



Surface degradation of strontium-based perovskite electrodes of solid oxide fuel cells



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HIGHLIGHTS

- Determined degradation mechanisms for strontium-based perovskite electrodes.
- Phase decomposition and increase in surface resistance was found.
- Provides non-operating conditions for manufacturers to prevent degradation.

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ABSTRACT

Solid oxide fuel cells (SOFCs) are chemical-to-electrical energy conversion devices that consist of ceramic and metallic materials. The electrodes of SOFCs function as sites for electrochemical reactions, and as electronic conductors to transfer charge. The strontium-based perovskite electrode has been considered because it offers ionic and electronic conductivity, and tolerance to reduction-oxidation cycling. However, as shown in this work, exposure to humidity greater than 40% relative humidity, that may be present during non-operation conditions, including storage, can result in changes in the electrode surface composition with resulting degradation of electrical performance. This study investigates the physical-chemical and electrical characteristics of electrode surfaces when subjected to various humidity and temperature conditions, using scanning electron microscopy, energy dispersive spectroscopy, X-ray fluorescence spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction techniques. Electrode phase decomposition, along with strontium-based degradation mechanisms, were found at humidity levels greater than 40% relative humidity.

1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that converts chemical energy into electrical energy with energy conversion efficiencies in the range of 40–80% as compared to ~35% for a diesel engine and 29–42% for a steam generator [1–5]. An SOFC usually consists of two porous electrodes separated by a dense, oxide-ion conducting electrolyte. Oxygen is supplied at the cathode and reacts with incoming electrons from the external circuit to form oxide ions. These oxide ions migrate to the anode through the oxide-ion conducting electrolyte. At the anode, oxide ions combine with hydrogen in the fuel to form water and liberate electrons. These electrons flow from the anode through the external circuit to the cathode. The materials for the electrodes and electrolytes are selected based on suitable electrical and chemical properties required of these components to perform their intended cell functions [6]. The operating principle described above is

shown as a schematic in Fig. 1.

1.1. Role of electrode surface in performance of SOFCs

Typically, the three major functions of the electrodes of an SOFC are: (1) allowing access to reacting gases, (2) allowing transport of electrons as well as ions, and (3) providing active catalytic sites. The operating temperature of an SOFC is more than 500 °C making them capable of running directly on practical hydrocarbon fuels without the need for a complex and expensive external fuel reformer. The hydrocarbon fuel can be reformed internally using a fuel reforming catalyst on the anode (especially on the surface), thereby increasing efficiency and reducing system complexity and cost [7]. Hence, electrodes for SOFCs should exhibit high ionic and electronic conductivity as well as a high catalytic activity for the desired chemical and electrochemical reactions [8]. Additionally, the microstructure of the electrodes should display a large

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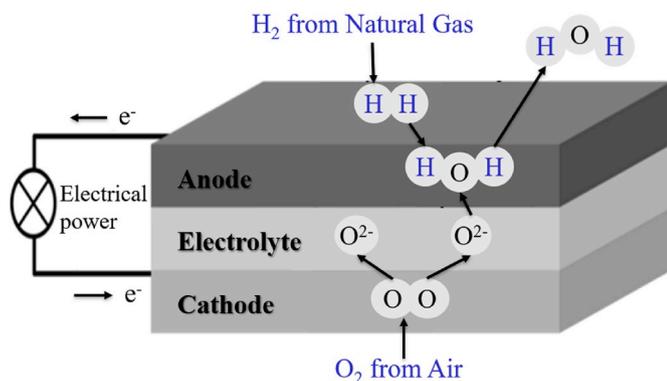


Fig. 1. Schematic of the operating principle of an SOFC cell.

number of active reaction sites [9]. To produce the required voltage and power, multiple cells are combined in an SOFC stack using interconnects. The cells (i.e., surface of the electrodes) in the stack are interconnected to collect current. The interconnecting medium requires high electronic conductivity at the operating temperatures of an SOFC [10].

Perovskite compounds are prominent candidates for the electrode material in SOFCs. A perovskite has the same crystal structure as calcium titanium oxide (CaTiO_3). Typically for SOFC electrodes, the structure ABX_3 contains an alkaline earth metal on the A-sites, a transition metal on the B-sites, and oxygen on the X-sites. Perovskite compounds are common among electrodes of SOFCs because they can provide: (1) mixed ionic and electronic conductivity, (2) structurally stable chemistries throughout a wide range of oxygen partial pressure and temperatures, and (3) little to no reactivity with the other components of the cells [11]. Strontium is a common choice for the A-sites of perovskite electrodes of SOFCs because it adds structural stability to the crystals at operating temperatures, in addition to providing good electronic conductivity to conduct electrons to the interconnecting medium.

