Thermal and Mechanical Properties of $LaCoO_3$

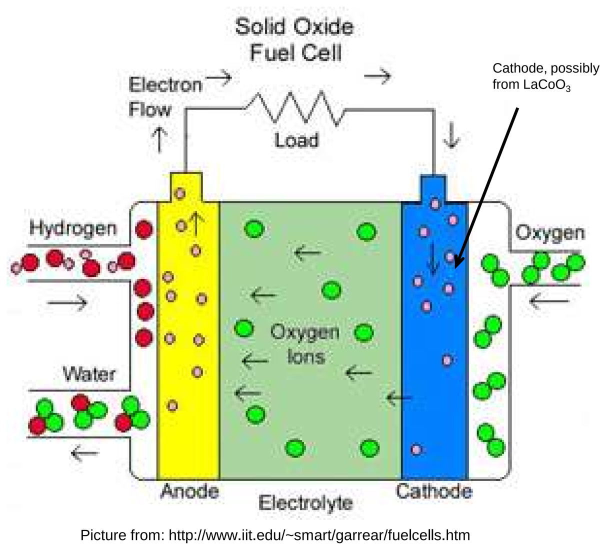
John Lloyd*, Laura Fegely*, Nina Orlovskaya*, Miladin Radovic#, Edgar Lara-Curzio#

*Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

#Metals and Ceramics, Oak Ridge National Lab, Oak Ridge, TN 38301

1. Introduction

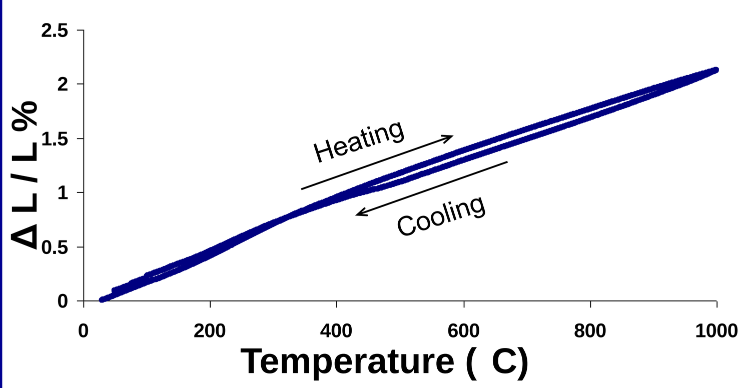
High ionic conductivity and electronic conductivities and excellent catalytic properties make $LaCoO_3$ potentially good cathode material for low temperature Solid Oxide Fuel Cells (SOFSs). However, $LaCoO_3$ should have thermo-mechanical properties close to those of electrolyte and anode materials to avoid generation of residual stresses and possible failure of multilayered SOFCs during processing and service. Also, as a good candidate material for SOFC $LaCoO_3$ should be stable in both, reducing and oxidizing environments.



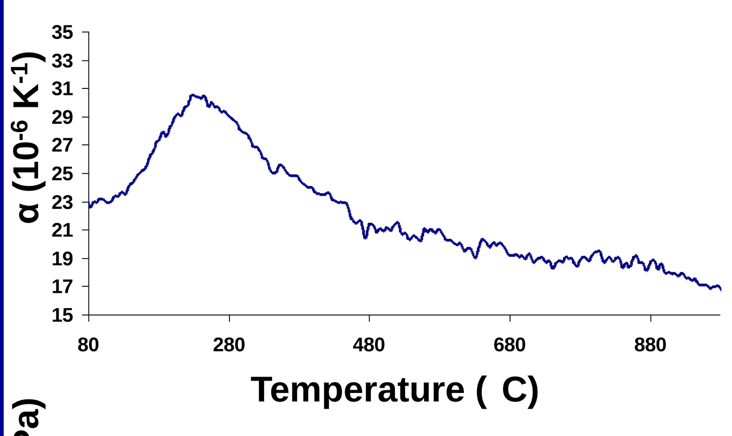
Picture from: http://www.iit.edu/~smart/garrear/fuelcells.htm

The goals of this work are to determine the thermal and mechanical properties, and the structural stability of $LaCoO_3$ in different environments.

