

# Long-term Cell Testing of Interlayer-free Lanthanum Strontium Cobalt Ferrite Cathodes for Solid Oxide Fuel Cells

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**Abstract:** Sub-stoichiometric LSCF nanopowders with composition of  $(\text{La}_{0.6}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.80}\text{O}_{3-\delta}$  were prepared using a nitrate-glycine process. The particle size is estimated to be 28.8 nm using the Scherrer equation. A sintering study and pull test was done to determine the quality of LSCF adhesion to the YSZ electrolyte. It was found that firing the cathode at 850°C does not provide the best adhesion, but button cell testing data indicate that the performance is stable over relatively long-term tests. The cell performance is not up to par to *state-of-the-art* Ni-YSZ/YSZ/SDC/LSCF where a barrier layer is used and the cathode is fired at high temperatures. Impedance data indicate that the reason for lower performance is due to higher cathode polarization. However, the results are promising and further studies are warranted because low temperature processing and the removal of the ceria layer can decrease fabrication costs.

**Keywords:** Solid oxide fuel cells, LSCF, Cathodes, YSZ, SDC.

## 1. INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) are candidates for a variety of applications where electrical power is needed. SOFCs are not Carnot limited, are highly efficient, modular, and possess cogeneration abilities. SOFC systems are expected to make ways into a variety of market such as portable, automotive, residential, commercial building, and large power plants [1, 2]. SOFCs can operate over a wide range of temperatures because several material sets are available thereby making them more versatile for different applications. In addition, SOFC systems are fuel flexible and can use different fuel sources such as natural gas, syngas, and hydrogen [3]. Of special interest is the reduction of the operating temperature to allow stacks to withstand thermal cycling more effectively where the application requires it. In recent years, SOFC development has been accelerating with several prototypes being built and tested at different sites [4]. Despite the progress made, the cathode remains a strong subject of research because of long-term degradation due to strontium segregation and chromium poisoning from metallic interconnects and balance of plant components [5, 6]. For intermediate temperature SOFCs operating around 750°C, it is common to use lanthanum strontium cobalt ferrite (LSCF) cathodes because they possess high mixed conductivity and high electro-catalytic activity for the reduction of oxygen. To prevent unwanted reactions

with the YSZ electrolyte, namely the formation of the nonconductive  $\text{SrZrO}_3$  phase, LSCF cathodes requires a buffer layer usually made of ceria either doped with Sm or Gd [7]. However, some studies indicate that these unwanted reactions with YSZ do not occur if the LSCF cathode ink is fired at temperatures below 900°C [8]. This firing step is necessary to attach the LSCF cathode to the electrolyte. Additional studies have indicated that adding a ceria-zirconia (CZ) mixture to LSCF and firing at 850°C further prevents the formation  $\text{SrZrO}_3$  at the cathode and YSZ electrolyte interface [9]. These studies are limited because they do not address the long-term stability of a cathode that has been fired at lower temperatures that is commonly done at around 1100°C [10]. In addition, the above studies do not address the concern of adhesion strength when firing at these low temperatures. Hence, the objective of this work is to address adhesion concerns and the long-term performance of LSCF cathodes that are fired at 850°C. A sintering study, followed by a pull test, was performed. Then, button cells were fabricated and tested. The cell voltage was monitored under load for relatively long-term tests, and the cell electrochemical performance was evaluated using impedance spectroscopy. The necessary material characterization and post-mortem analysis were also performed.

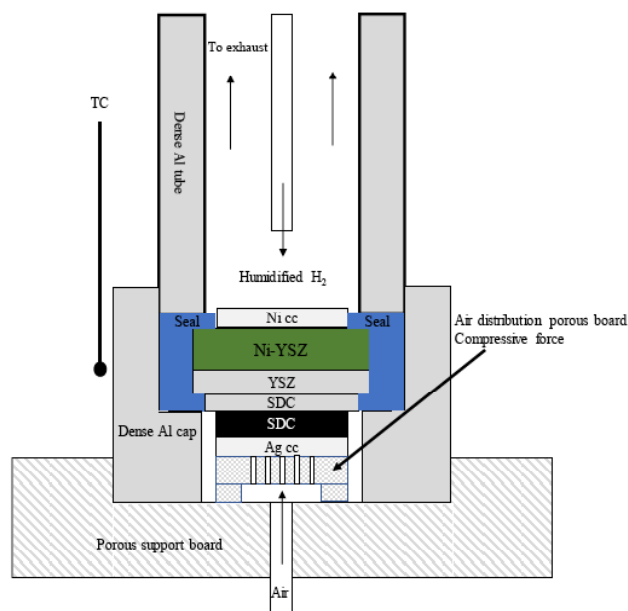
## 2. EXPERIMENTAL

LSCF cathode with composition of  $(\text{La}_{0.6}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.80}\text{O}_{3-\delta}$  was prepared using a nitrate-glycine process as described in the literature [8]. The nitrates of each elements were dissolved into DI water and then combined with a glycine solution. The combined solution had molar ratio of glycine to nitrates