1.2. Surface degradation of electrodes during operation of SOFCs

Long-term stability is a key requirement for the commercial application of SOFC technology. An SOFC consists of multiple components, each with its own failure mechanisms and criteria for failure. The performance degradation of SOFCs may be due to the following factors, some of which overlap: (1) the contact resistance between electrodes and current collectors may increase with time, (2) the electrode, electrolyte, and interconnect may become chemically unstable when they are in contact with each other, and (3) the electrode-electrolyte or the electrode-interconnect interfaces may become delaminated [12]. Additionally, the electrochemical reactions taking place (hydrogen oxidation on the anode and oxygen reduction on the cathode) depend on the composition of electrodes as they are highly sensitive to chemistry [13–16].

Young and Otagawa [17] studied the surface elemental composition on strontium metal plates during oxidation at room temperature and observed strontium carbonate peaks. They attributed this to the fact that strontium oxide and mixed oxides containing strontium are strongly susceptible to chemisorbed carbon dioxide and water vapor. Joo et al. [18] studied the effect of water on oxygen surface exchange kinetics and its degradation of dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3.6}$ (LSC) thin films at the operating temperatures of SOFCs ($>600^\circ\text{C}$). They reported that the degradation of catalytic activity of lanthanum strontium cobaltite (LSC) originates from strontium segregation towards the surface. The same result has been reported for lanthanum strontium cobalt ferrite (LSCF) materials at operating temperatures of SOFCs in $\text{H}_2\text{O}/\text{CO}_2/\text{O}_2$ atmospheres. Benson et al. [19] showed that quenching of perovskite electrode samples to room temperature in $\text{H}_2\text{O}/\text{CO}_2/\text{O}_2$ atmospheres results

in formation of additional compounds, such as SrCO_3 , which significantly modify the surface layer of ceramics, inhibiting subsequent oxygen exchange. Hence, Benson et al. [19] emphasized the need to preserve the surface composition and quality of ceramic upon cooling after annealing and after sudden shutdown of system. Jiang [20] 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 [21] studied the surface chemical composition of dense thin film $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3.6}$ electrodes after annealing at 650°C using X-ray photoelectron spectroscopy and found strontium peaks corresponding to strontium oxide, hydroxyl species ($\text{Sr}(\text{OH})_2$), and carbonate species (SrCO_3).

1.3. Potential degradation mechanisms during storage and other non-operating conditions

While the degradation of mixed conducting perovskites under SOFC operation conditions has been studied (see Section 1.2), far less is known for degradation under temperature/humidity conditions in non-operating conditions. Different stages of storage and other non-operating conditions for SOFCs are shown in Fig. 2. Temperature-humidity dependent degradation of mixed conducting perovskites can occur during cell storage, stack storage, SOFC storage, transportation, on-site storage, installation, spares storage and during repair. In general, the pre-startup storage period is for weeks to months, but storage of spare stacks for repair operations can be for years. During repair of SOFCs, if there is need to replace some faulty cell or stacks, this can 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 humidity higher than 40% relative humidity.

Different perovskite SOFC electrodes have been examined in this study under temperature/humidity conditions associated with non-operating conditions. Changes in the physical-chemical and electrical characteristics of lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) were observed to depend on the applied temperature and humidity conditions. LSC and LSCF have been developed as mixed electron and ion conductors for the intermediate-temperature SOFC cathode family, owing to their stability for operating temperature requirements and chemical stability with ceria-based electrolytes [22].

The present study investigates the degradation mechanisms responsible for temperature/humidity-dependent degradation of strontium-based perovskite electrodes that can manifest themselves during storage and other non-operating conditions of SOFCs. Section 2 describes the physical-chemical and electrical characterization techniques that have been used to assess the degradation of strontium-based perovskite electrodes. Section 3 presents the results obtained from elevated temperature/humidity exposures of electrode material. Section 4 postulates the degradation mechanisms responsible for the degradation of strontium-based perovskite electrodes in the presence of temperature/humidity and time conditions, and Section 5 presents the conclusions.

2. Characterization of electrodes of SOFCs

Four compositions of materials were studied: $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-x}$ (product LSCF-P) obtained from fuelcellmaterials.com denoted LSCF, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{CoO}_{3-x}$ (product LSC-P) obtained from fuelcellmaterials.com denoted LSC1, $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ obtained from Praxair denoted LSC2, and a newly developed strontium-based iron-doped perovskite electrode, denoted DEV1. LSCF, LSC1, and LSC2 electrodes were screen-printed on insulating substrates and fired at 1100°C for 2 h to form porous electrodes. DEV1 was a porous, free-standing sintered electrode.

