradation mechanisms. Hence, accelerated thermal and redox cycling test should be performed to determine the reliability of anodes and to ensure high thermal and

redox cycling durability to prevent the catastrophic failure of systems. Besides that, use of air leakage and fluctuation in fuel supply detection system is highly encouraged to prevent the failure due to crack in anodes of SOFCs.

Table 9. FMMECA for ceramic anodes

Potential Failure Mode	Failure Causes	Potential Failure Mechanisms	Failure Mechanism Type	Observed Effect	Severity	Occurrence	Detection
Anode-electrolyte interfacial delamination	Volume change in anode due to re-oxidation reaction (~1%)	Strain accumulation due to irreversible volume expansion	Chemo-mechanical mechanism - overstress	Decrease in conductivity, voltage drop, system shutdown	High	Low	High
Anode-electrolyte interfacial delamination	Mechanical stress due to thermal cycling	Strain accumulation due to CTE mismatch	Thermomechanical mechanism - overstress	Decrease in conductivity, voltage drop, system shutdown	High	Low	High
Change in metal catalyst surface morphology	Red-ox cycling	Outward metal diffusion and inward oxygen transport	Material transport mechanisms - wear out	Decrease in conductivity, voltage drop	Moderate	Moderate	Moderate
Reduction in catalyst porosity	Red-ox cycling	Ostwald ripening/coarsening	Material transport mechanisms - wear out	Decrease in conductivity, voltage drop	Moderate	High	Moderate
Crack	Air leakage (lack of fuel, shutdown and startup without reducing gas) causing anode oxidation during operation.	Fatigue of anode material	Thermomechanical mechanism - overstress	Sudden drop in voltage and CO formation.	High	Moderate	Low

Potential Failure Mode	Failure Causes	Potential Failure Mechanisms	Failure Mechanism Type	Observed Effect	Severity	Occurrence	Detection
Crack	Fuel supply fluctuation, unexpected hydrogen shortage causing partial re-oxidation	Fatigue of anode material	Thermomechanical mechanism - overstress	Drop in voltage, CO formation	High	Moderate	Low
Crack	Current overload	Fatigue of anode material	Thermomechanical mechanism - overstress	Drop in voltage	High	Moderate	Low
Corrosion of anode	Impurities in water/steam, humidity exposure, corrosive atmosphere	Chemical corrosion reaction	Deactivation and passivation mechanisms - wear out	Voltage drop	Low	Low	Moderate
Sulfur adsorption onto metal catalyst	Presence of sulfur impurities in fuel	Chemical reaction (metal particle migration)	Deactivation and passivation mechanisms - wear out	Sudden voltage drop initially and then gradual performance degradation.	Moderate	Low	Moderate
Coke deposition	No shift reaction (incomplete oxidation of fuel)	Coking	Deactivation and passivation mechanisms - wear out	Decrease in conductivity, voltage drop	Moderate	Low	Moderate

3. Discussion

Solid oxide fuel cells (SOFCs) are complex systems that are susceptible to many different degradation mechanisms, each of which individually and in combination can lead to performance degradation, failure, and safety issues. As a result, it is necessary to identify the ways an SOFC can degrade and assess the risk of each type of degradation process and failure mechanism. The development of an FMMECA is the first step in making a transition from empirical to physics-based SOFC failure models to account for the stresses experienced by ceramic anodes of SOFCs during their life

cycles. The FMMECA's most important contribution is the identification and organization of failure mechanisms and models that can predict the onset of degradation or failure.

It was found that anode-electrolyte interfacial delamination and cracks are the critical failure modes which can cause the abrupt failure of SOFCs. Hence, one should carefully design the ceramic anodes of SOFCs for redox cycling and thermal cycling as these are the dominant failure causes for aforementioned critical failure modes. It is worth noting that though mechanical failure due to redox cycling is still a concern with ceramic anodes, the susceptibility to the failure mode is expected to be dramatically reduced as compared to Ni-cermet cells. Additionally, these analyses can be used to develop degradation and failure test plans for ceramic anodes and to facilitate assessment of the reliability of anodes as well as the entire SOFC system. Standards organizations and industry groups can design better qualification and safety tests based on the findings of these analyses. Such assessments not only can predict a given application's life-cycle stresses on the SOFCs, but also capture the interactions between different failure mechanisms that exacerbate failure. Improved design and testing influenced by these analyses can lead to safer and more reliable SOFC systems.

Chapter 4: Strontium-based Perovskite Electrodes

Degradation Mechanisms

In the development of solid oxide fuel cells (SOFCs), the selection of electrode material is crucial because it not only functions as a site for electrochemical reaction, but also works as an electronic conductor to transfer charge. Strontium-based perovskite is a prominent candidate for the electrode material because it offers high conductivity and better performance. However, there is a concern that humidity, especially high humidity (~80% relative humidity) and high temperatures (~80 °C) during storage, can affect the properties of perovskite electrodes prior to installation of SOFCs.

1. Perovskite Electrodes for SOFCs

Perovskite compounds are a prominent candidate for the electrode material in SOFCs. Perovskite has the same crystal structure as calcium titanium oxide (CaTiO_3). The structure ABX_3 contains alkaline earth metal on the A-sites, a transition metal on the B-sites, and oxygen on the X-sites shown in Figure 6. Perovskite compounds are common among electrodes of SOFCs because they provide: (1) mixed ionic electronic conductivity, (2) structurally stable chemistries throughout a wide range of oxygen partial pressure and temperatures, and (3) no reactivity with other components.

The perovskite compounds have been studied because of the interest in the physical properties resulting from the presence of two oxidation states of the metallic cation. The composition of these oxides depends both on the annealing temperature and the oxygen partial pressure maintained during the synthesis, these parameters determining

the ratio of oxygen defects [88]. Strontium is common among the perovskite electrodes of SOFCs because it adds structural stability to the crystal at operating temperatures. However, there are some degradation mechanisms associated with strontium.

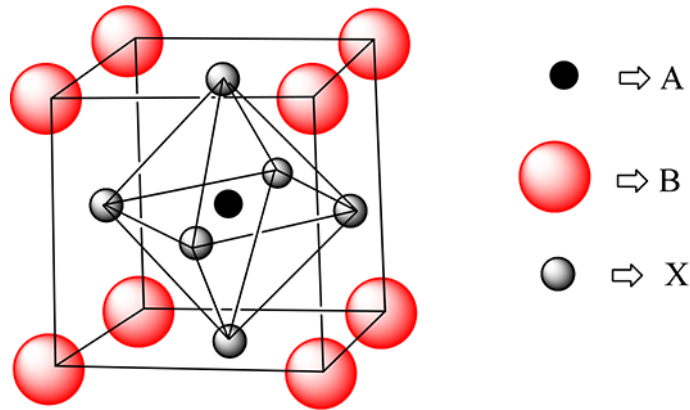


Figure 6. Perovskite crystal structure

2. Literature Review: Perovskite Electrode Degradation

Young and Otagawa [89] studied the surface elemental composition on strontium metal plates and observed strontium carbonate segregation due to the fact that strontium oxide and mixed oxides containing strontium are strongly susceptible to chemisorbed carbon dioxide and water vapor. According to the metal-rich surface model for the oxidation of strontium [90], the first stage consists of oxygen chemisorption with rapid movement of oxygen ions below the surface. Stage two consists of oxide nucleation and growth, and stage three consists of saturation with the formation of a semi continuous oxide layer over the bulk metal. As the thick oxide over layer forms at the surface, it adsorbs the water and carbon dioxide from the atmosphere, forms strontium carbonate, and contributes to the degradation of the perovskites. Campbell [91] developed an ionic model for strontium-doped magnesium oxide by assuming that strontium ions segregate to cation sites in the topmost ionic layer for the calculation of

the strontium surface enrichment ratio and found the increase in strontium segregation at higher bulk doping levels. Joo [92] studied the effect of water on oxygen surface exchange kinetics and its degradation of dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin films and reported the degradation of catalytic activity of LSC originates from strontium enrichment. The same result has been reported for LSCF materials in $\text{H}_2\text{O}/\text{CO}_2/\text{O}_2$ atmospheres, and the need to preserve the surface composition and quality of the ceramic upon cooling was emphasized by Benson et al. [93].