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of 2.5:1. The solution was then heated with continuous stirring until combustion occurred around 180°C. The combustion products were a porous, foamy like, and fragile material. The porous material was subsequently calcined at 800°C in air for 5 hours. After calcination, the powder was ball milled in ethanol for 24 hours and then air dried for 24 hours. LSCF ink were prepared using an organic vehicle purchased from Fuel Cell Material (FCM). For reference and comparison purposes, an additional LSCF ink from FCM with the same composition was purchased as well. Anode-supported bilayers were obtained from Delphi Automotive, PLC. The anode consists of *state-of-the-art* nickel and yttria-stabilized zirconia (Ni-YSZ) cermet while the electrolyte is *state-of-the-art* YSZ. Both inks were screen printed on the bilayers and fired at 850°C for 2 hours for the fabrication of button cells. Additional samples were prepared using the ink from FCM for a pull test study and fired at different temperatures and times.

All SOFC button cells were tested at 750°C. A baseline long-term performance was established using a commercial Ni-YSZ/YSZ/SDC/LSCF based cell technology (Cell 02), which includes a ceria barrier layer, and the LSCF has been fired at around 1100°C. The LSCF inks obtained from FCM (Cell 08) and prepared in house (Cell 13) were also tested in button cells. The details of the cell testing setup are shown in Figure 1. For Cell 08 and 13 the cathode current collector was fired in situ to prevent a thermal cycle. To ensure a good cathode contact, a small compressive force was applied via an air distribution porous board



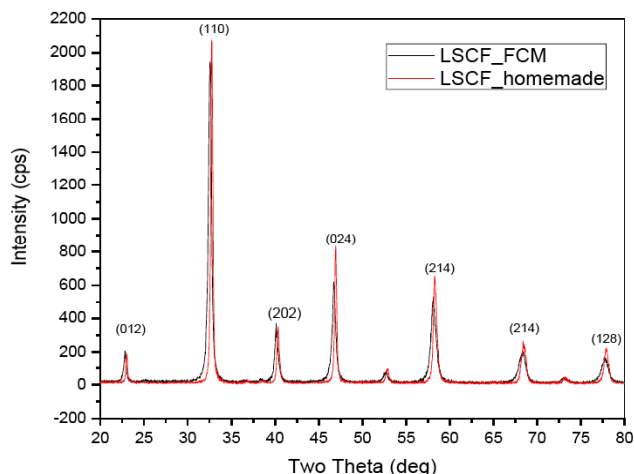
**Figure 1:** Schematics of the button cell testing setup used for this work.

as described in the figure. However, this approach was not used or needed for the Cell 02 where the cathode current collector was fired on a separate step. The temperature was closely monitored by placing a thermocouple very close to the cell. In the anode side, humidified hydrogen was used at room temperature with a flow rate of 1 SLPM. In the cathode side, air was used as an oxidant with a flow rate of 1 SLPM. Voltage-time curves as well as impedance measurements were made using a PARSTAT 2273 apparatus coupled with a power booster obtained from AMETEK Princeton Applied Research. Impedance data were obtained at open circuit voltage. The frequency range was between 0.01 Hz and 1 MHz with an AC amplitude of 10 mV and 12 datum points per frequency decade.