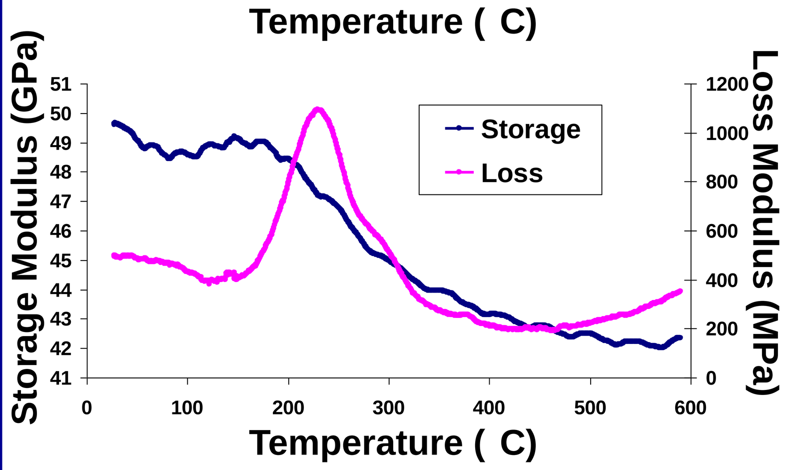
2. Properties in Air



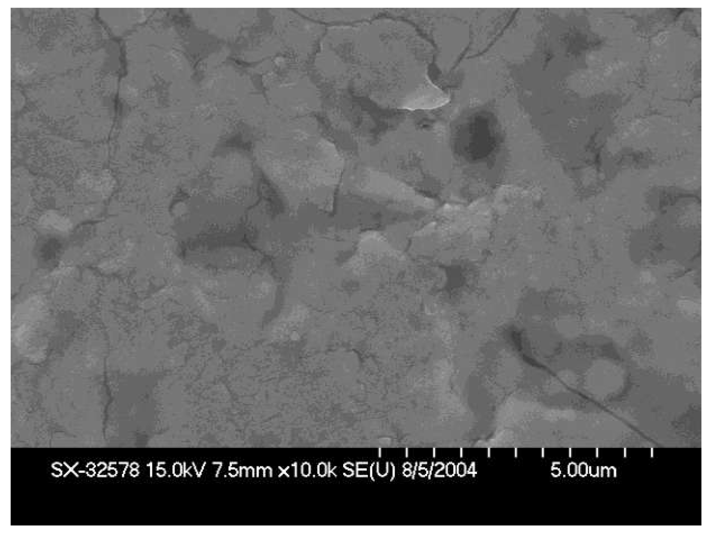
← Dimensional changes of $LaCoO_3$ during heating and cooling at the rate of 3 ºC/min determined by Thermo Mechanical Analyzer, TMA. The average coefficient of thermal expansion, α, was found to be 22×10^{-6} K^{-1} in ≈300-1000 ºC temperature range.



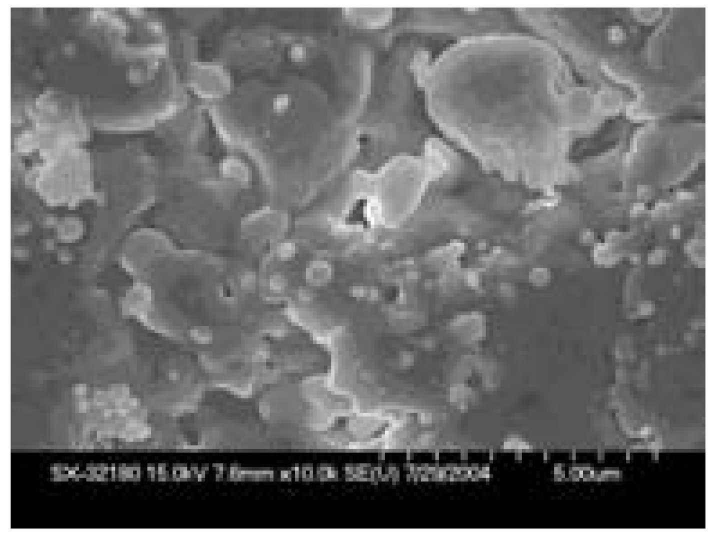
← The Coefficient of thermal expansion has a peak value of 31×10^{-6} K^{-1} at 230 ºC, which is believed to occur due to a spin state transition.