Jiang [94] observed strontium enrichment for screen-printed lanthanum strontium manganite (LSM) sintered at 1200 °C with a lanthanum/strontium ratio of 2.4 and claimed the strontium segregation to be a function of temperature, oxygen partial pressure, and polarization. Jung and Tuller [95] studied the surface chemical composition of dense thin film $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ electrodes using XPS technique and found strontium peaks corresponding to strontium oxide, hydroxyl species ($\text{Sr}(\text{OH})_2$), and carbonate species (SrCO_3). They claimed strontium segregation represents the formation of strontium oxide. Based on the differences in mobility of the involved cations under an applied gradient, either thermal, electrical, mechanical, or chemical in nature, Szot and Speier [96] reported that only kinetic demixing can account for strontium segregation on a macroscopic scale in ternary oxides, i.e., for distances greater than 10 nm. Hence, Szot and Speier [96] claimed that the kinetic demixing, driven by mechanical strain gradients, is a relevant driving force for strontium oxide segregation in mixed conducting perovskites at the operating temperature of SOFCs (i.e., above 500 °C). However, no study has been published related to the degradation

of mixed conducting perovskites at low temperature conditions, i.e., at storage conditions (shown in several phases in Figure 7).

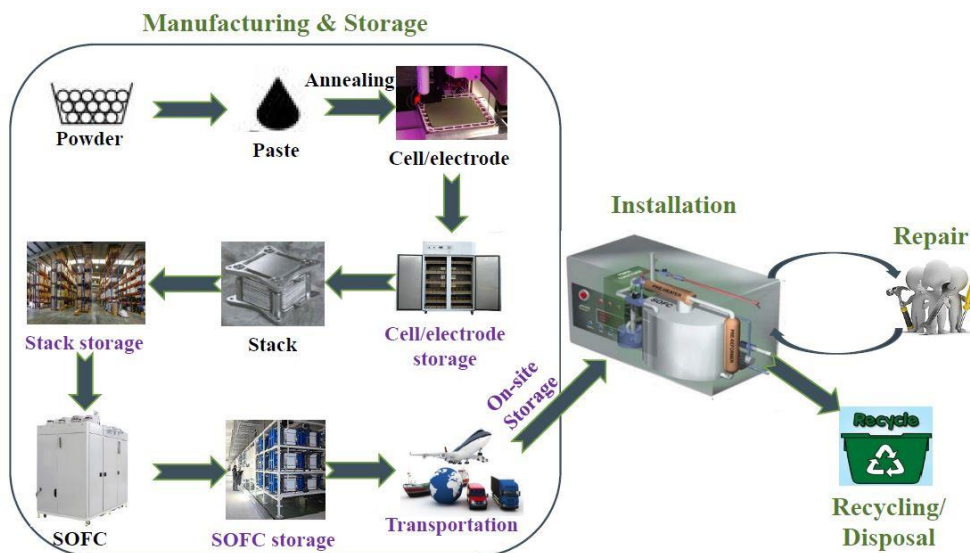


Figure 7. Life cycle of SOFCs, which involves manufacturing, storage (in several phases), transportation (also included in storage for this project), installation, operation, and disposal/recycling

Strontium based degradation mechanisms for the electrodes of SOFCs have been studied in the past. But all those studies are performed at operating temperature of SOFCs (above 500 °C). This study was performed to find the degradation mechanisms that can occur during the storage of these electrodes. Additionally, the goal of study was also to find the storage conditions to minimize/prevent the degradation of electrodes prior to installation of SOFCs.

3. Methodology

The different perovskite electrodes of SOFCs have been studied under various humidity and temperature conditions. Sintered, porous electrode samples were prepared and provided by Redox Power Systems, LLC.

Changes in the physical–chemical and electrical characteristics of lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) were observed depending on the applied temperature and humidity. LSC and LSCF have been developed as excellent mixed electron and ion conductors in the intermediate-temperature SOFC cathode family owing to their good resistivity for rigid environmental requirements and reasonable chemical suitability with ceria-based electrolytes [97]. The study on LSC and LSCF was conducted to investigate the degradation mechanisms responsible for temperature/humidity-dependent degradation of perovskite electrodes and to determine the effect of degradation on the performance of these electrodes. An accelerated testing plan was also developed and performed to characterize the degradation behavior of perovskite electrodes and to determine the storage specifications for electrode materials and assembly.

3.1. Physical and Chemical Characterization

The changes in surface elemental composition and phase decomposition due to temperature humidity dependent degradation have been investigated by a variety of X-ray analysis techniques. XPS was used to determine if there is any segregation due to temperature humidity dependent degradation. XRD was used to determine if there is any phase decomposition and if that phase decomposition is attributed to chemical restructuring or physical migration.

SEM and EDS analysis was performed using a FEI Quanta environmental scanning electron microscope (ESEM) with energy dispersive X-ray spectroscopy (EDS). SEM analysis was performed in high-vacuum/high-accelerating-voltage mode to determine the morphological changes in electrodes due to temperature/humidity-dependent

degradation. Elemental composition analysis was performed using EDS at the penetration depth of approximately 3 μm using a 15 kV accelerating voltage. Calibration was achieved using an external Cu standard.

X-ray diffraction of the aged and unaged samples was carried out with a Bruker D8 Discover X-ray diffractometer equipped with a secondary graphite-crystal monochromator and using Cu radiation at 40kV/40 μm . A Vantec-500 area-detector was used. The phase analysis was performed at a penetration depth of approximately 5 μm , and an additional phase of SrCO_3 was observed in the aged samples.

XPS was performed using a Kratos AXIS 165 spectrometer by exciting the electrode sample surfaces with mono-energetic Al X-rays at the accelerating voltage of 12 kV. An eight channeltron detection system was used to measure the energy of the emitted photoelectrons. The equipment was calibrated to adventitious hydrocarbon at the binding energy of 284.8 eV. Surface elemental composition analyses were performed on unaged and aged samples, and angle probe measurements at 20° and 90° were performed to confirm the strontium segregation in the perovskite electrode materials.

3.2.Electrical Characterization

Two-point conductivity measurements of the unaged and aged samples were performed using surface mount devices test tweezer (SMD Test TweezerTM 5678 Series) manufactured by Pomona Electronics with sleeved banana plugs and an Agilent 34411A multimeter. A block of plastic was superglued between the legs of the tweezer so that inter-probe spacing would remain fixed. Gold-plated brass ball bearings were

soldered on the legs of the SMD test tweezer to prevent penetration of the surface while measuring the surface resistance (shown in Figure 8). The change in surface resistance of the electrode samples due to change in elemental composition at the surface due to temperature humidity dependent degradation was measured. The measurement setup consisting of an electronic balance, a ring-stand and clamp, and a scissor jack was used to apply constant force during measurements.

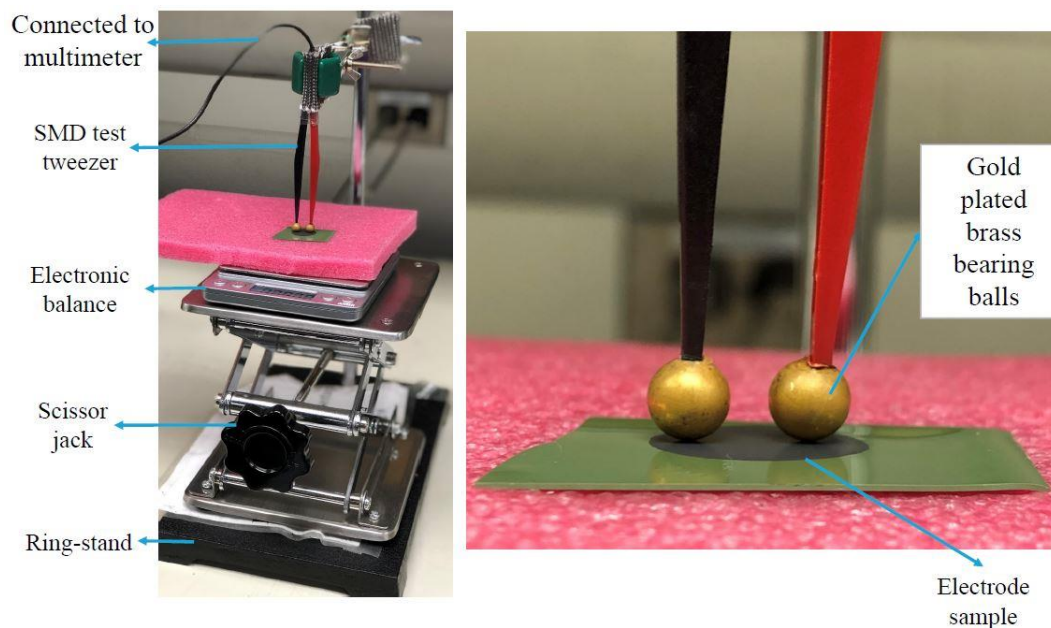


Figure 8. Two-point conductivity measurements setup

In order to select the appropriate force to minimize any variance in resistance measurements due to applied normal force on the samples during conductivity measurement, resistances of unaged strontium-based perovskite electrodes samples were measured at a series of forces (shown in Figure 9). An 80 gF was chosen as a constant force to measure the conductivity of unaged and aged samples. It was found through experimental analysis that an 80 gF is the minimum constant force that results in minimum variance in the resistance of unaged samples.

