

MATERIAL AND PROCESS DEVELOPMENT LEADING TO ECONOMICAL HIGH-PERFORMANCE THIN-FILM SOLID OXIDE FUEL CELLS

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ABSTRACT

This document summarizes the technical progress from September 2002 to March 2003 for the program, Material and Process Development Leading to Economical High-Performance Thin-Film Solid Oxide Fuel Cells, contract number DE-AC26-00NT40711. The causes have been identified for the unstable open circuit voltage (OCV) and low performance exhibited by the anode-supported lanthanum gallate based cells from the earlier development. Promising results have been obtained in the area of synthesis of electrolyte and cathode powders, which showed excellent sintering and densification at low temperatures. The fabrication of cells using tape-calandering process for anode-supported thin lanthanum gallate electrolyte cells and their performance optimization is in progress

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1 INTRODUCTION

This document summarizes the technical progress from September 2002 to March 2003 for the program, Material and Process Development Leading to Economical High-Performance Thin-Film Solid Oxide Fuel Cells, contract number DE-AC26-00NT40711. The document includes program technical background and discusses technical progress.

The program goal is to advance materials and processes that can be used to produce economical, high-performance solid oxide fuel cells (SOFC). The overall objective is to demonstrate an SOFC cell that is capable of achieving extraordinary high power densities at reduced temperatures (with the goal of $1\text{W}/\text{cm}^2$ at 600°C). An integrated approach to develop a high-performance, reduced-temperature SOFC is based on the development of materials and structures that result in superior electrolyte and electrode properties. These properties, when combined, are capable of increased performance in the 550° to 800°C temperature ranges while maintaining function integrity up to 1000°C for short periods. The materials and fabrication processes are economical, scalable, and amenable to high-volume manufacture of fuel cells. This proposed approach is consistent with Department of Energy (DOE)/National Energy Technology Laboratory (NETL) Vision of Fuel Cells for the 21st Century.

The cell package is based on a thin-film multilayer electrolyte supported on an anode substrate combined with a multilayer multifunctional cathode to achieve the performance goal of $0.25\text{ ohm}\cdot\text{cm}^2$ area-specific resistance (ASR) at 600°C . Thin-film electrolytes with high ionic conductivity at low temperatures are used to minimize ohmic losses. The predominant performance losses in SOFCs with thin-film electrolytes have been observed from the cathode. To achieve the cell performance goal, it is estimated that the cathode ASR is required to be less than $0.18\text{ ohm}\cdot\text{cm}^2$ at 600°C . However, it is possible to achieve such a cathode using advanced cathode materials, catalytic activity enhancement for oxygen reduction reaction, and engineered electrode structures.

The ability to fabricate multilayer structures is an important element in the development of a fuel cell with high performance at lower temperatures. The tape-calendering process is well suited to the fabrication of multilayer composites discussed above and studies have shown tape calendering as a reliable and potentially the most economical among known processes for fabricating supported thin-film solid oxide electrolytes. As reported in the previous report [1], we have demonstrated fabrication of an anode-supported thin-LSGMF-electrolyte solid oxide fuel cell, which incorporated $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ -based cathode. Promising results were obtained for anode supported thin-LSGMF-electrolyte cells based on high conductive electrolyte, high performance cathode materials, and fabricated by tape calendering manufacturing process. However, with LSGMF electrolyte, $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ cathode and Ni/ceria anode, the endurance test showed that the cell voltage slowly decayed with time under a nominal load. Also, the cell OCV was low and gradually decayed with time.

2 EXPERIMENTAL

2.1 CELL FABRICATION

The tape calendering process has been modified for fabricating $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Fe}_{0.05}\text{O}_3$ (LSGMF)-based cells. In this process, the electrolyte (LSGMF) and support anode (NiO/ceria) materials are mixed with organic binders and plasticizer in a high-shear mixer. The heat generated by the mixing process softens the organics and forms a homogeneous plastic mass. Each plastic mass (electrolyte and electrode) is then rolled to produce a flexible sheet. Self-supported LSGMF tape is then sized and fired. For anode-supported thin LSGMF electrolyte fabrication, the electrolyte (LSGMF) and the support electrode tapes are laminated together to form a bilayer tape and subsequently rolled to reduce thickness of each layer. Another electrode tape is added to the bilayer tape and again rolled to a thin tape. Such a process is repeated until the desired thickness of electrolyte is reached. At this point, the bilayer tape is cut to the desired shape and size and then fired at elevated temperatures to remove the organics and sinter the ceramics.

