The influence of cation segregation on SOFC cathode aging behavior

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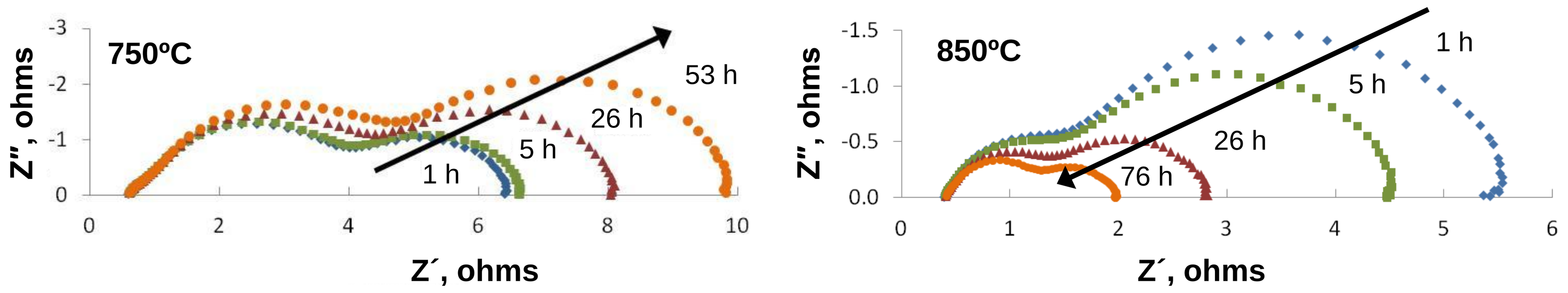
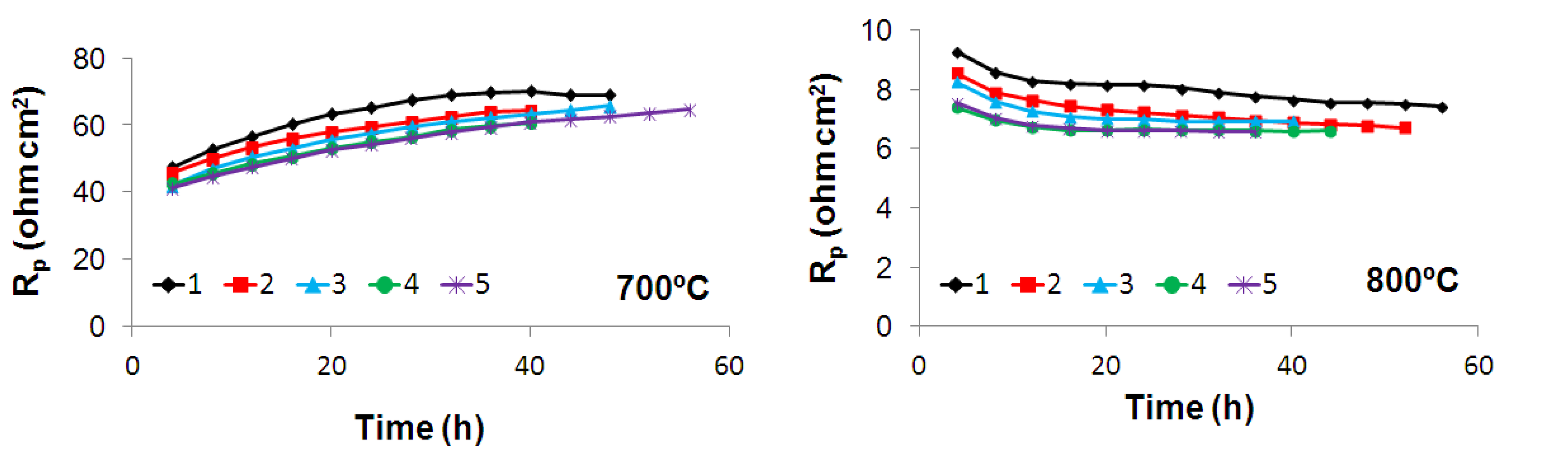
Overview

The polarization resistance of an $La_{0.8}Sr_{0.2}MnO_3$ (LSM) SOFC cathode has been found to age differently at 750ºC compared to 850ºC 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 700ºC and 800ºC. The results indicate that the reversible trend in 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 structure of LSM **thin films** 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 700ºC or 800ºC.