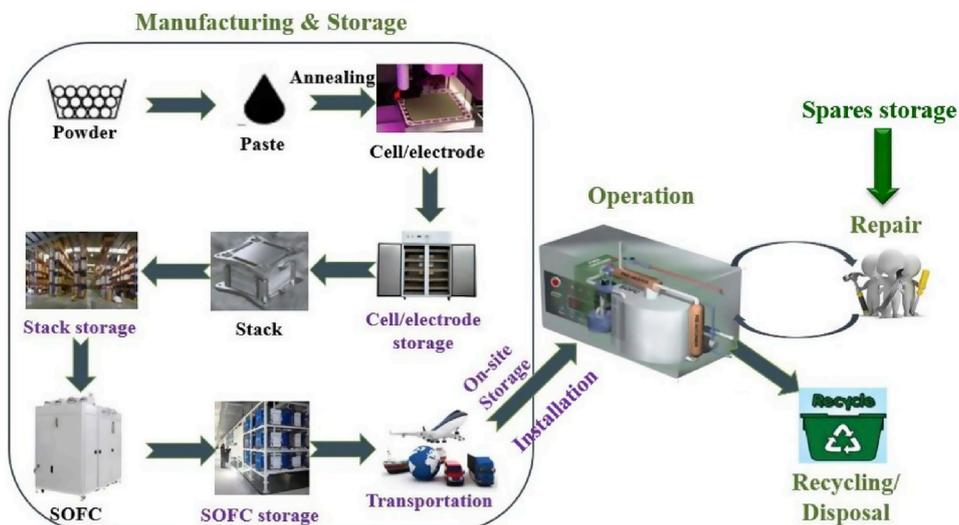


Fig. 2. Life cycle of SOFCs, which involves manufacturing, storage (in several phases), transportation (also included in storage for this project), installation, operation, and disposal/recycling.

2.1. Physical and chemical characterization

SEM and EDS analyses were conducted using an FEI FEG Quanta 200 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 conducted 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 fluorescence (XRF) was carried out with a Fischerscope XDAL X-ray spectrometer, which has a detection range from 0.1% to 100% (w/w). The depth of penetration varies depending on the materials used and can be over 50 μm. Using this XRF at tube voltages of 30 kV and 50 kV, penetration depths for the DEV1 samples will reach approximately 50 μm and 200 μm, respectively.

X-ray diffraction (XRD) of aged and unaged strontium-based perovskite samples was carried out with a Bruker D8 Discover X-ray diffractometer equipped with a secondary graphite-crystal monochromator and using Cu radiation at 40 kV/40 μm. A Vantec-500 area-detector was used. The phase analysis was performed at a penetration depth of

approximately 5 μm.

X-ray photoelectron spectroscopy (XPS) was conducted 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 conducted on unaged and aged samples, and angle probe measurements at 20° and 90° were performed.

2.2. Electrical measurements: two-point and four-point resistance measurements

Two-point conductivity measurements of the strontium-based perovskite samples were performed using a surface-mounted test tweezer (SMD Test Tweezer™ 5678 Series) manufactured by Pomona Electronics with sleeved banana plugs and an Agilent 34411 A multimeter. Gold-plated brass bearings balls were soldered on the legs of the SMD test tweezer to prevent penetration of the surface while measuring the surface resistance (shown in Fig. 3). The measurement apparatus consisting of an electronic balance, a ring-stand and clamp, and a scissor jack, was used to apply constant force during measurements. Two-point

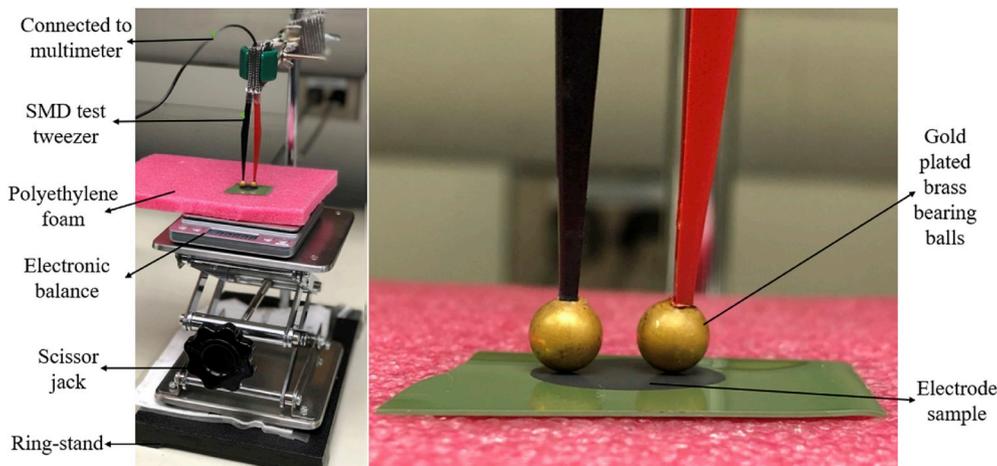


Fig. 3. (a) Two-point conductivity measurements apparatus; (b) Enlarged view of gold-plated brass bearings balls used for two-point conductivity measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