For self-support LSGMF-based cells, $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ and $\text{NiO/Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ were applied on two electrolyte surfaces as cathode and anode, respectively. For anode-supported thin-LSGMF-electrolyte cells, cathode $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3/\text{LSGMF}$ was applied on the electrolyte surface to produce a complete cell. The electrode firing temperature was 1000-1100°C.

2.2 CELL AND MATERIALS ANALYSIS

Cell microstructure and composition were analyzed with Scanning Electron Microscopy (SEM) and Auger spectroscopy. Powder morphology was characterized with SEM and BET surface analyzer. Power composition and structure were characterized with X-ray diffractometry (XRD).

3 RESULT AND DISCUSSION

3.1 PROGRESS HIGHLIGHTS

During this reporting period, work has been focused on analysis and identification of issues related with the observed low OCV and performance degradation of thin-electrolyte anode supported cells and development of superior materials for cell fabrication. Key progresses have been made:

- Detail microscopic and chemical analyses of the cells fabricated have been performed. These samples were prepared using commercially available coarse powders.
- The cause for unstable open circuit voltage and poor performance has been identified. It was concluded that poor sintering characteristics of the coarse LSGMF powder led to inadequate densification of the electrolyte layers. The poor cell performance was believed to be caused by gas leakage through thin electrolyte layers, possible contamination of Ni through the interlayer at the anode side, and non-optimized electrode structures.

- Several attempts were made to prepare electrolyte powders with appropriate sintering properties in parallel to the efforts searching for vendors to supply the electrolyte materials with desired properties. Powders synthesized using a reactive milling process have achieved superior densities at lower temperatures.
- A number of candidate cathode materials have been obtained through outside vendors as well as in-house modification and synthesis. Progress has also been made in establishing suitable rheological properties of the cathode inks that will result in appropriate microstructures and superior cell performance. Cathode performance evaluations are in progress.

3.2 CELL COMPONENT ANALYSIS

Structural and chemical analyses of the cells fabricated/tested during the previous reporting period were performed using Scanning Electron Microscopy (SEM) and Auger spectroscopy. These cells were fabricated using a vendor supplied LSGMF electrolyte (Praxair, Inc.) and $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ (SSC) cathode powders (Nextech). The surface areas of these powders were quite low, $0.5\sim 0.6 \text{ m}^2/\text{g}$. We were able to make relatively dense LSGMF electrolyte in the temperature range of $1450\text{-}1500^\circ\text{C}$. $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3$ cathode was applied on the electrolyte surface by screen printing and fired at $1000\text{-}1100^\circ\text{C}$ to produce a complete cell. In order to avoid chemical interaction between LSGMF electrolyte and NiO in the anode support, a thin buffer layer of ceria at the anode/electrolyte interface was also introduced. The sketch of the anode-supported structure is shown in Figure 1.

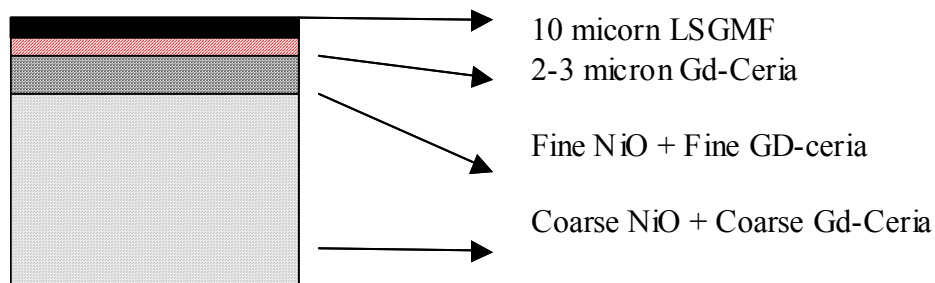


Figure 1. Schematic of the thin-LSGMF bilayers fabricated.