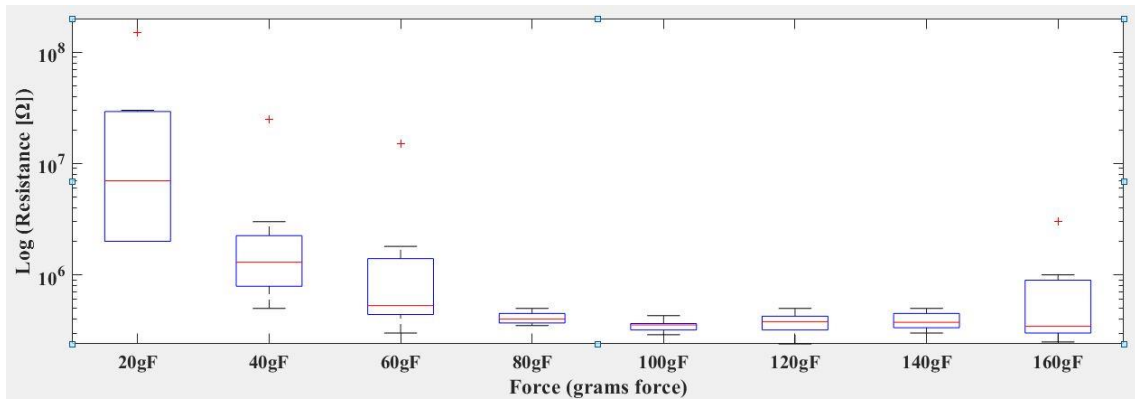


Figure 9. Two-point resistance of unaged strontium-based perovskite electrodes

4. Results

Temperature humidity dependent degradation of mixed conducting strontium-based perovskite electrodes was observed through temperature humidity exposure testing. Visual degradation modes during temperature humidity exposure were discoloration and the appearance of white precipitates on the surface of the electrodes. The morphological changes due to white precipitate formation on the surface of the electrodes are shown in Figure 10.

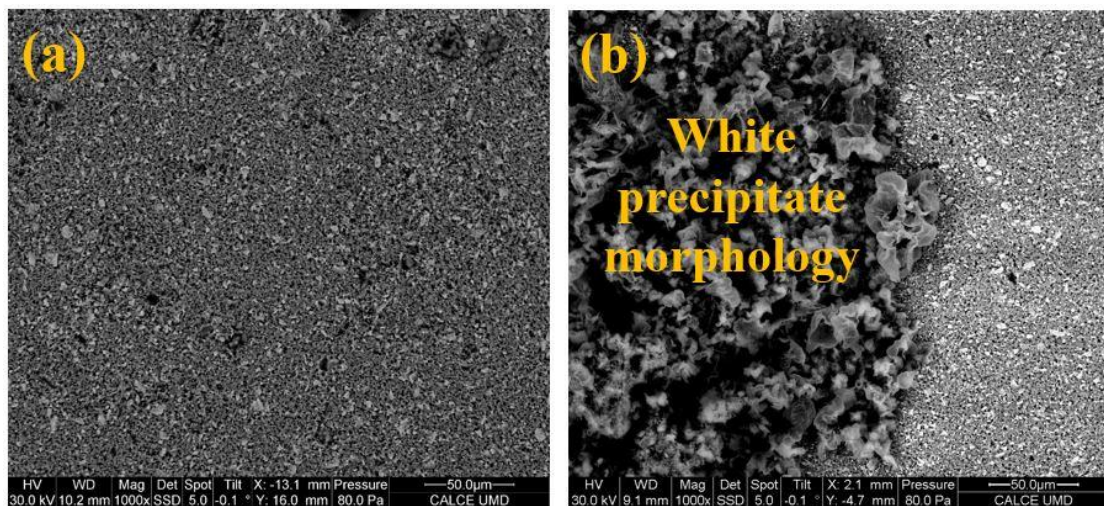


Figure 10. (a) Perovskite electrode before aging, (b) perovskite electrode after aging for 140 hours at 80 °C and 80%RH

4.1.Elevated Temperature Humidity Aging

Accelerated testing was performed on two set of LSC samples (LSC set A and LSC set B are from different vendors) and LSCF samples. Exposure to temperature humidity conditions resulted in black discoloration of LSC set B samples while there were no visual changes in LSC set A and LSCF samples. Electrical characterization using two-point conductivity measurements showed that the LSC set B samples have undergone the maximum percentage increase in resistance while LSCF has undergone minimum percentage increase in resistance. Results from two samples of each set is shown in Figure 11. In order to find the factor responsible for increase in resistance of LSC set B samples as compared to LSC set A samples, irrespective of similar stoichiometry, elemental composition analysis was performed. Through SEM-EDS analysis, it was found that LSC set B samples have higher strontium weight percentage as compared to LSC set A samples shown in Figure 12.

XRD and XPS analysis was also performed on different strontium based perovskite electrodes. XRD analysis showed that the aged electrodes show peaks of strontium carbonate while this peak is absent in unaged samples. Similarly, XPS showed higher weight percentage of strontium on the surface of aged perovskite electrodes as compared to unaged samples.

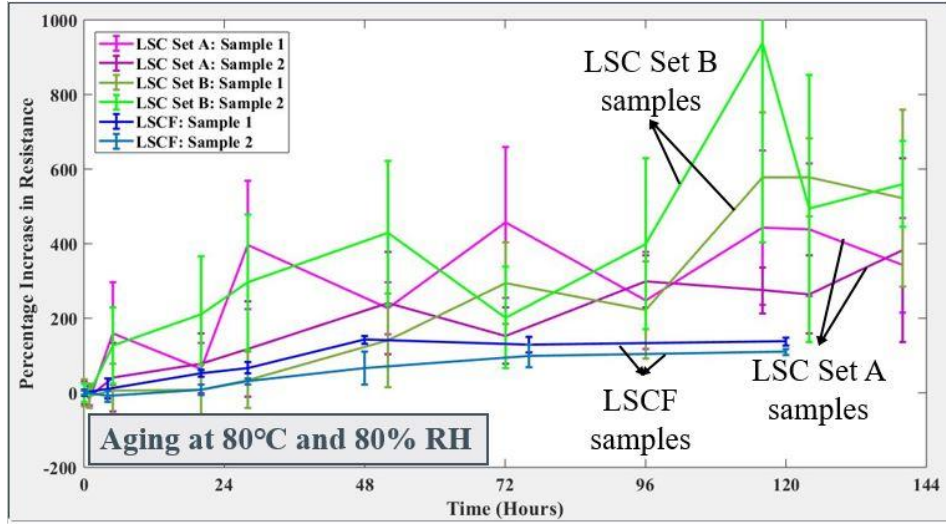


Figure 11. Mean value of 8 resistance measurement for each sample after each inspection interval is plotted