← The storage (Young's) and loss moduli were determined in air, in the 22-600 ºC temperature range using a Dynamic Mechanical Analyzer, DMA. The sample was tested in a single cantilever fixture at 1 Hz frequency with amplitude of 2 µm. High mechanical losses at about 230 ºC can be attributed to the spin state transition.



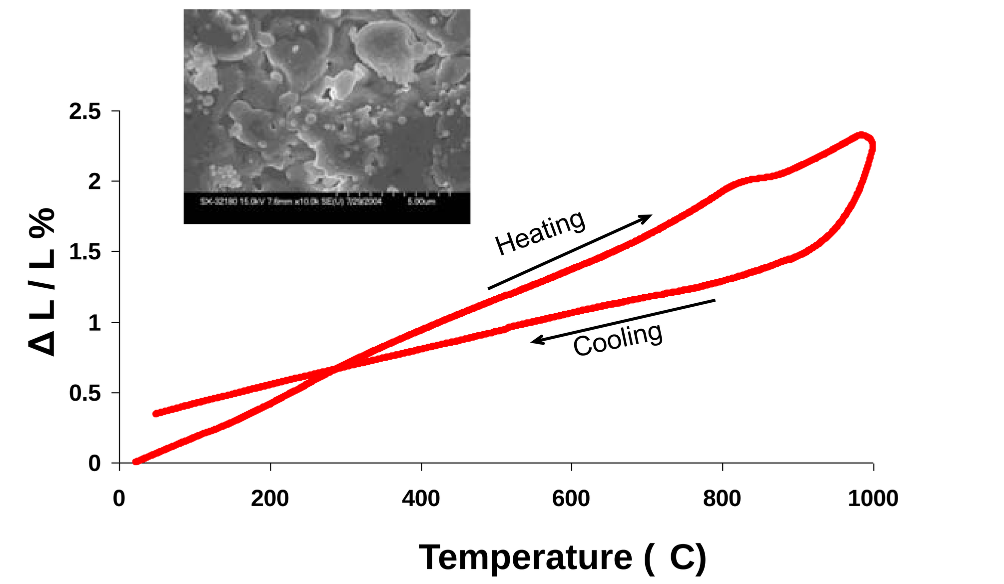
← Scanning Electron Microscopy, SEM image of $LaCoO_3$ surface after heating to 1000ºC in air. Notice the contrast in porosity between this sample and the sample tested under the same conditions in 4% H_2+96% Ar gas mixture (see below).