Analysis of the cell microstructure is shown in Figure 2. As seen in the micrographs, the electrolyte layer contains large grain size combined with porosity. In the cathode, large SSC particle was also evident. The chemical analysis of the cell assembly was performed using SEM backscatter images as well as Auger spectroscopy (Figure 3). Surprisingly, a considerable amount of Ni was found in the LSGMF electrolyte even though a ceria interlayer was implemented between the LSGMF electrolyte and Ni-ceria anode. It is possible that Ni migration occurred during the sintering at 1450°C and poor sintering characteristics of the starting electrolyte powder with large particle size ($d_{50} \sim 4 \mu\text{m}$, $\text{SA} \sim 0.58 \text{ m}^2/\text{g}$). It is likely that main cause of the poor OCV exhibited by these cells and sharp degradation in the power leading to infantile failures are related to gas cross-over caused by poor density of the electrolyte layer.

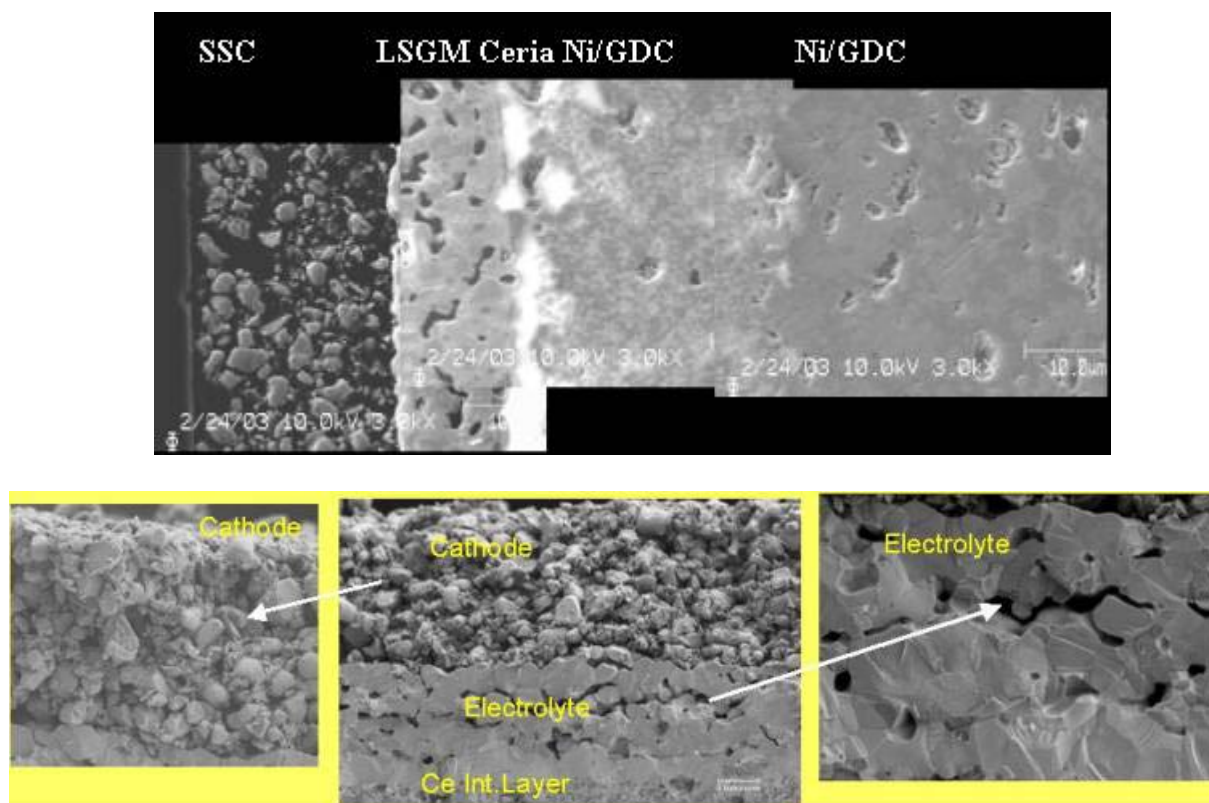


Figure 2 SEM examinations on the cell showing low OCV under hydrogen

Analysis of the cell microstructure is shown in Figure 2. As seen in the micrographs, the electrolyte layer contains large grain size combined with porosity. In the cathode, large SSC particle was also evident. The chemical analysis of the cell assembly was performed using SEM backscatter images as well as Auger spectroscopy (Figure 3). Surprisingly, a considerable amount of Ni was found in the LSGMF electrolyte even though a ceria interlayer was implemented between the LSGMF electrolyte and Ni-ceria anode. It is possible that Ni migration occurred during the sintering at 1450°C and poor sintering characteristics of the starting electrolyte powder with large particle size ($d_{50} \sim 4 \mu\text{m}$, $SA \sim 0.58 \text{ m}^2/\text{g}$). It is likely that main cause of the poor OCV exhibited by these cells and sharp degradation in the power leading to infantile failures are related to gas cross-over caused by poor density of the electrolyte layer.