conductivity measurements show the combination of contact resistance and sample resistance. Four-point conductivity measurements, using a modified version of the 2-probe design, but with collinear 4 probes, were also performed to determine the degradation behavior of sample resistance. All the 4 probes were equally spaced. The current was supplied through the two outer probes and the voltage was measured across two inner probes to determine the sample resistivity. Since, 4 probe resistance measurement uses two additional contacts for voltage measurement, the voltage drops across wire resistance and contact resistance are negligibly small due to high impedance of voltmeter (more than $10^{12}\Omega$) and the measured voltage is essentially the voltage drop across the electrode material. The increase in four-point resistance measurements can be used to show that not only contact resistance but also resistance of the sample material increases with degradation.

To select an appropriate force to minimize variances in resistance measurements due to applied normal force on the samples during conductivity measurement, resistances of unaged strontium-based perovskite electrodes (DEV1 samples) were measured with a series of normal forces (shown in Fig. 4). A constant force of 80 gF was chosen for measuring the conductivity of unaged and aged samples based on the results shown in Fig. 4.

3. Degradation under temperature/humidity conditions

Temperature/humidity-dependent degradation of strontium-based perovskite electrodes was observed through elevated temperature/humidity testing in air. Aging of DEV1 samples (80 °C and 80% relative humidity) resulted in black discoloration of the normally dark grey samples within 12 h. Long exposure (one week) of these samples at 80 °C and 80% RH (relative humidity) resulted in formation of white precipitate on the surface. Morphological changes were found through SEM analysis along with visual observation of white precipitate formation on the electrode surfaces (shown in Fig. 5).

Elevated temperature/humidity in air testing was also conducted on the LSC1, LSC2, and LSCF samples. Black discoloration of one of the strontium-based perovskite electrodes (LSC2) after aging at 80 °C and 80%RH is shown in Fig. S1 in supplementary file. Electrical characterization using two-point conductivity measurements showed that the LSC2 samples have undergone the maximum percentage increase in resistance, whereas LSCF had undergone the minimum percentage increase. The results from two samples of each set are shown in Fig. 6. It is worth noting that the initial two-point resistance of unaged LSC1 samples were $\sim 15\Omega$ as compared to $\sim 10\Omega$ for LSC2 samples and $\sim 150\Omega$ for LSCF samples. Elemental composition analyses were conducted to determine the factor(s) responsible for increase in resistance of LSC2 samples as compared to LSC1 samples, in spite of their having similar chemical compositions. SEM-EDS analysis indicated that the LSC2 samples have higher strontium weight percentage ($\sim 18\%$) as compared

to the LSC1 samples ($\sim 6\%$), in agreement with the greater fraction of Sr in the as received material.

3.1. Changes in surface resistance due to temperature/humidity aging

The surface resistances of the DEV1 samples were measured after they were aged at 80 °C and 80% RH. It was found that the surface resistance of electrode samples shoots up on the order of 500% of initial surface resistance with the black discoloration. With white precipitate formation, the surface of the electrodes becomes highly resistive with increases in resistance greater than 1000% of initial surface resistance. The increases in resistance of three DEV1 samples due to temperature/humidity aging at 80 °C and 80% RH for 228 h are shown in log scale in Fig. 7.

Additionally, 2-point resistance measurements were performed for the DEV1 samples exposed to all combination of two temperatures (60 °C and 80 °C), and three humidity conditions (70% RH, 50%RH, and 30%RH), shown in Fig. S3 in supplementary file. Linear interaction model was developed as a function of temperature, relative-humidity, and time which will be presented in follow-up paper. 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 Fig. S4 in supplementary file). 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.

3.2. Changes in elemental composition at different depths due to temperature/humidity aging

Since strontium segregation [21] has been reported in the literature (albeit at the much higher temperatures typical of SOFC operation) and can eventually result in an increase in surface resistance of the samples, the strontium weight percentage was measured at a penetration depth of $\sim 200\mu\text{m}$ and $\sim 50\mu\text{m}$ using XRF. No significant increase in weight percentage of strontium with annealing time or depth was found in the bulk material of the DEV1 samples. EDS analysis was also conducted before and after aging the DEV1 samples for 10 days. Table 1 shows the initial and final average strontium weight percentages for three samples at different penetration depths before and after aging.

