Transient aging behavior of LSM in response to thermal gradients

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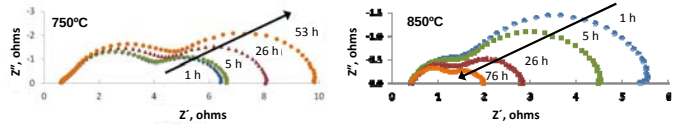
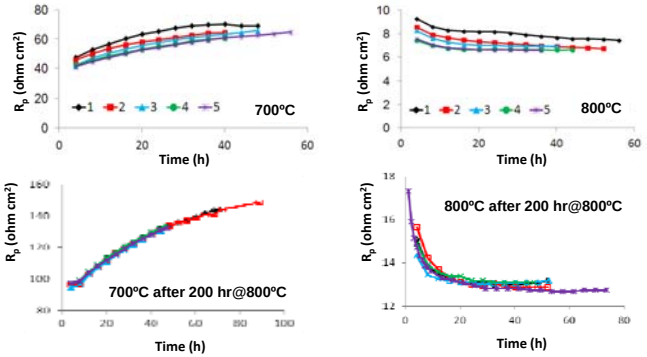
Overview

The polarization resistance of an $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ (LSM) SOFC cathode was found to age differently at 750°C compared to 850°C when held at open circuit.[1] At the lower temperature, the polarization resistance increases with time, while the resistance decreases with time at the higher temperature. To better isolate the cause of this behavior, symmetrical cells containing different combinations of porous cathodes (LSM or $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)) and electrolyte materials (GDC and YSZ) were thermally cycled between 700°C and 800°C and between 800°C and 850°C. The results indicate that the reversible, transient LSM aging behavior stems from a temperature-dependent reorganization of the electrode surface, which in turn effects the catalytic properties of that surface. Changes in the surface composition and microstructure of LSM **thin films** and **powders** due to temperature and atmospheric effects have been previously reported.[2-5] To better link the surface characterization of **thin films** with the electrochemical characterization of **porous electrodes**, commercial LSM powder (Fuel Cell Materials) was sintered into **dense pellets**. The pellet surfaces were examined using SEM, TEM, and XPS after aging the pellets at 700°C or 800°C.



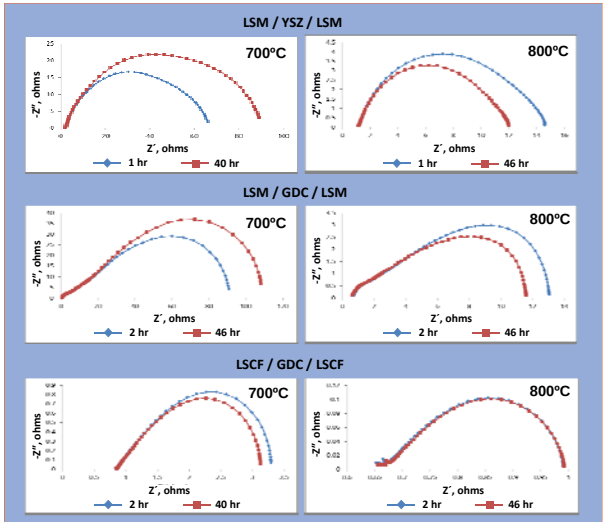
Impedance spectra of an **electrolyte-supported SOFC** with an **LSM/GDC** cathode, Hionic™ electrolyte, and Ni-YSZ anode aged at open circuit at 750°C or 850°C.



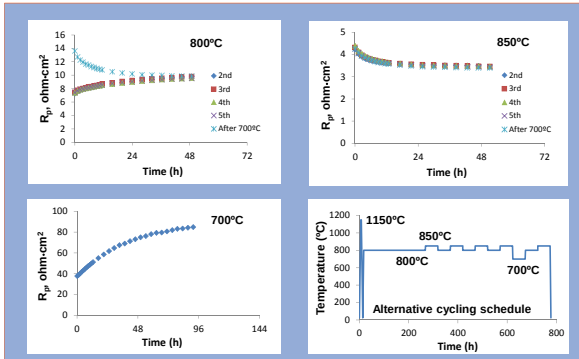
Change in the polarization resistance (R_p) of an **LSM/YSZ/LSM symmetrical cell** thermally cycled 5 times between 700°C and 800°C. Marker number indicates thermal cycle number. The reversible portion of the aging behavior can be isolated by annealing the sample at 800°C for 200 hrs before cycling between 700°C and 800°C.