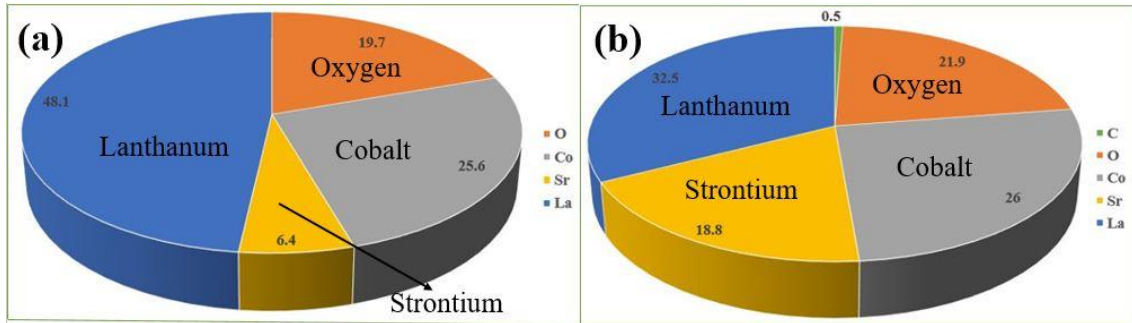


Figure 12. (a) Weight percentage for LSC set A samples, and (b) weight percentage for LSC set B samples

4.2.Elevated Temperature Aging

Temperature aging of perovskite electrodes were performed at 80°C (relative humidity < 5%) to find if the degradation is dependent on both stresses i.e., temperature and humidity. No discoloration, morphological changes and percentage increase in resistance was observed for LSC set A and LSC set B samples (shown in Figure 13)

which indicates that the interaction term between temperature and humidity is significant in degradation of strontium based perovskite electrodes.

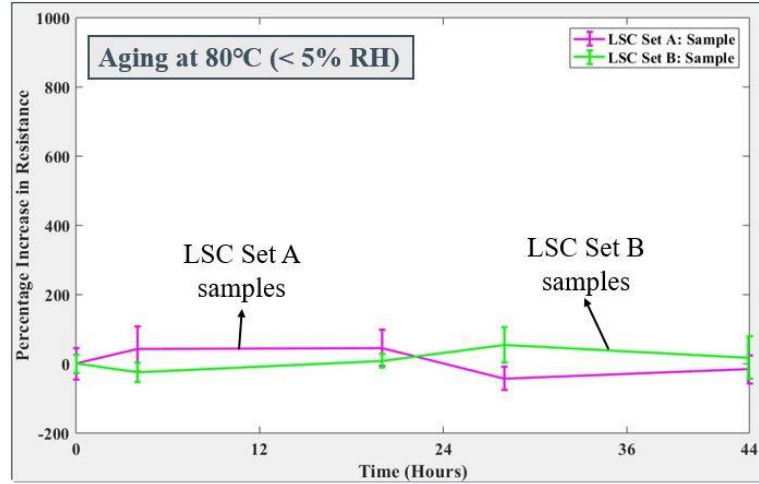


Figure 13. Mean value of 8 resistance measurement of each sample after each inspection interval is plotted

5. Temperature-Humidity Dependent Degradation Mechanisms

Additional phase formation along with discoloration and white precipitate formation was observed for strontium-based perovskite electrodes upon exposure to temperature – humidity and time conditions. Despite the fact that the previous studies on perovskite degradation in water and carbon dioxide atmosphere [90] [92] have been performed at operating temperatures of SOFCs, typically higher than 500°C, the results obtained through accelerated storage aging of perovskite electrode are consistent with previous studies.

XPS analysis of unaged and aged electrode samples showed that approximately 75% of the strontium present on the surface of unaged samples is in the form of strontium carbonate. This suggests that either the strontium has the capability to segregate even at room temperature or enough strontium was present on the surface of

the strontium based electrode samples due to high temperature annealing. This result is consistent with [89] [93] where researchers reported that high temperature annealing of strontium-based perovskite materials followed by cooling to room temperature results in modifications to the surface of ceramic. This was ascribed to $\text{CO}_2/\text{H}_2\text{O}$ species that physisorbed on the surface of the sample upon removal and cooling from the annealing environment may subsequently form the stable, exchange-blocking compounds, post anneal. Besides that, high temperature aging can result in strontium segregation through kinetic demixing, driven by mechanical strain gradients, while such changes on a macroscopic scale in ternary oxides at room temperature are not expected. This explanation leaves us with the hypothesis that annealing of the perovskite electrode and then quenching at room temperature results in strontium segregation in the form of strontium oxide. So, it is recommended to preserve the surface composition and quality of the ceramic upon cooling, for example in an air separator, which is consistent with the surface model for oxidation of strontium [90]. The strong susceptibility of strontium oxide to chemisorbed water vapor and carbon dioxide from surrounding atmosphere in the presence of favorable thermodynamic environment results in the formation of strontium compounds when strontium based electrode samples get exposed to temperature-humidity combination. The black discoloration due to temperature – humidity aging is attributed to electrode phase decomposition accompanied by strontium carbonate formation, while the formation of white precipitate is attributed to thick strontium carbonate layer.

6. Discussion

A stable perovskite electrode material with high electrochemical performance is crucial for the long – term stability of SOFCs. In general, the stability of the perovskite layer depends on its chemical components and crystal structure [98]. Anderson [99] found that higher strontium content leads to a less stable perovskite which is consistent with our study where we found that LSC set B has undergone maximum degradation in temperature – humidity conditions. LSC set B has higher strontium weight percentage as compared to LSC set A sample. The strong susceptibility of strontium oxide present on the surface of LSC set B samples results in the formation of strontium carbonate after exposure to high humidity conditions which resulted in maximum surface increase in resistance.

LSCF showed minimum percentage increase in resistance in temperature – humidity conditions which is consistent with previous studies where they found doping perovskite with iron increases the structural stability of the material [100, 101]. In general, the perovskite phase is stable over a very large range of oxygen partial pressures. In addition the crystal lattice can accommodate significant changes in oxygen content through the generation and consumption of oxygen vacancies. These properties of good oxygen transport and oxygen exchange without undergoing crystal phase changes are not possessed by transition metal oxides, such as iron oxides, which makes iron containing perovskites superior to simple metal oxides in terms of material stability [102].

The electrode materials with higher strontium weight percentage showed maximum degradation irrespective of similar material structure, which proved that higher

strontium content leads to a less stable perovskite. Iron-doped perovskite electrode material showed minimum percentage increase in resistance which is attributed to higher structural stability of iron-doped perovskite materials. This study showed that strontium based perovskite electrode materials are susceptible to degradation under high humidity storage conditions, and thus affect the reliability of SOFCs.

Chapter 5: Temperature Humidity Degradation Model for Strontium-based Perovskite Electrodes

Degradation of solid oxide fuel cells (SOFCs) is often referred as the decrease of a cell's electrical performance (electrical performance is measured in resistance which has been used for model development) or mechanical failure. The consequences of temperature/humidity-dependent degradation are performance degradation and shortening of the SOFC lifetime. Elevated temperature-humidity stress exposure confirmed degradation of strontium-based perovskite electrodes of SOFCs. Perovskite electrode samples have been aged to a number of temperature and humidity conditions shown in Table 10 and the results from tests will be used to determine the storage condition specifications.

Table 10. Design of experiment for strontium-based perovskite electrodes

Humidity/ Temperature	30%RH	50%RH	70%RH	90%RH
60 °C	✓	✓	✓	✓
80 °C	✓	✓	✓	✓

Two samples were exposed for the same duration with inspection points of 0, 1, 5, 10, 25, and 30 hours at each condition in order to develop resistance degradation model as a function of temperature and relative humidity. Surface resistance was measured at 5 random locations of each sample at each inspection point. The plot of resistance data in linear scale and in log scale is shown with time in Figure 14 and Figure 15 respectively. Rapid degradation occurred at 90% relative humidity conditions and resistance of the samples crossed the failure threshold within first inspection. Different data-analysis and model-development approach have been used and it is found that data from 90%RH conditions represent highly accelerated stress conditions which can be

useful to understand failure-mechanisms while it might not be useful for model development. Resistance data from 90% relative humidity was found to skew results and hence further analysis is performed after removing the data from 90% relative humidity conditions.