Based on these results a plan was devised to

- Specify LSGMF electrolyte material characteristics and find a vendor(s) to supply the materials
- Explore in-house synthesis/modification of electrolyte powder, which may have superior sintering characteristics, achieving high densities at lower temperatures

Two important benefits were envisioned for a high surface area electrolyte powder; a) higher density leading to superior performance, and b) low firing temperature leading to less interdiffusion related problems.

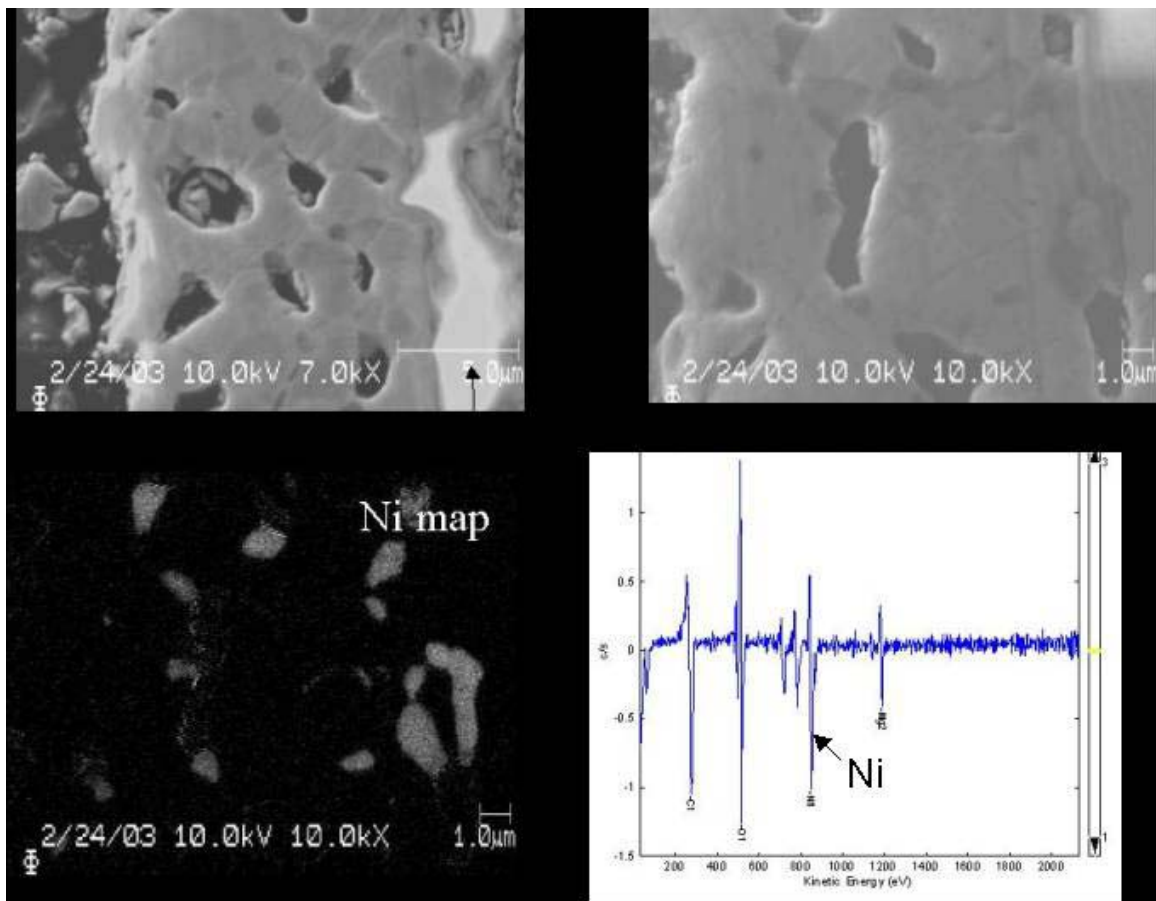


Figure 3 Analysis showing presence of Ni in the electrolyte

3.3 LSGMF ELECTROLYTE ENGINEERING

In order to achieve low temperature densification of the electrolyte layer, attempts were made to prepare/modify LSGMF electrolyte powders with high surface area and superior morphologies. Four alternatives were considered:

- 1) size reduction of the vendor (Praxair) powder via ball milling,
- 2) preparing powders from solid-state reaction,
- 3) reactive milling to form fine powder via low temperature calcining of the metal oxalates, and
- 4) different vendors to meet the specifications

While searching for right vendors to meet the requirements, powders modification and preparation are in progress. The microstructures of the different types of powders and sinterability of these powders are shown in Figure 4. As seen in the Figure, the as-received vendor powder and powder synthesized using solid-state reacted powders do have large sintered aggregates of about 4-5 μm. These powders were ball milled to break the aggregates and reduce the size to ~ 1 –2 microns. However, the size distribution was found to be wide, combined with irregular morphology not suitable for processing, proper packing and densification at low

temperatures. On the other hand, the reactive milled powder was found to be spherical and typically submicron (0.3-0.5 μm) in size.

Lower sintering temperature and high densification were achieved with these powders as seen in the Figure 4. Please note that the high density was achieved at a much lower sintering temperature of 1250°C for the powders derived from reactive milling process. However, the phase analysis using XRD showed the presence of (~3%) of second phases; SrLaGaO_4 and $\text{SrLa}_3\text{GaO}_7$ in these powders, which tend to form at lower temperatures <1200°C. Similar results have been also seen in the sintered tapes at 1450°C from these powders. The coarser and milled powders reached > 96% density, while the reaction milled powder reached > 99% density.

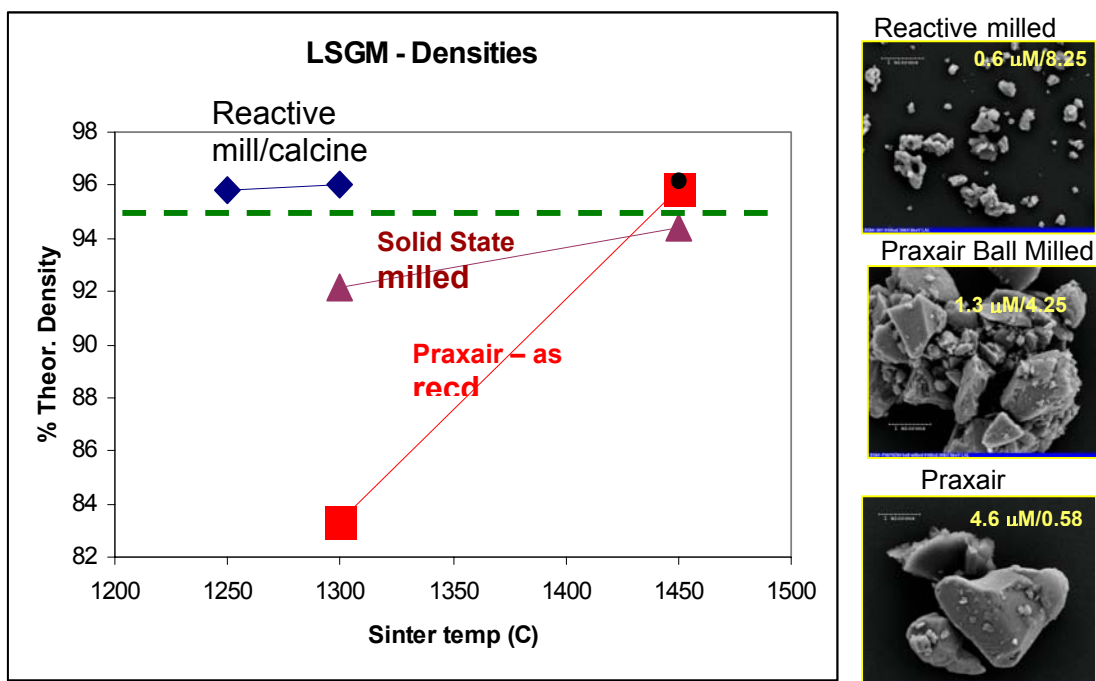


Figure 4 Sintering characteristics of different LSGM powders

3.4 CATHODE DEVELOPMENT:

Microscopic examination of tested cells revealed poor microstructure of the cathode layer also. As seen in Figure 2, the particle to particle bonding appears inadequate with clear lack of any neck formation between SSCo particles. In order to improve this, several of SSC-based cathode powders were prepared. Modifications of the samarium strontium cobaltite with substitutions on the A (Sm,Sr) with isovalent and size matching ions were also attempted, as listed in the Table below.