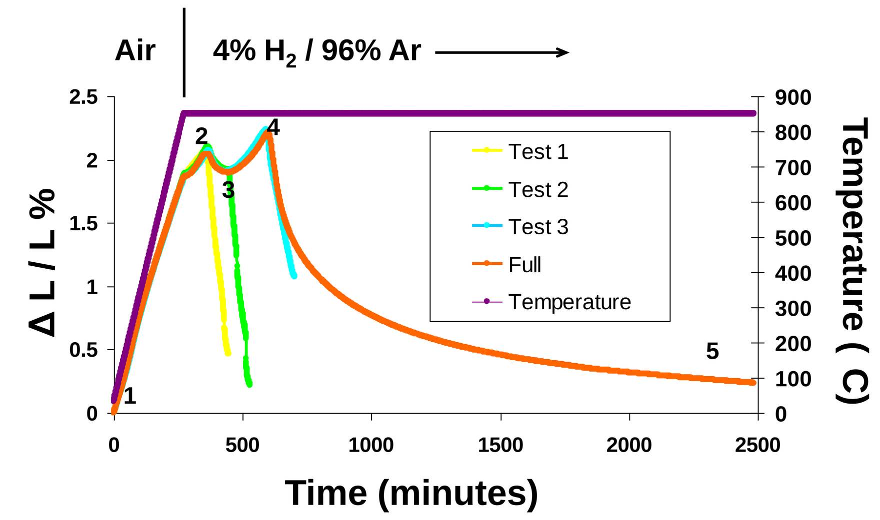


← SEM image of $LaCoO_3$ surface after heating to 1000ºC in 4% H_2+96% Ar gas mixture. The dramatic structural changes occurred during the reduction. The presence of Co_3O_4, CoO, and metallic cobalt has been confirmed using XRD. The EDS analysis clearly revealed the formation of Co rich and Co deficient phases.

3. Properties in 4% H_2 / 96% Ar

→ Dimension changes of $LaCoO_3$ during heating and cooling in 4%H_2+96%Ar gas mixture. The difference between heating and cooling curve indicate the structural changes in reducing environment. Most dramatic changes occur in 850-1000 ºC temperature range, suggesting that structural changes in reducing atmposphere occur in that temperature range. The inset SEM picture shows the porosity that developed during the test.

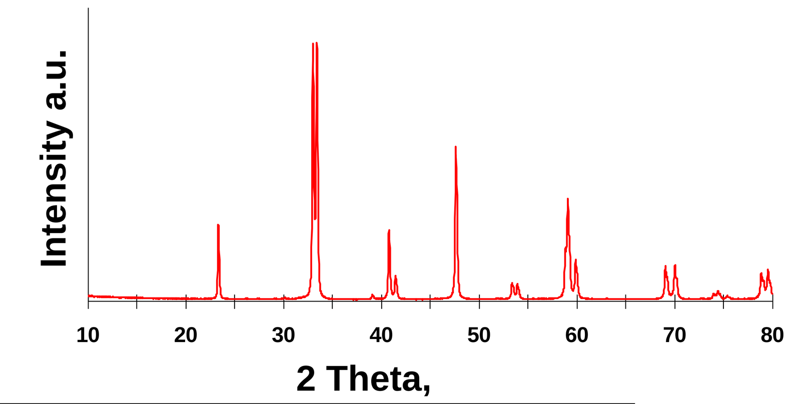




← To determine the composition of the sample during each phase of reduction, four samples were heated to 850 ºC in air. Each sample was then reduced in 4%H_2+96% Ar gas mixture at 850ºC for a different amount of time that correspond points labeled from 2-5 on the plot. After soaking, the samples were rapidly cooled to room temperature (10 C/minute) in the 4%H2+96% Ar gas mixture X-Ray Diffraction was then performed on each sample to determine its composition.

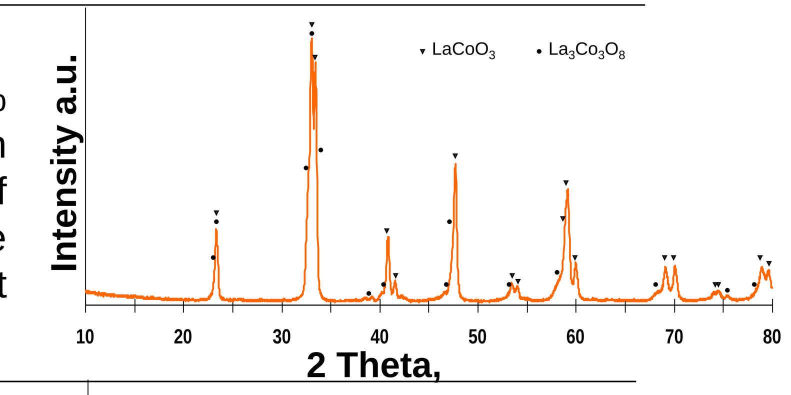
1) Sample before heating in H_2

→ $LaCoO_3$ control sample, heated to 1000 C in air. The peak around 33 2θ is a doublet. The rhombohedral symmetry (R3C space group) has been found for $LaCoO_3$ perovskite heated to 1000 C in air. This results are in good agreement with data published in literature.