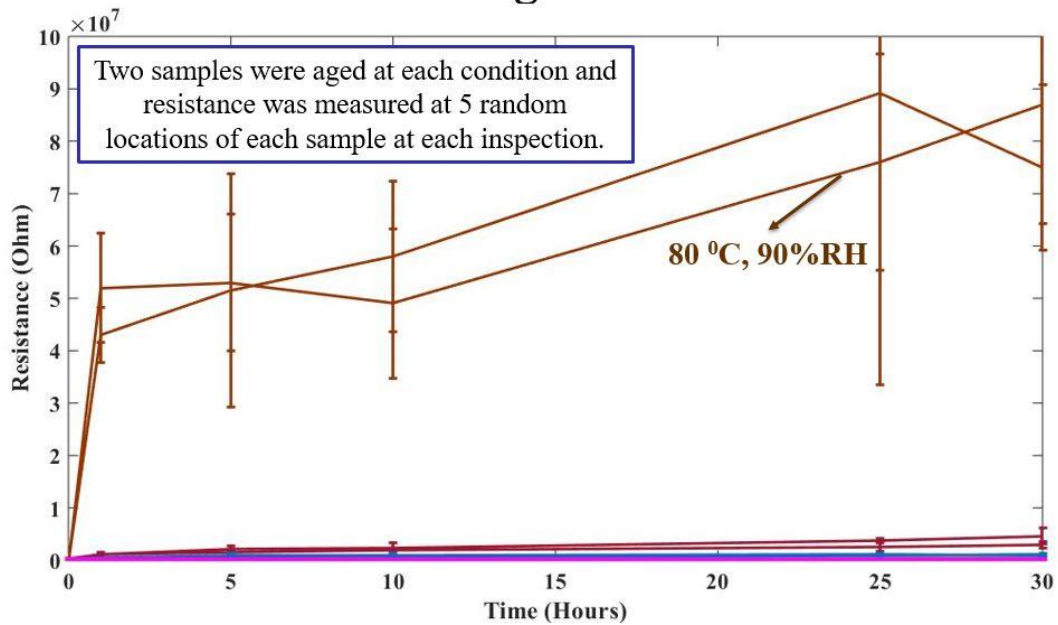


Figure 14. Resistance data with time in linear scale (error bar: one standard deviation)

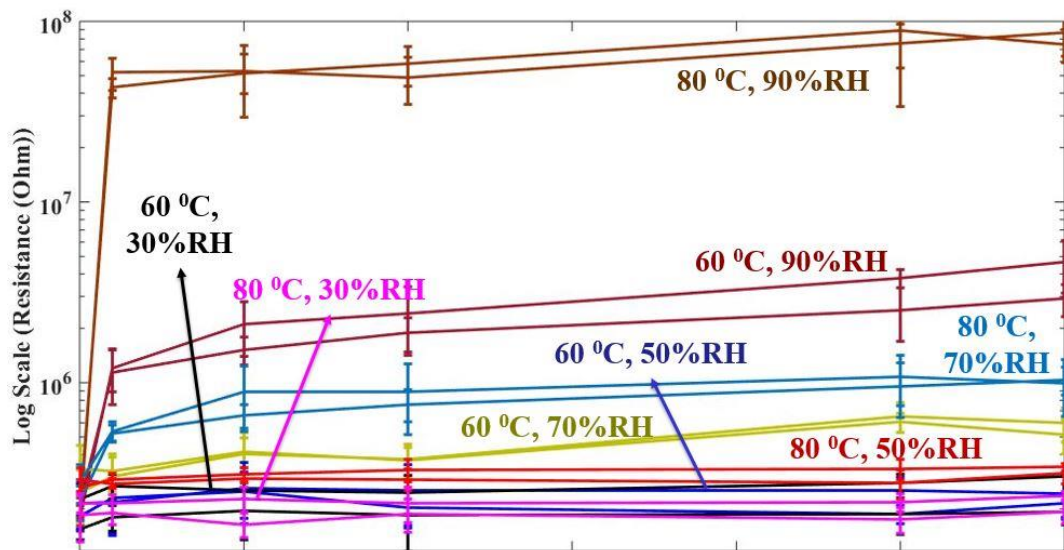


Figure 15. Resistance data with time in log scale (error bar: one standard deviation)

1. Data Analysis Approach

Resistance degradation model as a function of temperature, relative humidity and time was developed using two approaches. Since aging was performed at every combination of temperature and humidity stress levels (shown in Figure 16), first, a full factorial linear interaction model was developed to understand the impact of interaction term in degradation. Secondly, stress interaction sensitivity based model was developed by performing the sensitivity analysis on different interaction terms to find factors which represent the degradation of strontium-based perovskite electrodes.

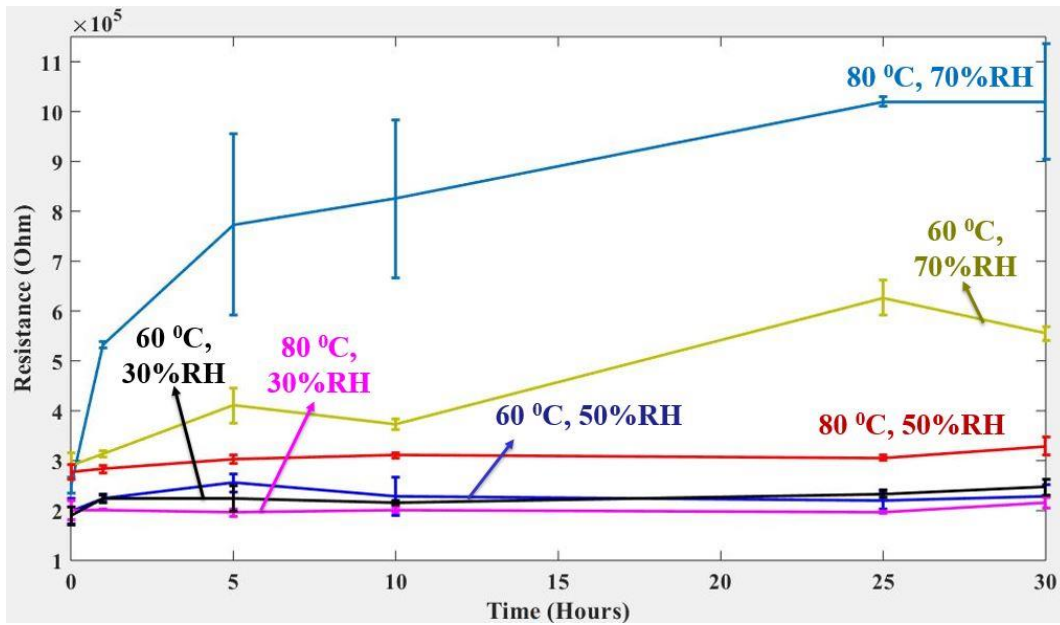


Figure 16. Mean resistance of two samples (error bar: mean resistance of each sample) from each condition measured at each inspection is plotted against time

1.1.Full Factorial Linear Interaction Model

A linear interaction model has been developed to predict failure time under individual conditions with R-square of 0.79. The resistance of strontium-based

perovskite electrodes as a function of temperature, relative-humidity, and time is given by the following equation:

$$R(T, H, t) = 6083 \times T + 9250 \times H + 5613 \times t + (T - 343) \times [(H - 50) \times 408] + (H - 50) \times [(t - 11.8) \times 358.9] - 2262450$$

where R is the two-wire resistance of strontium-based perovskite electrodes in Ω at 350 gf, T is the temperature in Kelvin, H is the percentage relative humidity, and t is time in hours. The model output is compared with the actual test data shown in Figure 17.