The XRD data were collected using a Rigaku Mini Flex 600, a Benchtop X-ray Diffraction System. The scan step was setup at 0.02 degrees with a duration of 0.8 seconds. The SEM/EDS equipment used is an analytical Quanta 200s Environmental Scanning Electron Microscope produced by the Phillips Electron Optics Company. The TEM used is a JEM 2100 Plus, using a thermal LaB<sub>6</sub> gun operated at 200 keV. EDS was performed with a X-Max TEM 65T silicon drift detector, using the Cliff Lorimer method for quantification. Samples were prepared by sonication in ethanol, then the suspension was dropped and dried on a carbon grid.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the LSCF powders used in this work. Both LSCF powders have a rhombohedral perovskite structure as observed and reported by other researchers [11]. The purchased LSCF powder shows wider peaks indicating a smaller



**Figure 2:** XRD data for FCM and homemade LSCF.

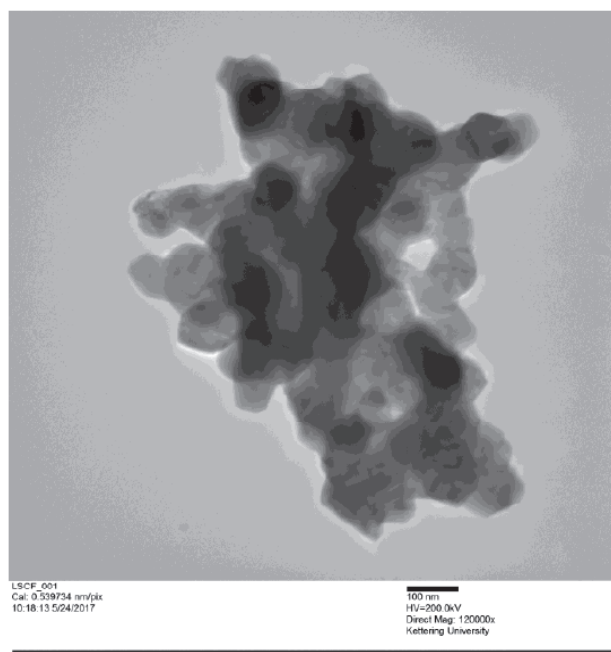
crystallite size. The particle size can be estimated using the x-ray line broadening technique and the Scherrer equation as shown below:

$$d_p = \frac{0.94 \lambda}{B \cos \theta_B}$$

where  $d_p$  is the crystal size in nm,  $\lambda$  is the x-ray wavelength (1.540593 Å) of CuK $\alpha$  radiation,  $B$  is the width (measured in radians) of the XRD diffraction peak at half of its maximum intensity, and  $\theta_B$  is the Bragg diffraction angle of the peak [12]. Using Figure 2 and the (110) peaks, the grain sizes are estimated to be 19.7 and 28.8 nm for the purchased and homemade LSCF powders respectively. This result indicates that the in-house synthesis still needs some optimization to reduce the particle size further. Figure 3 reports the high magnification TEM picture of the homemade LSCF powder. Particles are agglomerated and some indicate a neck formation. The TEM data indicate that the grain size is larger (around 90 nm) than the one estimated from the Scherrer formula. One possible explanation for the observed difference is that the XRD peak broadening has increased due to the presence of some possible amorphous crystals. This is would not be possible with TEM because the crystals are fewer given the high magnification of this technique.

Both LSCF powder were analyzed using SEM/EDS to verify their chemical composition. Table 1 compares the expected atomic percent calculated based upon the chemical formula of  $(\text{La}_{0.6}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.80}\text{O}_{3-\delta}$  with the measured values using EDS. The results obtained from the SEM machine are reasonably in line for what it is expected, but relative large differences are seen for both powders. This observation is probably due to the bulk analysis nature of the SEM and some element segregation may also be playing a role. To verify this, the homemade powder was also analyzed using the EDS portion of the TEM machine. These results are also shown in Table 1. The measured differences are

smaller except for the Sr and La elements. It is unclear at this time why some elements would have high errors and others would not. However, the localized nature of the TEM may be responsible for this behavior.



**Figure 3:** HR-TEM photograph for the homemade LSCF.

A total of eight samples or button cells were prepared for the pull test study. The cathode firing temperature and time was varied, and a scotch tape test was performed after the firing step. Table 2 reports the various parameters and pull test results. At a firing temperature of 850°C for two hours, the pull test is positive; however, the tape has a heavy cathode residue which indicates poor bonding among cathode particles. The sample that failed at 900°C did not fail completely, but a small chunk of material came off. Heavy residue on the tape was still observed. Increasing the temperature to 950°C or above, produces better adhesion to the bilayer and leaves no residues on the tape. Increasing the sintering time also