XRF and EDS analysis showed no significant change in concentration of strontium in the bulk of the DEV1 samples, irrespective of an observed increase in surface resistance of the samples. XRD analysis was conducted to determine whether there is any phase decomposition in the near surface region ($\sim 5\mu\text{m}$ penetration depth) of the material producing the observed increase in resistance. XPS analysis was conducted to look for changes in elemental composition on the surface of the sample

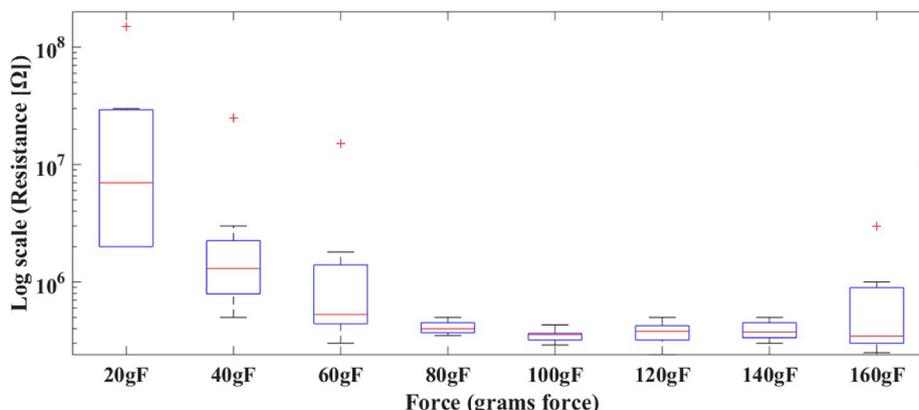


Fig. 4. Two-point resistance of unaged DEV1 samples at different forces and at 1 V.

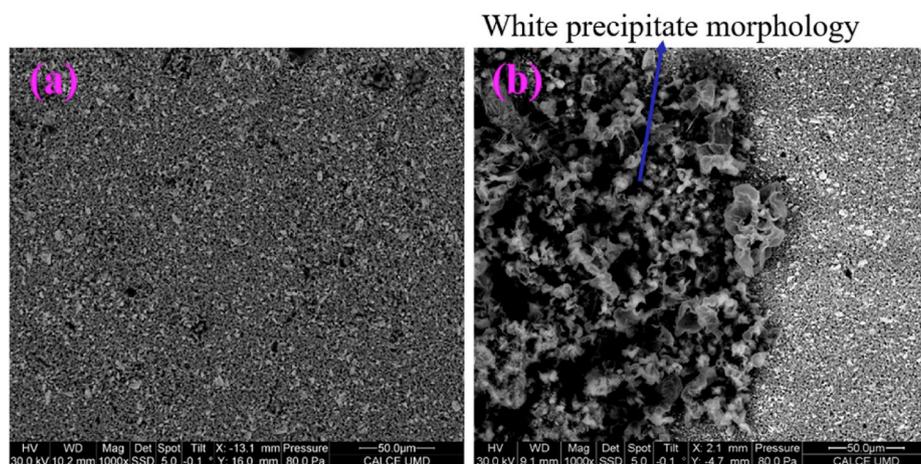


Fig. 5. (a) Perovskite electrodes before aging, (b) Perovskite electrodes after aging for 131 h at 80 °C and 80%RH.

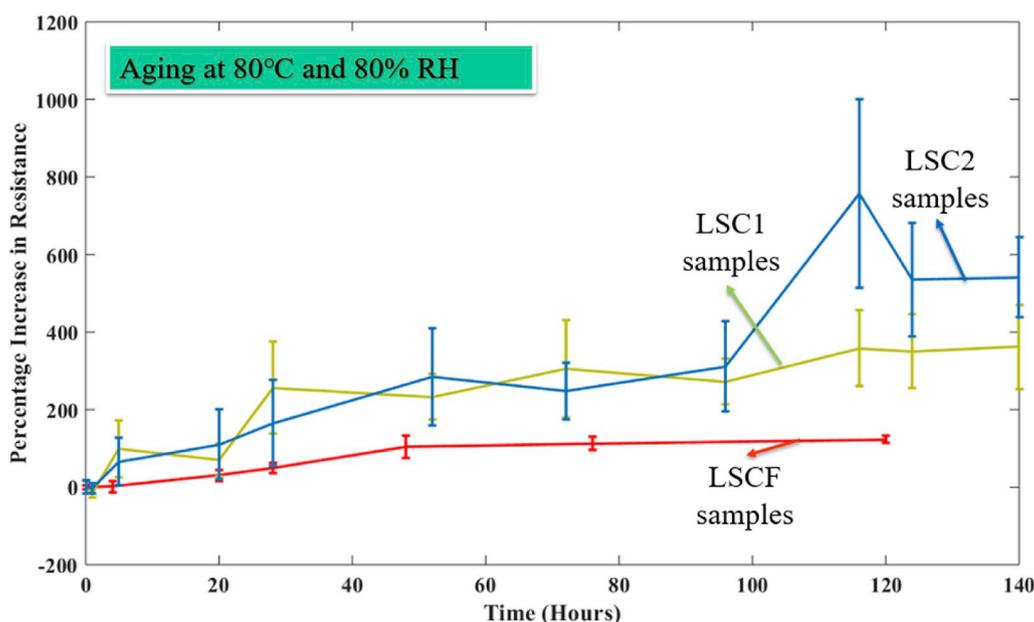


Fig. 6. Mean value of 16 resistance measurements from two samples of each set (error bar: 90% confidence interval) after each inspection interval is plotted against time.