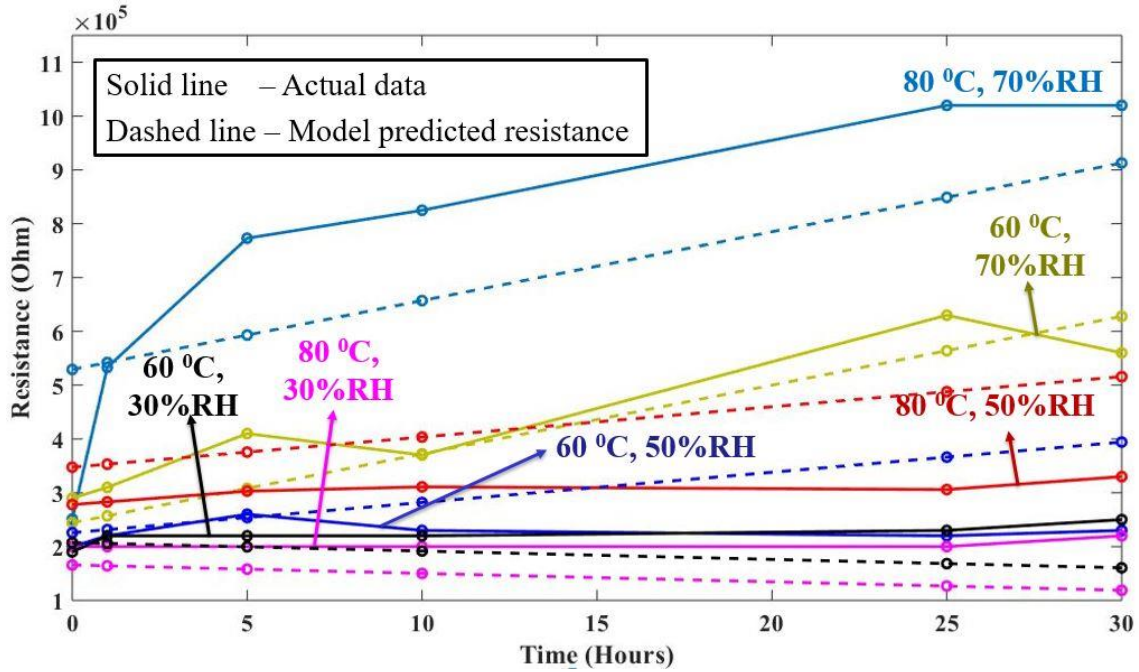


Figure 17. Actual data vs. model predicted resistance

Since, linear interaction model has linear terms of temperature and humidity which resulted in variation in predicted resistance at time zero on the basis of temperature and humidity conditions. It was found that the relative humidity is highly significant. Linear interaction model gave positive slope for temperature and time when samples were aged at relative humidity greater than 40%RH which suggests increase in resistance of

samples with increase in time and temperature (shown in Figure 18). However, storing these electrode samples below 40%RH predicted close to zero slope which suggests no significant degradation or increase in resistance below 40%RH for strontium-based perovskite electrodes.

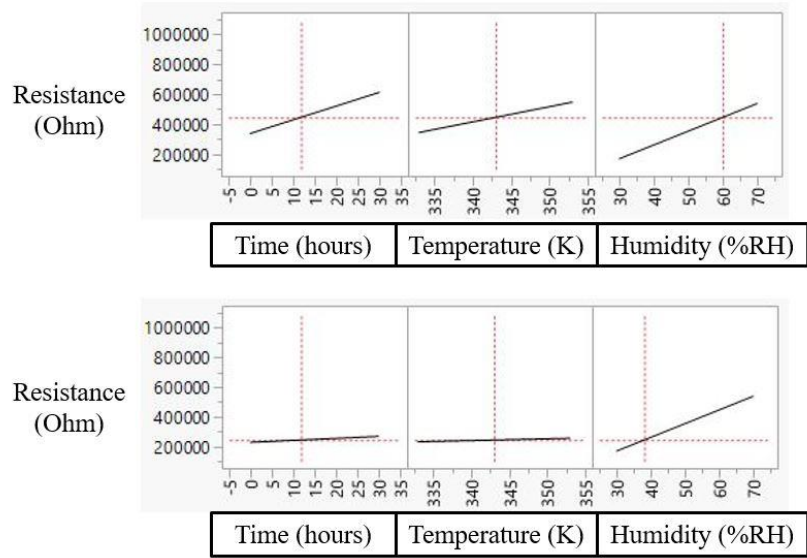


Figure 18. Effect of relative humidity on resistance of perovskite electrodes

1.2.Stress Interaction Based Empirical Model

Stress interaction sensitivity based model was developed, first to find the interaction terms which represent the degradation of strontium-based ceramic electrodes by performing sensitivity analysis, and second to constrain the initial resistance value at different temperature humidity conditions. Empirical degradation model has following terms:

$$R = R_0 + t \times f(T,H)$$

where R is the two-wire resistance of strontium-based perovskite electrodes in Ω at 350 gf, R_0 is initial resistance, T is the temperature in kelvin, H is the percentage relative

humidity, and t is time in hours. 35 different linear, polynomial, exponential, and logarithmic interaction of stresses have been considered for sensitivity analysis shown in Table 11.

Table 11. Coefficient of correlation between resistance and stress interaction terms

Factors	Correlation Coefficient	Factors	Correlation Coefficient
$t*T$	0.30	t/T^2	0.27
$t*H$	0.56	t/H^2	-0.18
$t*T*H$	0.57	$t*H/T^2$	0.53
$t*exp(T)$	0	$T*t/H^2$	-0.18
$t*exp(H)$	0.81	$t*T^2/H^2$	-0.17
t/T	0.28	$t*H^2/T^2$	0.66
t/H	-0.01	$t*exp(1/T^2)$	0.29
$t*H/T$	0.54	$t*exp(1/H^2)$	0.29
$t*T/H$	-0.01	$t*exp(T/H^2)$	0.18
$t*exp(1/T)$	0.29	$t*exp(H/T^2)$	0.29
$t*exp(1/H)$	0.28	$t*exp(H^2/T^2)$	0.30
$t*exp(H/T)$	0.33	$t*exp(T^2/H^2)$	-0.19
$t*exp(T/H)$	-0.26	$t*log(T)$	0.29
$t*T^2$	0.31	$t*log(H)$	0.37
$t*H^2$	0.69	$t*log(T*H)$	0.32
$t*T^2*H$	0.58	$t*log(T/H)$	0.13
$t*T*H^2$	0.70	$t*log(H/T)$	-0.13
$t*T^2*H^2$	0.72		

First, interaction terms have been shortlisted on the basis of threshold correlation coefficient value of 0.2 and then remaining interaction terms have been removed on the basis of significance i.e., Prob < 0.05. There is no rule for determining what size of correlation is considered strong, moderate, or weak. However, it has been suggested in literature that correlation above 0.4 is considered to be relatively strong, correlation between 0.2 and 0.4 are moderate, and those below 0.2 are considered weak or no correlation [103, 104]. Correlation coefficient threshold of 0.2 has been used to

consider even the weak correlation because the combination of many weak predictors often outperforms a few strong predictors. Empirical degradation model is given by the following equation:

$$R(T, H, t) = 286634 + t \times [3931 \times T + 7229 \times RH + 1.08 \times 10^{-26} \times \exp(H) - 2170826 \times \exp(H/T) + 9.4 \times 10^{10}/T^2]$$

where R is the two-wire resistance of strontium-based perovskite electrodes in Ω at 350 gf, T is the temperature in kelvin, H is the percentage relative humidity, and t is time in hours. Diffusion-reaction mechanisms responsible for degradation of strontium-based perovskite electrodes suggest combination of linear and non-linear term. Moreover, carbonation of strontium was found to be major factor responsible for degradation is first order reaction and suggests exponential degradation trend [105]. Degradation model was found to be representative of degradation since it has both linear and exponential of stresses along with interaction of temperature and humidity stress. Parameter estimates for empirical degradation model is shown in Table 12.