**Table 1: EDS Results for LSCF Powders**

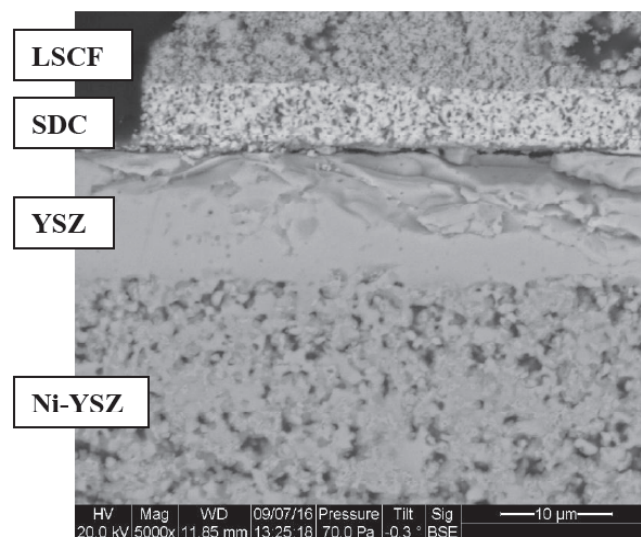
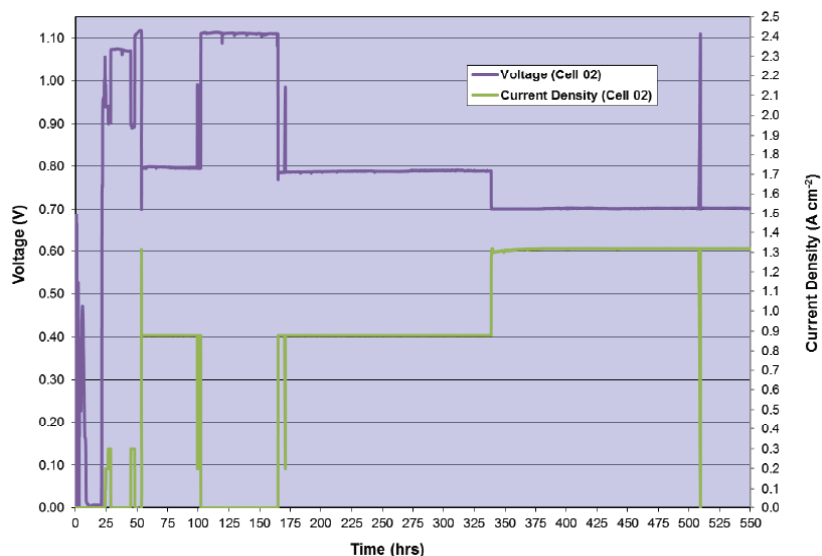
Element	Expected Atomic%	LSCF from FCM		Homemade LSCF		Homemade LSCF (HR-TEM)	
		Atomic%	Error%	Atomic%	Error%	Atomic%	Error%
O K	60.61	64.26	6.03	55.83	7.9	59.54	1.8
Fe K	16.15	14.21	11.96	18.77	16.3	16.82	4.2
Co K	4.04	3.60	10.86	4.64	14.8	4.07	0.7
Sr L	7.67	6.96	9.29	6.93	9.6	6.65	13.3
La L	11.52	10.97	4.77	13.83	20.1	12.88	11.9

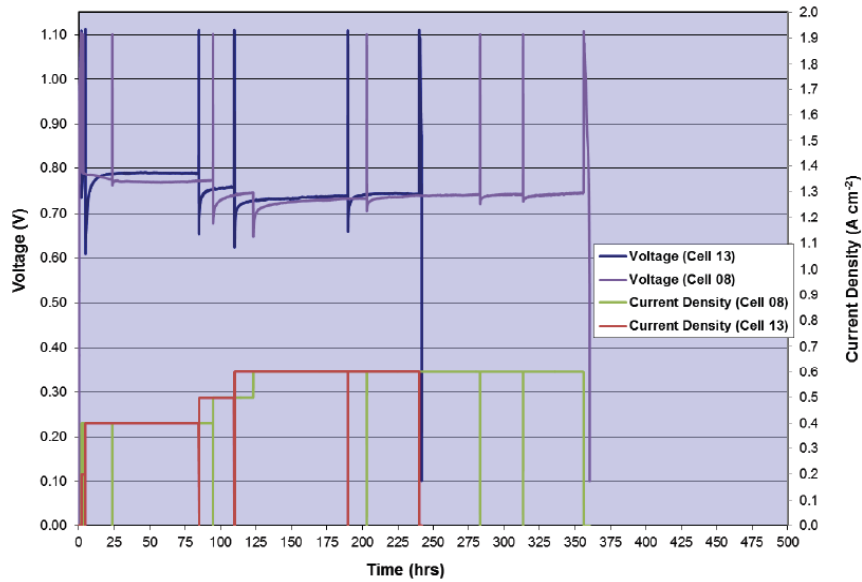
**Table 2: Pull Test Study Results at Different Firing Temperatures and Times for LSCF Inks**