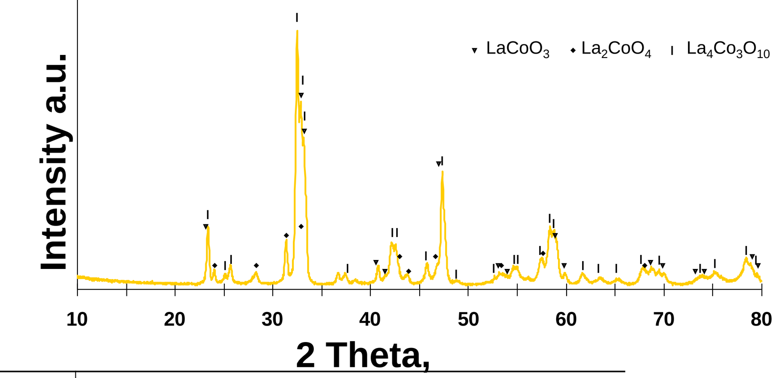
2) Sample after 88 minutes in H_2

→ $LaCoO_3$ heated to 850 C in air and soaked in 4%H_2+96% Ar for 88 minutes. An oxygen deficient form of $La_3Co_3O_8$, in addition to the original form, is identified. The removal of oxygen from the perovskite lattice and formation of the oxygen deficient phase resulted in the appearance of the first maximum on the expansion curve.



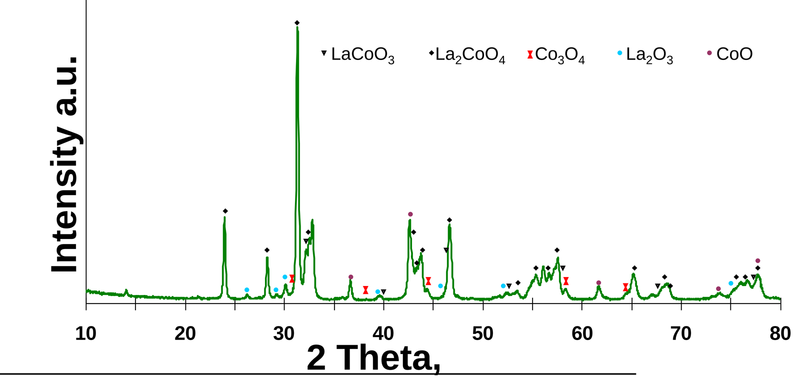
3) Sample after 172 minutes in H_2

→ $LaCoO_3$ heated to 850°C in air and soaked in 4%H_2+96% Ar for 172 minutes. The $LaCoO_3$ perovskite is still found, but $La_4Co_3O_{10}$ and La_2CoO_4 Co-deficient phases have been formed. This resulted in a significant shrinkage of the material and a formation of the minimum on the expansion curve.



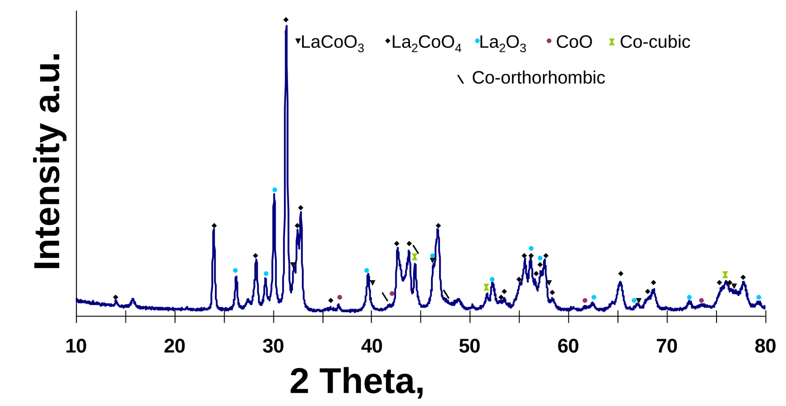
4) Sample after 325 minutes in H_2

→ $LaCoO_3$ heated to 850°C in air and soaked in 4%H_2+96% Ar for 325 minutes. Further reduction of the sample resulted in the formation of pure La_2O_3 and CoO oxides via a route $La_4Co_3O_{10}$ => $2La_2O_3$ + Co_3O_4 with Co_3O_4 being further reduced to CoO oxide.