Table 12. Parameters for stress-interaction sensitivity based model

Term	Estimate	Std Error	Prob > t
Intercept	286634	24710	<0.0001
$t \times T$	3931	997	0.0004
$t \times H$	7229	1859	0.0005
$t \times \exp(H)$	1.08×10^{-26}	1.97×10^{-27}	<0.0001
$t \times \exp(H/T)$	-2170826	565602	0.0006
t/T^2	9.4×10^{10}	2.5×10^{10}	0.0010

The model output is compared with actual test data shown in Figure 19. It shows that stress interaction sensitivity based model fits the test data. Time to failure can be predicted using this model at different temperature and humidity conditions. It was

found that degradation can be represented by combination of linear and exponential terms. The degradation model has two terms similar to Eyring model i.e. exponential of humidity term and term representing interaction between temperature and relative

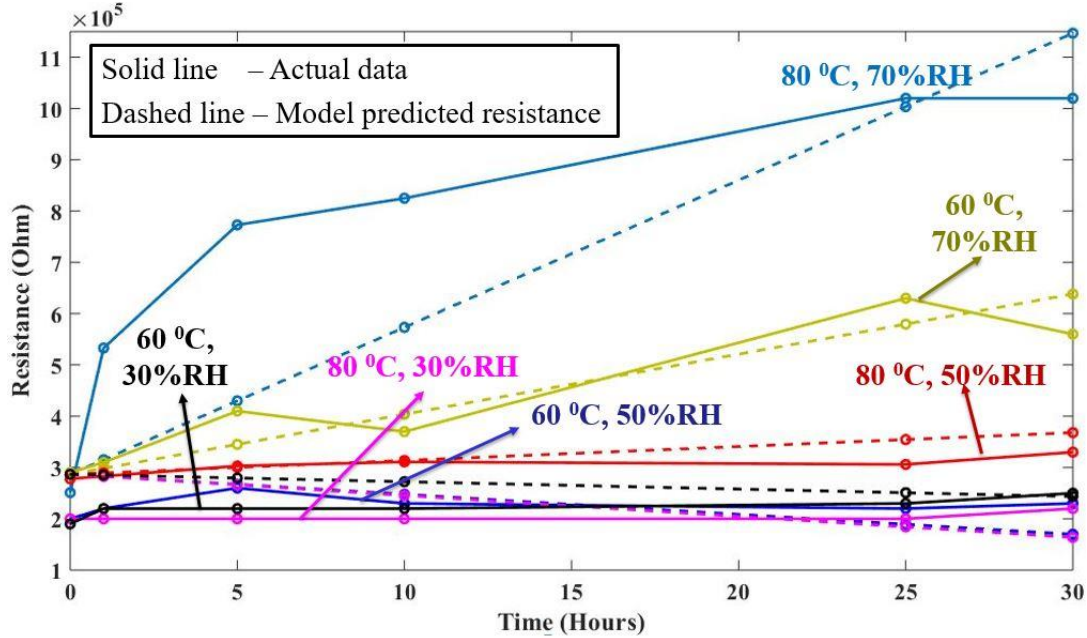


Figure 19. Actual data vs. model predicted resistance

humidity. These two terms represent the degradation due to chemical reaction (carbonation of strontium oxide which is first order reaction and suggests exponential degradation). Similarly, Eyring model has exponential terms and is used to predict time to failure if a chemical process is causing degradation leading to failure which suggests degradation of strontium-based perovskite electrodes can be modeled using Eyring equation with some modifications [106] [107] [108].

2. Discussion

The carbonation of strontium oxide was studied where Bagherishereski [109] divided it into three stages: (1) an initial induction period, (2) a rapid kinetically-controlled carbonation stage primarily on the surface of sample, and (3) a slow

diffusion controlled regime that takes place as CO₂ diffuses through a layer of strontium carbonate formed on the surface. The carbonation reaction of strontium oxide was found to be first order reaction (exponential with time) where strontium carbonate formation is dependent on reaction rate. Similarly, Parker et al. [110] studied the temperature dependence of equilibrium constant for the formation of strontium carbonate between 0 and 80°C and found equilibrium constant for the reaction is exponential with time. Considering strontium carbonate as major factor responsible for increase in resistance of strontium based perovskite electrodes suggest exponential degradation model. Physical explanation was provided for the terms in stress-interaction sensitivity based model except for $1/T^2$ term. Physics of failure suggests stress-interaction sensitivity based model as representative degradation model for strontium-based perovskite electrodes. Life of strontium-based perovskite electrodes at 80 °C using stress-interaction sensitivity based model is shown in Figure 20 including and excluding $1/T^2$ term. However, further study is required to provide the physical explanation for $1/T^2$ term in degradation model for strontium-based perovskite electrodes.

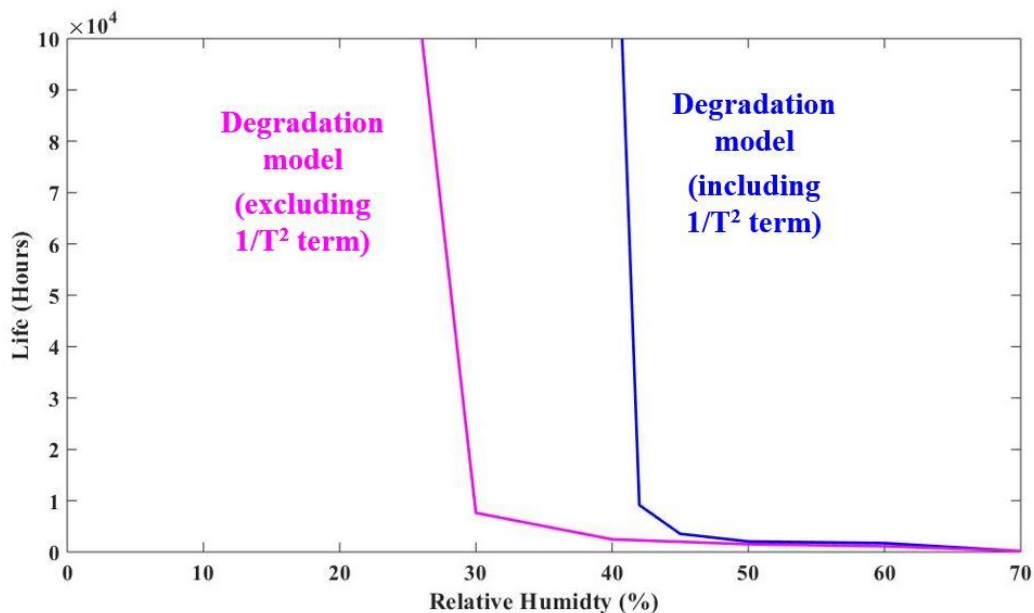


Figure 20. Life of strontium-based perovskite electrodes at 80-degree C

The data generated from elevated stress testing of perovskite electrodes were analyzed using an empirical degradation model to assess the reliability of their storage life. It was found that the carbonation of strontium oxide in the presence of high humidity and temperature is the major factor responsible for physical–chemical and electrical degradation of perovskite electrodes. An empirical degradation model (stress–interaction sensitivity based model) is developed and used to determine storage specifications and showed that degradation is highly attributable to relative humidity. Strontium-based perovskite electrodes stored at relative humidity less than 40% present no storage concerns for any practical length of time.

The physical–chemical and electrical properties of strontium-based perovskite electrodes were investigated by means of a variety of X-ray analysis techniques, focusing on phase decomposition and changes in surface elemental composition due to temperature/humidity loading conditions. This study showed that strontium-based

perovskite electrode materials are susceptible to degradation under high-humidity storage conditions, and thus affect the reliability of SOFCs. Based on the observations of a variety of strontium based-perovskite electrodes, it is recommended to store these electrodes at relative humidity less than 40% to minimize degradation during storage and to improve the efficiency and life of SOFCs.

Chapter 6: Conclusions and Recommendations

A significant amount of research has been conducted with improvements noted in the area of both cermet and ceramic anodes of SOFCs. Despite this, the fundamental issues associated with SOFC durability was insufficiently characterized and identified. This study used the existing methodologies such as Ishikawa diagram and FMMECA to illustrate different paths toward failures in SOFCs system. FMMECA was used to highlight the potential failure mechanisms, root causes and failure modes, the likelihood of occurrence, severity and detection of the associated failure mechanisms. The FMMECA's most important contribution is the identification and organization of failure mechanisms and models that can predict the onset of degradation or failure. It was found that anode-electrolyte interfacial delamination and cracks are the critical failure modes which can cause the abrupt failure of SOFCs. Hence, one should carefully design the ceramic anodes of SOFCs for redox cycling and thermal cycling as these are the dominant failure causes for aforementioned critical failure modes. It is worth noting that though mechanical failure due to redox cycling is still a concern with ceramic anodes, the susceptibility to the failure mode is expected to be dramatically reduced as compared to Ni-cermet cells. The purpose of this study is to use the existing technologies such as Ishikawa diagram and FMMECA to analyze and utilize existing data for the purpose of reliability assessment and improvement.