Sample ID	Firing Temp. (°C)	Firing Time (hr)	Scotch Tape Test	Residue on Tape
PT1	850	2	Pass	Heavy
PT2	900	2	Fail	Heavy
PT3	950	2	Pass	No
PT4	1000	2	Pass	No
PT5	1050	2	Pass	No
PT6	1100	2	Pass	No
PT7	850	4	Pass	Light
PT8	850	6	Pass	Light

influences the residue found on the tape, but still some can be observed though much lighter. The results of this test indicate the adhesion to the electrolyte maybe problematic especially when an SOFC is subjected to thermal cycles.

To establish a performance baseline, a commercial SOFC cell that comprises of Ni-YSZ/YSZ/SDC/LSCF, labeled Cell 02, was first tested at 750°C. The test results for this cell are shown in Figure 4. From the figure, it can be observed that the cell voltage is stable over the tested period of more than 500 hours. The various voltage or current spikes are simply loading and unloading cycles. The cell performance is quite good with a final operating condition of 0.7 V at 1.3 A/cm<sup>2</sup>. The SEM cross section of this cell can be seen in Figure 5. Visible is the ceria barrier layer that is generally used to prevent un-wanted reaction with the LSCF and the electrolyte.

**Figure 5:** Cross section SEM picture of Cell 02.**Figure 4:** Lifetime performance for Cell 02.

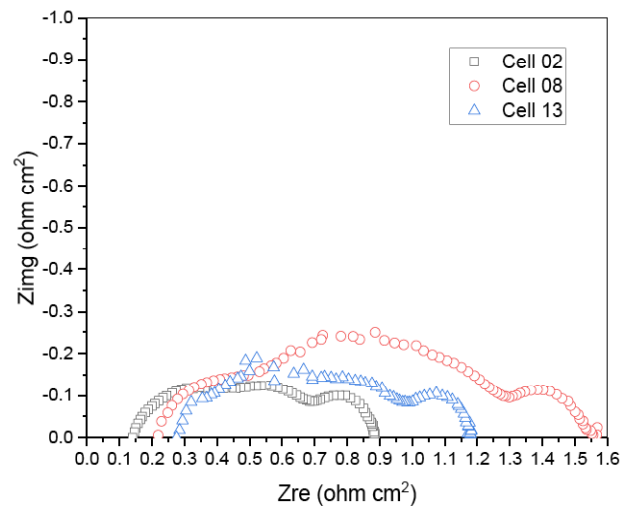


**Figure 6:** Lifetime performance for Cell 08 and Cell 13.

Two additional button cell tests were performed where no ceria barrier layer was used. The cell tests are labeled as Cell 08 with Ni-YSZ/YSZ/LSCF (from FCM) and Cell 13 with Ni-YSZ/YSZ/LSCF (homemade). The cathode was fired at 850°C for 2 hours to prevent the unwanted insulating phases in the LSCF/YSZ interface. Since the low firing temperature results in a less robust cathode adhesion to the electrolyte, the current collector was fired in-situ with the cell testing rig which prevented or delayed the thermal cycle. Figure 6 compares the lifetime performance of Cell 08 and Cell 13 tested at 750°C. The two different inks have similar performance, but the homemade LSCF powder has slightly better power density and better initial voltage stability. Both cells have good voltage stability when tested for relatively long term. Again, the various voltage or current spikes are simply loading and unloading cycles. It is very unlikely that an insulating phase of SrZrO<sub>3</sub> is being produced over time otherwise a steady drop in voltage should be observed. Cell 08 shows this behavior at the very beginning of the test but ends very quickly. Upon cooling down of Cell 08 it was found that the cathode delaminated because of the incurred thermal cycle. Cell 13 with the homemade cathode showed better adhesion upon cool down and did not result in delamination. However, a simple pull test removed the cathode reasonably easily. The observed difference could be explained in two ways. First, the homemade cathode probably has better sintering properties. Second, the in-situ firing of the cathode requires a

contact force which may have varied from one test to another.