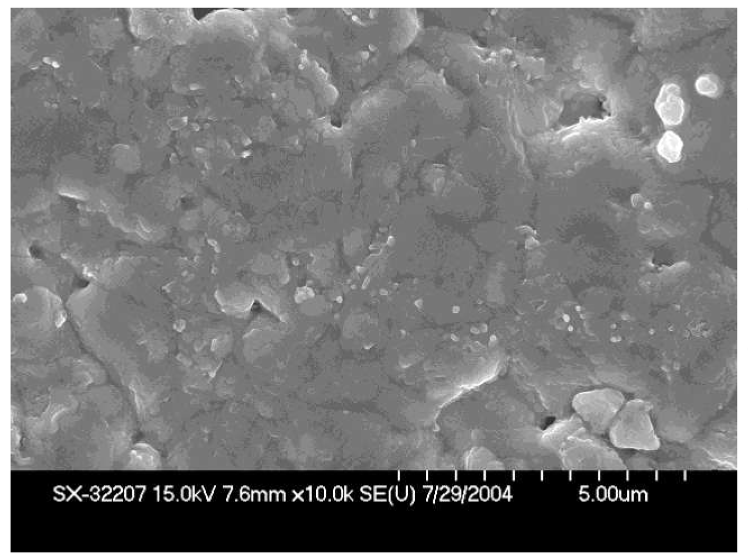


5) Sample after 2211 minutes in H_2

→ $LaCoO_3$ heated to 850°C in air and soaked in 4%H_2+96% Ar for 2211 minutes. $LaCoO_3$, La_2CoO_4, La_2O_3, and traces of CoO are identified. A mixture of two phases (cubic and hexagonal) metallic Co have been detected on the surface of the ceramic sample after 2211 minutes in 4% H_2 96% Ar.