Additionally, degradation mechanisms was found for the prominent electrode material i.e., strontium-based perovskite electrode by elevated temperature and humidity aging. Strontium is common among the perovskite electrodes of SOFCs because it adds structural stability to the crystal at operating temperatures. However,

carbonation of strontium oxide in presence of high humidity can degrade the conductivity of strontium-based perovskite electrodes. The formation of strontium compound is attributed to the strong susceptibility of strontium oxide to chemisorbed water vapor and carbon dioxide from surrounding atmosphere in the presence of high humidity and temperature conditions. The dark-black discoloration failure mode suggests that electrode material has reached the second stage of degradation while white-precipitate formation suggests that materials has reached the third stage of degradation. The empirical degradation model was developed and used to determine allowable temperature humidity conditions during storage of strontium-based perovskite electrodes.

1. Recommendations on Product Development

Listed below are the recommendations based on the findings of this study can be used by standards organizations and industry groups. Improved design influenced by these recommendations can lead to safer and more reliable SOFC systems.

1.1.Spare Storage

The degradation mechanisms for strontium-based perovskite electrodes that can manifest themselves during non-operating conditions of SOFCs has been found in this study. These temperature-humidity dependent degradation mechanisms can occur during cell storage, stack storage, SOFC storage, transportation, on-site storage, and during spares storage for repair (shown in Figure 21).

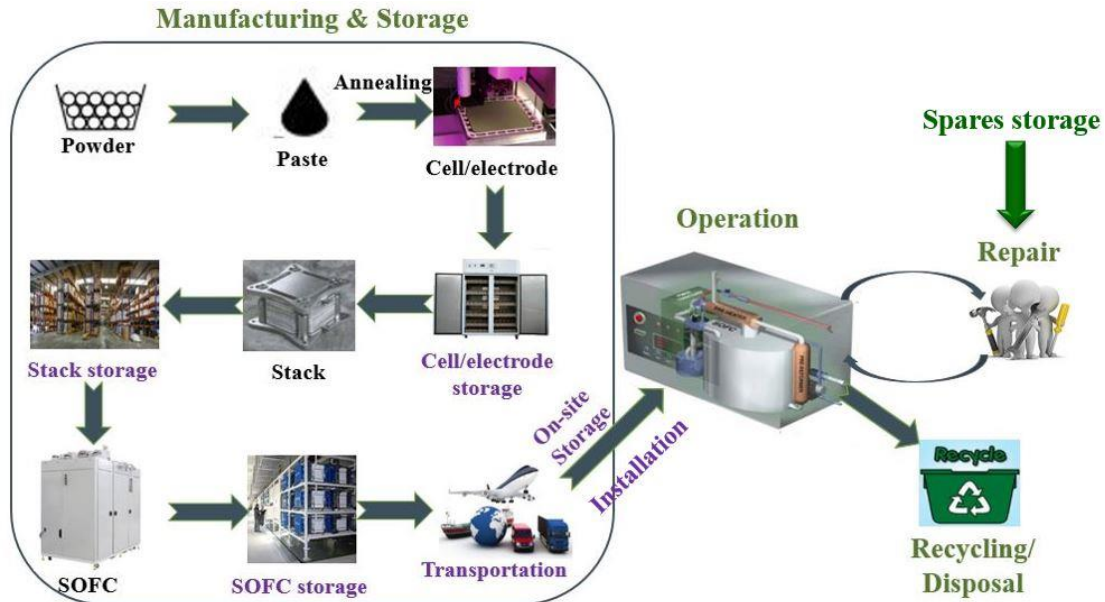


Figure 21. Storage phases for electrodes of SOFCs

In general, the pre-startup storage period is for weeks to months, but storage of spare stacks for repair operations can be for long periods. If degradation occurs, there can be imbalance in the generating unit. During repair of SOFCs, if there is need to replace some faulty cell or stacks, this can be easily be done with onsite, spare cells or stacks. But there is concern that long term storage of spare electrode materials can induce degradation in presence of high-humidity and hence continuous monitoring of these spare parts and storage in low relative humidity conditions ($\leq 40\% \text{RH}$) is recommended.

1.2. Analogy of Cell Specifications with Junction Specifications

The specifications provided for the storage of strontium-based perovskite electrodes are for cell temperature and relative humidity. This can be understood with Figure 22, where cell temperature is analogous to the junction temperature of integrated circuits (ICs). In ICs, the junction temperature can't be measured properly and hence estimated through case temperature and ambient temperature. Similarly, the specifications for storage provided are for cells of SOFCs. Further research is required to understand how ambient conditions might affect cell temperature and humidity.

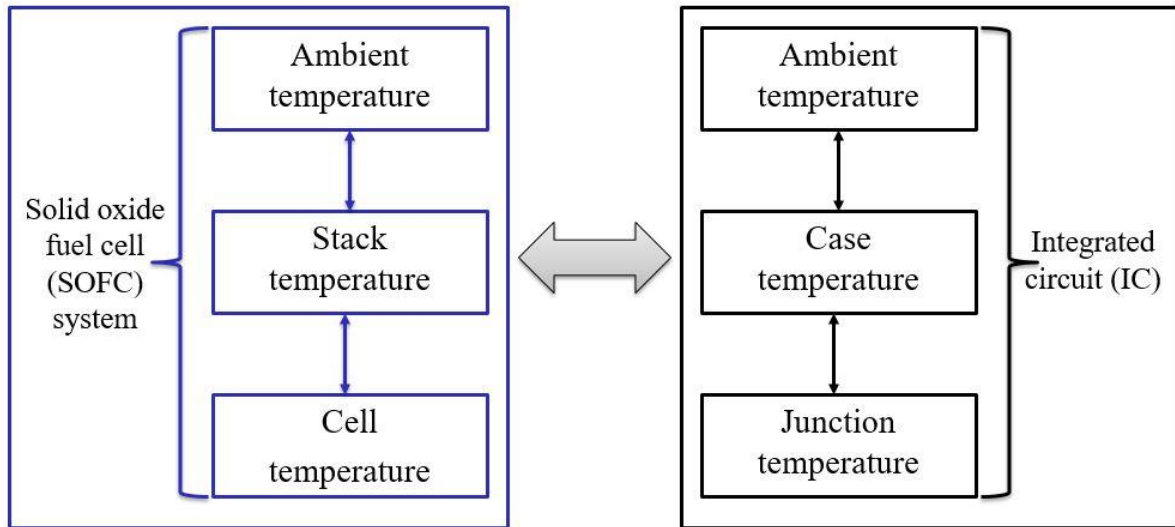


Figure 22. Analogy of cell specifications with junction specifications for ICs

1.3. Fuel/Oxidant Channel Sealing

Strontium-based perovskite electrodes are susceptible to degradation when get exposed to high humidity. Hence, sealing the fuel and air channel prior to installation is recommended to prevent exposure of electrode materials to ambient temperature-humidity conditions. The specification for temperature and relative humidity provided by empirical degradation model applies to the cell, which is analogous to junction temperature in integrated circuits. The relationship between junction temperature and

ambient temperature has been studied for integrated circuits and similar research is required to find the relationship between ambient temperature and cell temperature for SOFCs. It is difficult and expensive to directly monitor the temperature of cells of SOFCs, but it can be estimated through knowledge of ambient and stack temperature. The relationship between cell, stack and ambient temperature for SOFCs can help prevent condensation, which is thought to be more harmful for the electrode materials. It was found that surface-condensed water can result in carbonation of strontium oxide and thereby conductivity degradation of perovskite electrode materials.

2. Future Work

This study has found the degradation mechanisms that can occur during the storage of electrodes of SOFCs which has not been studied before. The degradation of electrodes prior to installation of SOFCs can affect the performance, and life of SOFCs which makes it crucial to prevent degradation prior to installation. However, this study emphasized on the physical, chemical, and morphological changes that can occur in the surface of strontium-based perovskite electrodes and performing the similar study to find the changes in bulk of these materials due to elevated temperature and humidity aging can be crucial to completely understand the degradation mechanisms.

Additionally, data generated from this study has been used to develop empirical degradation model and physical explanation has been provided for each individual and interaction terms in the model. However, understanding of bulk degradation mechanisms will might help in developing physics of failure based degradation model

for perovskite electrodes materials which will be valid for all temperature-humidity combinations.

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