The impedance spectroscopy data for all cells are shown in Figure 7. From the figure, the ohmic resistance (high frequency intercept), total polarization (low frequency intercept) are read for each cell and reported in Table 3. Also reported in Table 3 is the electrode polarization which is the distance from the high to the low resistance intercept [13]. Cell 02 has the lowest ohmic resistance of the three cells which indicates a properly sintering cathode. Cell 13 has a lower electrode polarization than Cell 08 but larger than Cell 02. The impedance data indicate that the cathode properties are not the same when fired at 850°C and leads to higher ohmic and electrode resistances.



**Figure 7:** Impedance data for Cell 08 and Cell 13.

**Table 3: Comparison of Ohmic, Electrode, and Total Polarization for Different Cells**

ID	Ohmic (ohms/cm <sup>2</sup> )	Total (ohms/cm <sup>2</sup> )	Electrode (ohms/cm <sup>2</sup> )
Cell 02	0.141	0.884	0.743
Cell 08	0.222	1.557	1.335
Cell 13	0.284	1.179	0.895

The SEM pictures for Cell 08 and Cell 13 are shown in Figure 8. Note that no ceria layer is present. For both cells, the cathode has a different morphology than the cathode seen in Cell 02. Indeed, this difference results from the low firing temperature and shows a higher porosity but less interconnection within the cathode particles. The SEM pictures indicate that additional work is required to improve the cathode sintering properties so that a more uniform structure can be formed. A better adhesion with the electrolyte is also required for better tolerate thermal cycles.

## CONCLUSIONS

LSCF nanopowders were prepared using a nitrate-glycine process whose particle size was estimated to be 28.8 nm. A sintering study and pull test determined that the quality of LSCF adhesion to the YSZ electrolyte is poor. However, button cell testing data indicate that the performance is stable over relatively long-term tests. The cell performance is not up to par to *state-of-the-art* LSCF cells but the stable performance is promising. Impedance data indicate that the reason for lower performance is due to higher cathode

polarization. Further studies should concentrate on improving the cathode sinterability properties as this approach has the potential of reducing fabrication costs.

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## NOMENCLATURE

LSCF: lanthanum strontium cobalt ferrite

SOFCs: solid oxide fuel cells

Ni: nickel

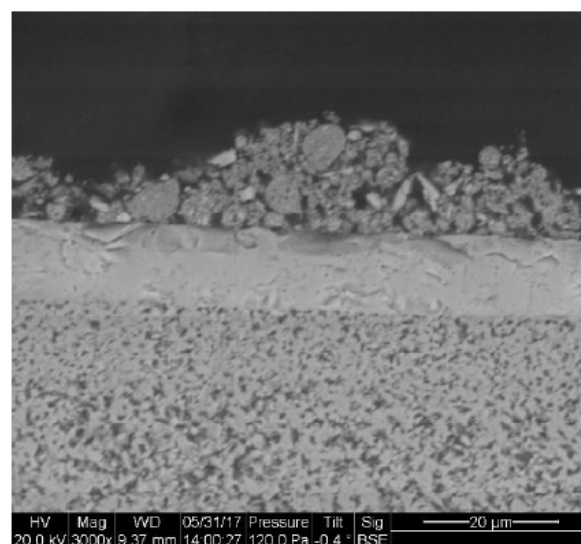
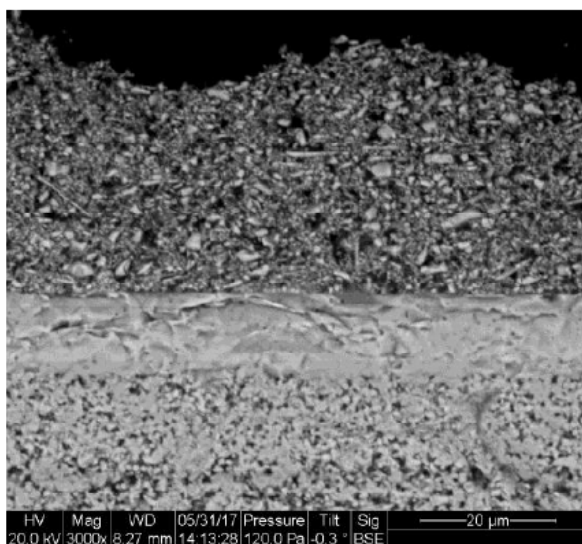
YSZ: yttria stabilized zirconia

SDC: samaria doped zirconia

SrZrO<sub>3</sub>: strontium zirconate

Sm: samarium

Gd: gadolinium



**Figure 8:** Cross section SEM picture of Cell 08 and Cell 13.

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