(~3 nm penetration depth). XRD analysis showed phase decomposition and an additional phase of strontium carbonate in all aged samples. XPS analysis of unaged samples indicated strontium oxide on the surface. After aging, all the strontium present on the surface was determined to be converted to strontium carbonate by XPS (shown in Fig. S2 in supplementary file) with visual degradation modes of black discoloration and white precipitate formation. XRD and XPS analysis showed phase decomposition of the electrode, strontium carbonate on the electrode surfaces was determined by XPS with the appearance of black discoloration, and formation of a phase of strontium carbonate was determined by XRD with the white precipitate. This suggests that the black discoloration due to temperature/humidity aging is attributable to electrode phase decomposition accompanied by strontium carbonate formation, while the formation of white precipitate is attributed to a thick strontium carbonate layer of ~>3 nm thick considering the fact that XPS analysis only showed peaks of strontium carbonate for aged perovskite samples. From the above composition and phase analysis and annealing studies described below, it was concluded that the apparently strong susceptibility of strontium oxide to chemisorbed water vapor and carbon dioxide from a surrounding atmosphere can result in the

formation of strontium compounds on electrode surfaces whenever strontium-based SOFC electrode samples are exposed to conditions humidity greater than 40% RH.

3.3. Surface degradation based on four-point resistance measurements

Two-point resistance values indicated degradation of contact resistance of electrode samples due to temperature/humidity aging. In order to determine if the conductivity of the bulk samples was also changing, 4-point resistance measurements were performed for the DEV1 samples exposed to two different temperature and three different humidity conditions (shown in Fig. 8). In the most aggressive annealing condition (80 °C and 90% RH) the 4-point resistance increased from ~2 kΩ to ~60 kΩ, indicating that the temperature/humidity-dependent electrode degradation impacts bulk resistance. It is worth noting, though, that the 2-point resistance is orders of magnitude larger than the bulk resistance and increased from ~3 MΩ to ~20 MΩ (at 80 °C and 80% RH), indicating that contact resistance, and its degradation, would dominate in a device using this configuration. In a real system, contact would be made using specially designed pastes or other contact materials that would aid

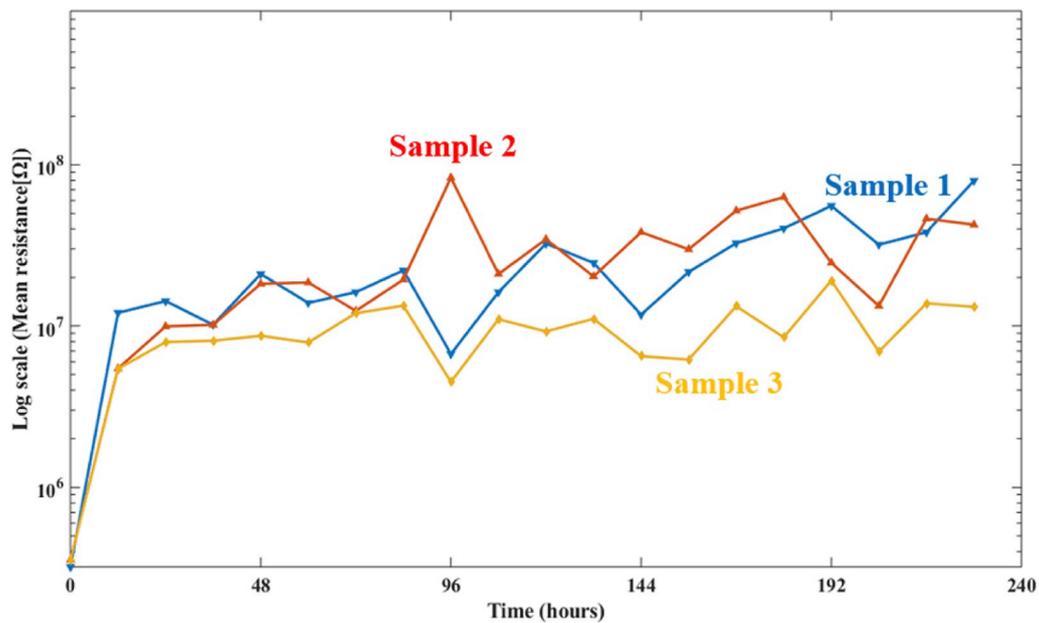


Fig. 7. Mean of 8 resistance measurements (2-point resistance) for three identical DEV1 samples after each inspection interval annealed at 80 °C and 80% RH.