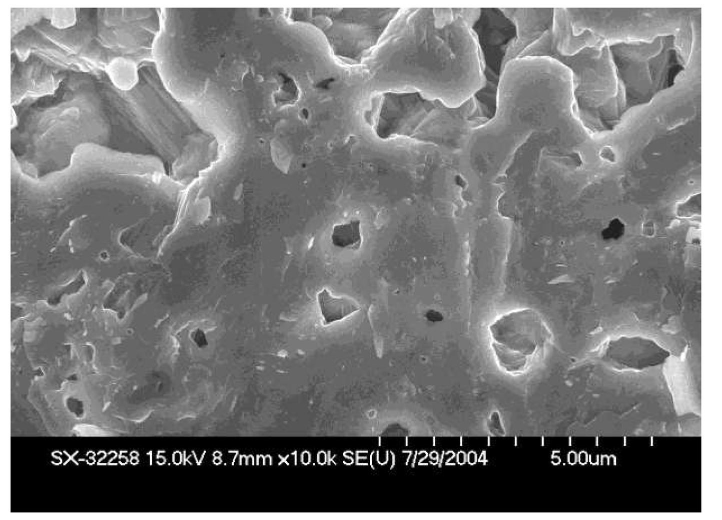


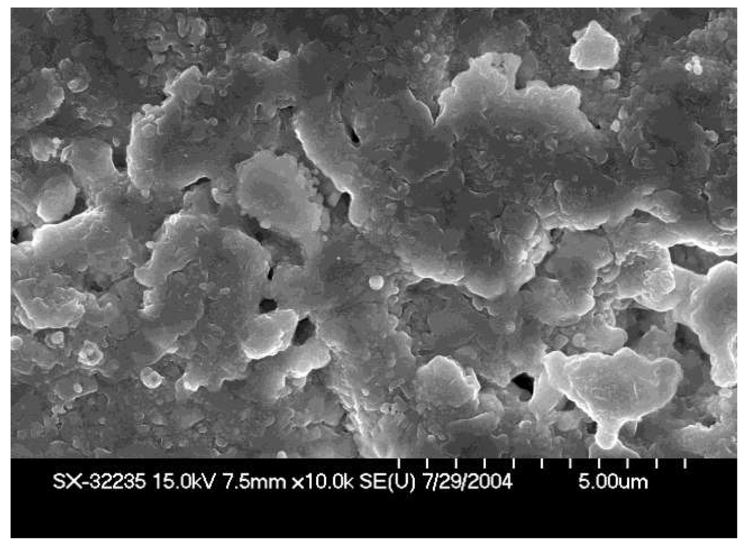
4. SEM of Samples in 4% H_2 / 96% Ar



← Microstructure of $LaCoO_3$ perovskite surface after soaking in 4%H_2 / 96%Ar for 88 minutes. The grain boundaries are revealed due to thermal etching at high temperature. The grain size was estimated to be in the range of 2-5 microns. This microstructure corresponds to point #2 on Δl/l vs. time plot.

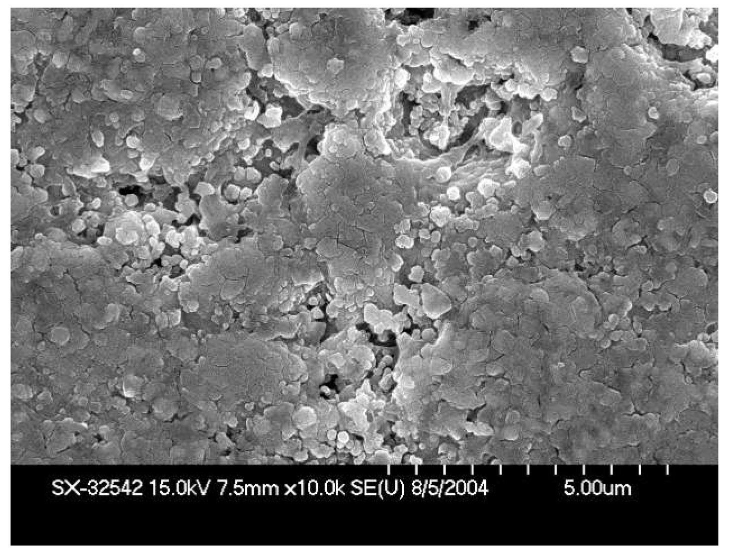
→ $LaCoO_3$ after soaking in 4%H_2+96%Ar for 172 minutes at 850ºC. Noticeable increase in porosity. This microstructure corresponds to point #3 (minimum) on Δl/l vs. time plot.





← As oxygen continues to diffuse from the center outward, the specimen becomes more porous. This microstructure corresponds to point #4 on the expansion plot.

→ After 2211 minutes, nearly 37 hours in a 4%H_2+96%Ar atmosphere the sample is very porous. This microstructure corresponds to point #5 on the expansion plot.



5. Conclusions

- A significant increase of the CTE and mechanical damping, along with a decrease in Young's modulus, occur in the 200-250 °C temperature range. This range corresponds to a spin state transition which occurs in pure $LaCoO_3$
- $LaCoO_3$ is not stable in a reducing atmosphere. It undergoes a series of expansions and contractions due to phase transitions beginning around 850 C. These expansions and contractions are seen to be directly related to the formation of $La_3Co_3O_8$, La_2CoO_4, $La_4Co_3O_{10}$, La_2O_3, CoO, and Co compounds due to the reducing atmosphere.
- Although $LaCoO_3$ is a good ionic and electric conductor, as well as having excellent catalytic properties, its high CTE of 22 x 10^{-6} K^{-1} is significantly higher than most materials used to make electrolytes and anodes. This difference may cause generation of residual stresses and eventually cracking of the multilayered SOFC.

6. Acknowledgements

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