Sample I.D	Composition	Powder process
	3.4.1.1.1 Sm/La/Gd/Nd/Sr	
SSCO1	70/0/0/0/30	Oxalate milling
SSCO2	50/0/0/0/50	Oxalate milling
SSCO3	40/10/0/0/50	Oxalate milling
SSCO4	40/0/10/0/50	Oxalate milling
SSCO5	40/0/0/10/50	Oxalate milling
SSCO6	40/5/5/0/50	Oxalate milling
SSCO7	40/0/5/5/50	Oxalate milling
SSCO8	50/0/0/0/50	Solid state

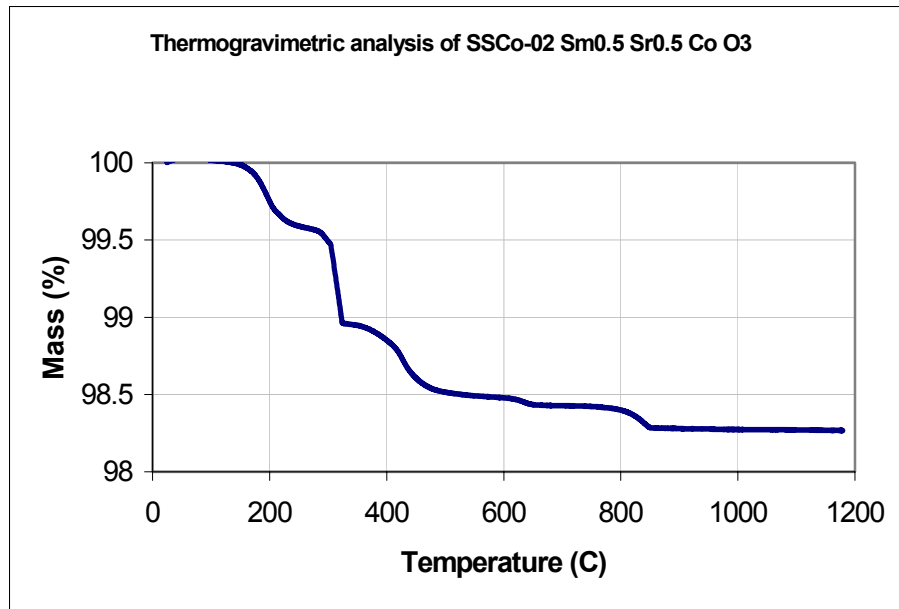


Figure 5 Thermo gravimetric analysis of SS Co-02

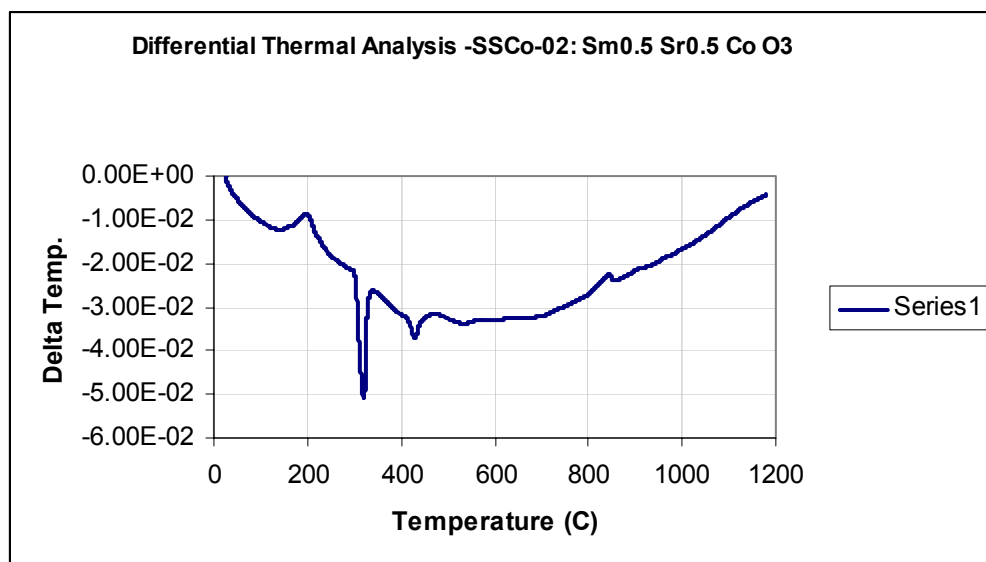


Figure 6. Differential Thermal analysis of SS-Co-02

These powders were synthesized using the reactive milling approach and were calcined at 900 °C for 3 hrs. Complete reaction was accomplished at such low temperatures as seen in the TGA and DTA traces (Fig 5 and Fig 6). The XRD analysis of the calcined powders showed single perovskites phase with varying degrees of crystallinity (Figure 7). Superior powder morphology and fine particle size, suitable for better cathodes microstructure is also clearly visible in the SEM (Figure 8). Selected powders are being made into cathode paste for performance evaluation.