Table 1
Strontium weight percentage at different penetration depths for DEV1 samples.

Elemental Composition Using Different X-ray Analysis Techniques	Strontium Weight Percentage Before Aging	Strontium Weight Percentage After Aging at 80 °C and 80% RH for 10 Days
XRF at 50 kV (X-ray penetration depth: 200 μm)	40.85	41.12
XRF at 30 kV (X-ray penetration depth: 50 μm)	40.65	41.97
EDS at 30 kV (X-ray penetration depth: 3 μm)	34.67	37.33

in alleviating the large initial resistance observed with the test stand used here.

4. Discussions: mechanisms responsible for degradation of the surface and sub-surface

Degradation of solid oxide fuel cells (SOFCs) is often quantified 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 [23]. The consequences of temperature/humidity-dependent degradation are conductivity degradation which will eventually lead to performance degradation and shortening of the SOFC lifetime. Elevated temperature/humidity stress exposure confirmed the degradation of strontium-based perovskite

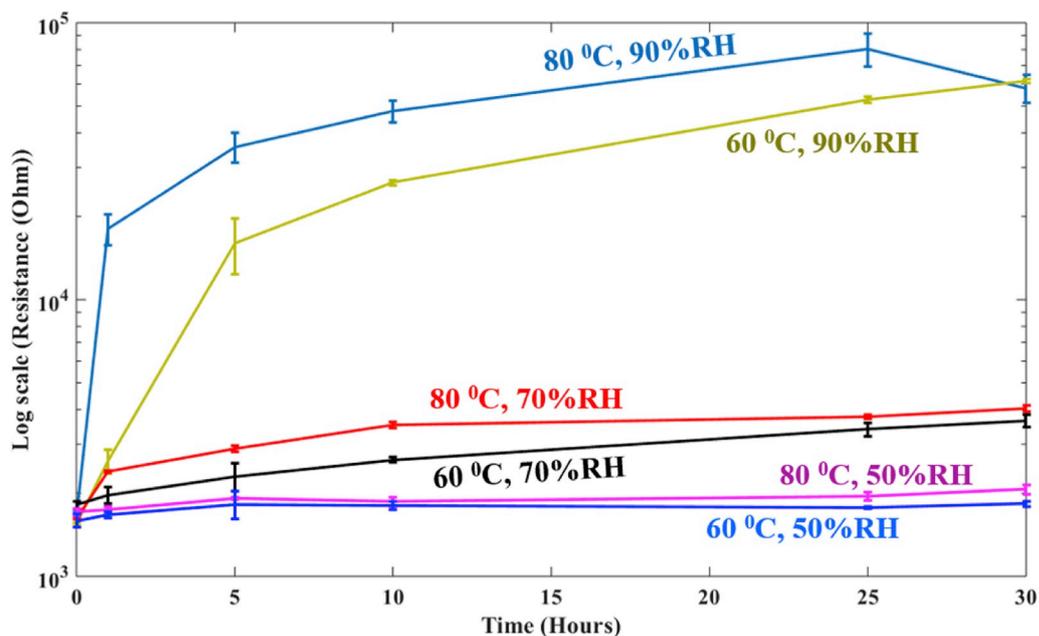


Fig. 8. Mean resistance (4-point resistance) of two DEV1 samples (8 measurements on each sample) per condition measured after each inspection interval (error bar: one standard deviation).

electrodes of SOFCs. Phase decomposition along with an increase in surface resistance of strontium-based perovskite electrodes were observed when they were exposed to the elevated temperature/humidity conditions.

4.1. Effect of surface degradation on the performance of SOFCs

The electrodes of SOFCs require high catalytic activity in addition to electronic and ionic conductivity to perform their intended functions. These catalytic activities are highly sensitive to surface chemistry. Consequently, any change in surface composition of electrodes will affect their performance. The composition and structure of these electrodes are designed for desirable electrochemical properties. Any deviations from these properties can impact performance. Through the elemental composition analysis techniques applied here, it was found that strontium-based perovskite electrodes show morphological changes and phase decomposition on the surface due to elevated temperature/humidity aging. Since strontium-based perovskite electrodes are porous (typically ~40% porosity), the accumulation of decomposed phase can occur on the surface and in the bulk of the electrodes. That is, also on the outer surfaces of the particles constituting the electrodes. It is inferred through 4-point resistance measurement values that the phase-decomposition of the electrode is not limited to the electrical probe contact surfaces.