References

1. H. Abernathy et al., **Journal of Power Sources**, 216:11-14 (2012).
2. J. W. Han et al, **ECS Transactions**, 35(1):2097-2104 (2011).
3. L.F.J. Piper et al., **Journal of the Electrochem. Soc.**, 158(2):B99-B105 (2011).
4. T.T. Fister et al., **Appl. Physics Letters**, 93:151904 (2008).
5. N. Caillol et al., **Appl. Surface Science**, 253:4641-4648 (2001).



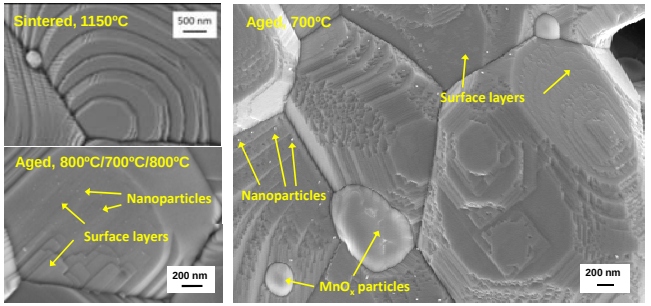
The nature of the aging mechanism was isolated by varying the character of the cathode/electrolyte and the cathode/air interface. The aging behavior of LSM is independent of electrolyte, ruling out specific interfacial phase formation such as zirconates. The behavior is also different from that of LSCF, indicating a reversible change in the thermodynamic state in LSM which does not occur similarly in LSCF in this temperature range.



Cycling between multiple temperatures reveals the aging behavior is not limited to the 700-800°C temperature range. The direction of the aging behavior is dictated by the relative step in temperature between 700°C and 850°C. The same equilibrium value of R_p for a given temperature is obtained whether stepping from a higher or a lower temperature, indicating the same final thermodynamic state in LSM.

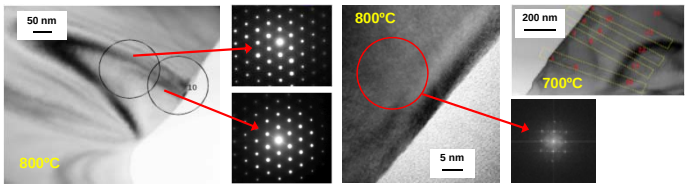
Dense LSM Pellet Studies

Pellets of LSM powder were sintered at 1150°C and cooled to room temperatures. Pellets were then annealed at 800°C for 200 hrs before being aged for 72 hrs at 700°C and then at 800°C. In situ X-ray diffraction studies revealed no bulk phase changes for pellets sintered at 1150°C and then aged at 700°C, 800°C, or 850°C.



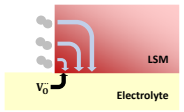
The as-sintered (and all subsequently fired) LSM pellets have manganese oxide particles on the surface, but clean terraces and edges on the LSM grains. Pellets aged in the 700°C to 800°C temperature range develop long planar growths on the terraces, as well as currently unidentified nanoparticles on the edges and terraces. Whether the nanoparticles reversibly form/decompose (or continue to grow) during thermal cycling is being currently examined.

TEM analysis of pellet **cross-sections** does not find any **prevalent** secondary phases forming or decomposing on the LSM surface during the thermal cycling. EDS analysis (20 nm beam size) does not reveal large changes in composition in the surface and subsurface layers between samples aged at 700°C or 800°C.



	Surface (~20 nm)		Subsurface (20-50 nm)	
Sample	(La+Sr): Mn	Sr:(La+Sr)	(La+Sr): Mn	Sr:(La+Sr)
72 hr 700ºC	1.00±0.02	0.15±0.01	0.95±0.05	0.18±0.01
72 hr 800ºC	1.03±0.08	0.10±0.02	0.97±0.06	0.15±0.01

Without conclusive evidence of reversible changes in chemical or phase composition in LSM between 700°C and 850°C, the transient behavior can instead be explained by changes in the intrinsic defect concentrations (e.g., Schottky) as the temperature changes. Slower cation diffusivities limit the speed at which the LSM can reach the equilibrium values. The change in the catalytic properties of the LSM associated with the creation/destruction of defects causes the observed changes in polarization resistance.



$$nil \rightleftharpoons 3V_O^{\cdot\cdot} + V_B^{'''} + V_A^{'''}$$

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