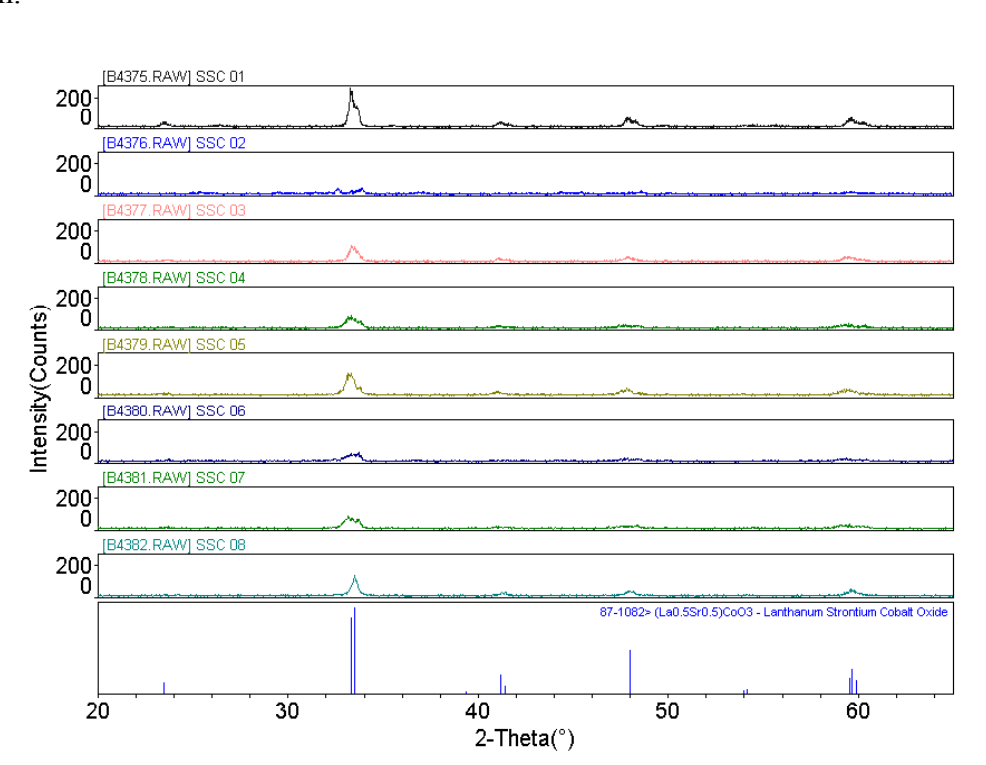


Figure 7 XRD of synthesized SSC-based cathode materials

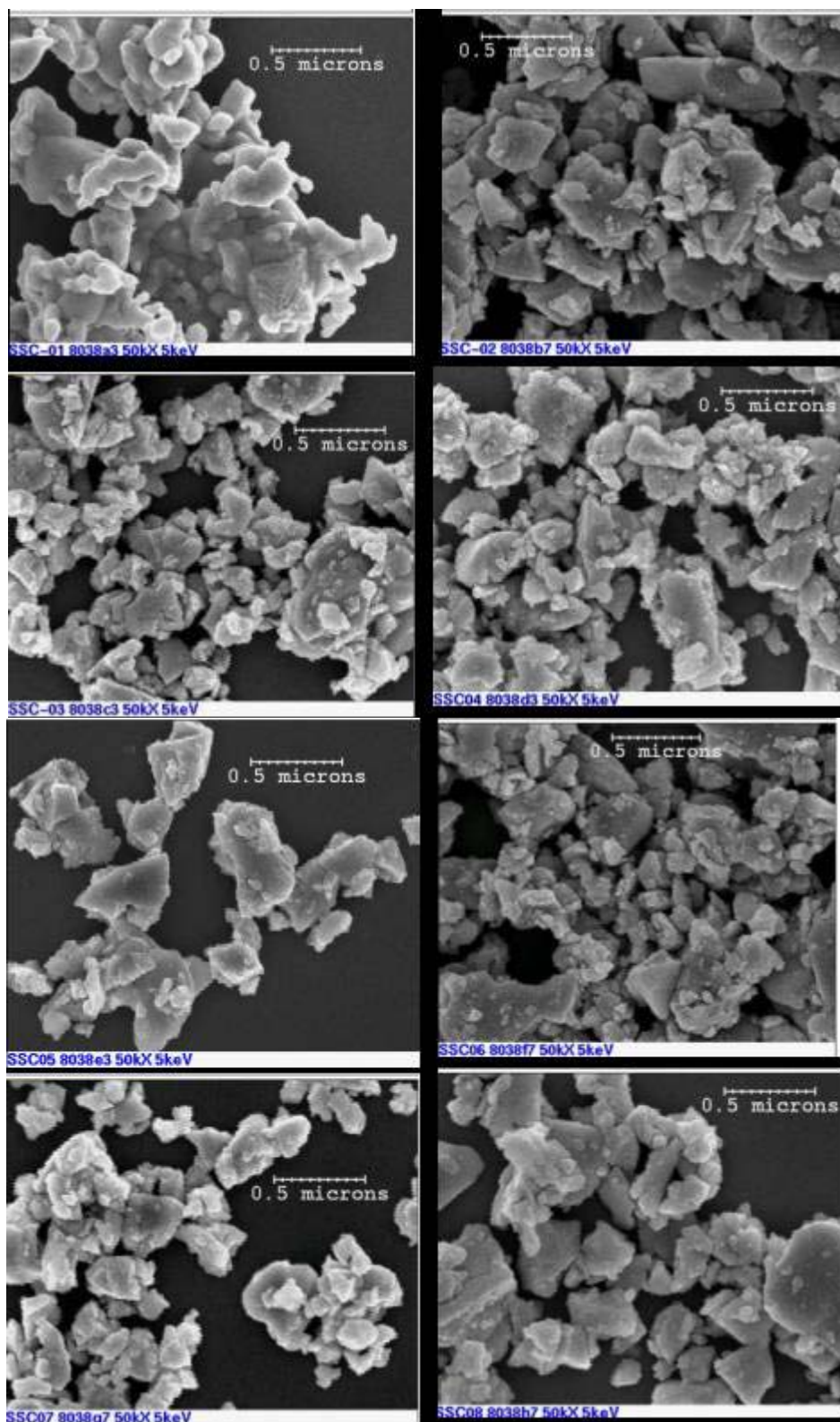


Figure 8 SEM examinations of synthesized SSC-based cathode materials

Several other promising cathode compositions including, $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_3$ and $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ were also been prepared and obtained from vendors. Paste formulation and evaluation with these cathode materials are in process.

3.5 FUTURE PLAN

Future work will be focused on the fabrication and evaluation of anode supported thin LSGMF electrolyte cells. Cell performance optimization will be accomplished through the microstructure development and fabrication process engineering with controlled powder compositions and desired characteristics.

4 CONCLUSION

The causes for the unstable OCV and low performance exhibited by the cells from the earlier development have been identified. Promising results have been obtained in the area of synthesis of electrolyte and cathode powders, which showed excellent sintering and densification at low temperatures. The fabrication of cells using tape calendering process for anode-supported thin LSGMF electrolyte cells and their performance optimization is in progress

5 REFERENCES

[1] J. Guan and N. Minh, "Material and process development leading to economical high-performance thin-film solid oxide fuel cells", Semi-Annual Report under contract DE-AC26-00NT40711, September 2002.