The interface between the interconnect that collects the current from the electrode and the electrode in a fuel-cell assembly are susceptible to humidity, which may result in the formation of an insulating phase growing between these two components. There are usually hundreds of these cells in a typical SOFC system. The whole system is assembled in an assembly facility and then shipped to an installation site where it stays in non-operating condition before and during installation. Systems should be assembled in dry environments and the assembled systems needs to be protected from humidity prior to installation on site. Humidity may also cause problem during operation as a system may be cooled down to the local environmental temperature a few times during its life.

4.2. Are these degradation mechanisms self-limiting?

It is suggested in the literature [18] that high-temperature (>500 °C) aging can result in strontium segregation through kinetic demixing, driven by mechanical strain gradients. However, such changes on a macroscopic scale in ternary oxides are not expected at room temperature [20], and this is only true when there is a single phase of perovskite and when strontium is migrating through that phase to the surface. This study shows phase decomposition along with strontium carbonate formation on the surface, which results in corrosion of the perovskite crystals from the outside in. Through this surface degradation study, it is hypothesized that the formation of strontium carbonate on the outside sample surface of LSC1, LSC2, LSCF, and DEV1 creates a concentration gradient for the strontium hydroxide within the porous sample. This concentration gradient causes strontium hydroxide to continually move to the outside surface as it is consumed with carbon dioxide in the air to form carbonate. Sufficiently long exposure may result in the entire perovskite being converted to decomposition products. Hence, it is hypothesized that the temperature/humidity-dependent degradation mechanisms for strontium-based perovskite materials are not self-limiting and cannot be contained by mere removal of surface products.

4.3. Surface resistance as a degradation predictor

It was observed that the surface resistance of strontium-based electrode increases by as much as 500% of initial surface resistance with the observed black discoloration. With white precipitate formation, the electrode surfaces become even more resistive, with increases in resistance greater than 1000% of the initial surface resistance. Black

discoloration and white precipitate formation are attributable to phase decomposition and strontium carbonate formation, which happened simultaneously with an increase in surface resistance of the electrode samples. This suggests that increases in surface resistance are attributable to phase decomposition and strontium carbonate formation. Hence, in addition to providing information about surface conductivity, an increase in surface resistance can be used to predict degradation of electrodes.

5. Conclusions

A stable perovskite electrode material with ionic and electronic conductivity 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. Based on physical, chemical, and electrical characterization of strontium-based perovskite electrodes, temperature-humidity dependent degradation mechanisms were found which can manifest themselves during storage and other non-operating conditions.

Experimental results showed that the lanthanum strontium cobaltite (LSC) electrode materials with strontium weight percentages of ~18% undergo an approximately 500% increase in surface resistance from initial surface resistance as compared to the LSC electrode materials with strontium weight percentage of ~6% which undergo an approximately 300% increase in surface resistance from initial surface resistance, after 140 h in 80 °C and 80% relative humidity. This increase in surface resistance implies that the surface degradation of strontium-based perovskite electrode materials with similar chemistries is dependent on the amount of strontium present in the materials. It was found that a three-fold increase in strontium weight percentage in LSC resulted in 1.5-fold percentage increase in surface resistance. The iron-doped perovskite electrode material (LSCF) studied here showed a 100% increase in surface resistance from initial resistance when aged at 80 °C and 80% relative humidity for 124 h. This surface resistance increase for LSCF implies that doping perovskite electrode materials with iron provides some resistance stability as compared to LSC electrode materials. This study showed that strontium-based perovskite electrode material goes through morphological changes, phase decomposition, and increase in surface resistance when subjected to high humidity (>40% RH).

The temperature/humidity-dependent degradation of the materials studied here is attributed to the susceptibility of strontium oxide to reaction with chemisorbed water vapor and carbon dioxide from the surrounding atmosphere in the presence of a favorable thermodynamic environment, especially relative humidity higher than 40%. This susceptibility results in the formation of an additional phase of strontium carbonate. The observed black discoloration, due to temperature/humidity aging, is attributed to electrode phase decomposition accompanied by strontium carbonate formation. The observed white precipitate is attributed to the formation of a strontium carbonate layer (~1 nm thick) on the surface.

This study shows the need to observe the necessary conditions to preserve the composition of strontium-based perovskite electrodes during storage and other non-operating conditions to improve the performance and durability of SOFCs. It was found that storing the strontium-based perovskite electrodes at relative humidity higher than 60% can degrade the surface composition of electrodes in less than a week. It was also found that storing it below 40% relative humidity will have negligible degradation. Hence, it is recommended to store these electrodes at low relative-humidity conditions (<40% RH) to prevent degradation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2019.227040>.

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