Impedance spectra of an electrolyte-supported SOFC with an LSM/GDC composite cathode aged at open circuit at 750ºC or 850ºC.



Change in the polarization resistance (R_p) of an LSM/YSZ/LSM symmetrical cell thermally cycled 5 times between 700ºC and 800ºC. Marker number indicates thermal cycle number.

References

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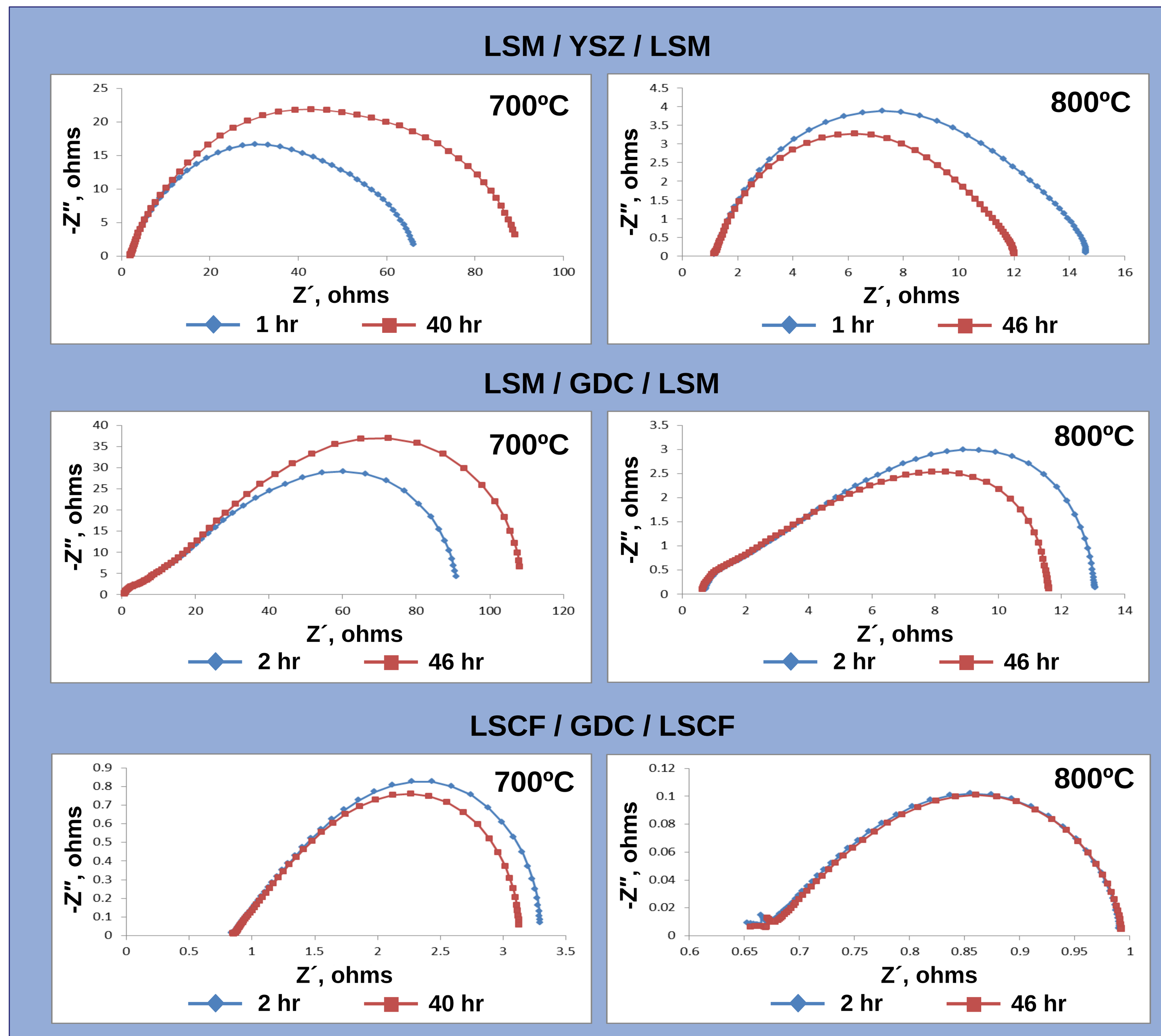
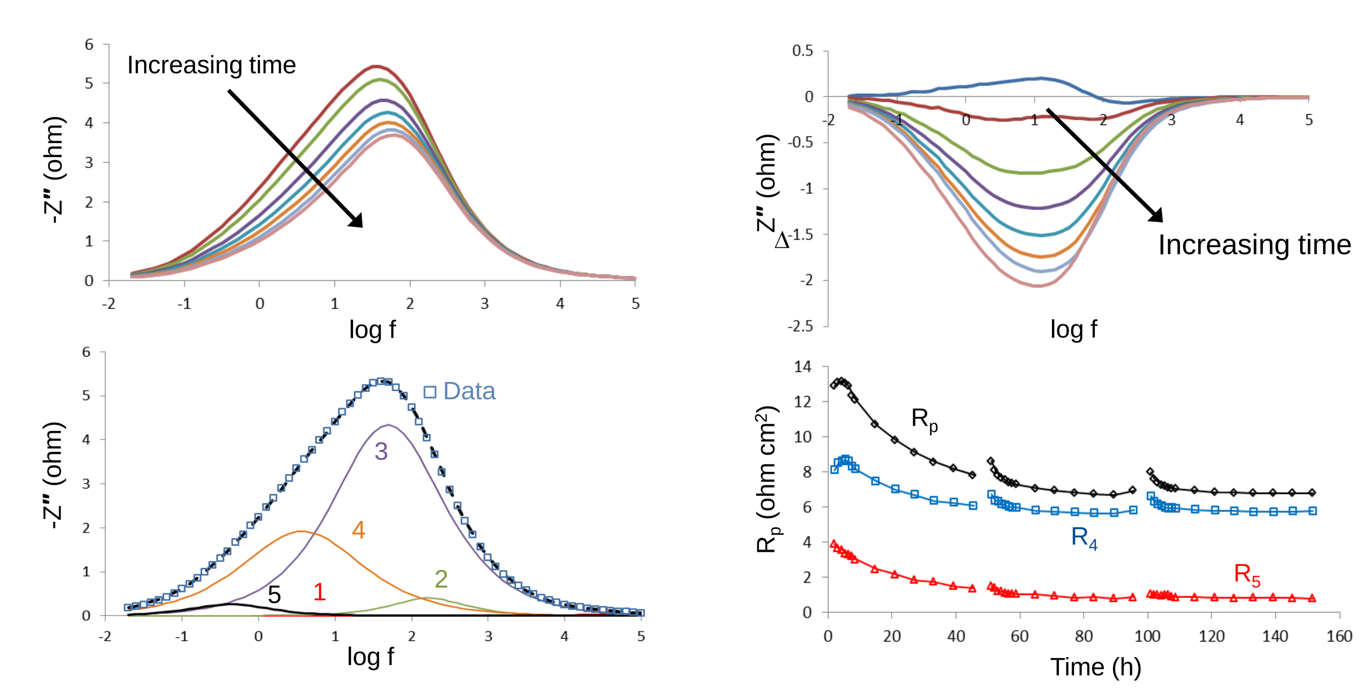
3. L.F.J. Piper et al., **Journal of the Electrochem. Soc.**, 158(2):B99-B105 (2011).
4. T.T. Fister et al., **Appl. Physics Letters**, 93:151904 (2008).
5. N. Caillol et al., **Appl. Surface Science**, 253:4641-4648 (2001).



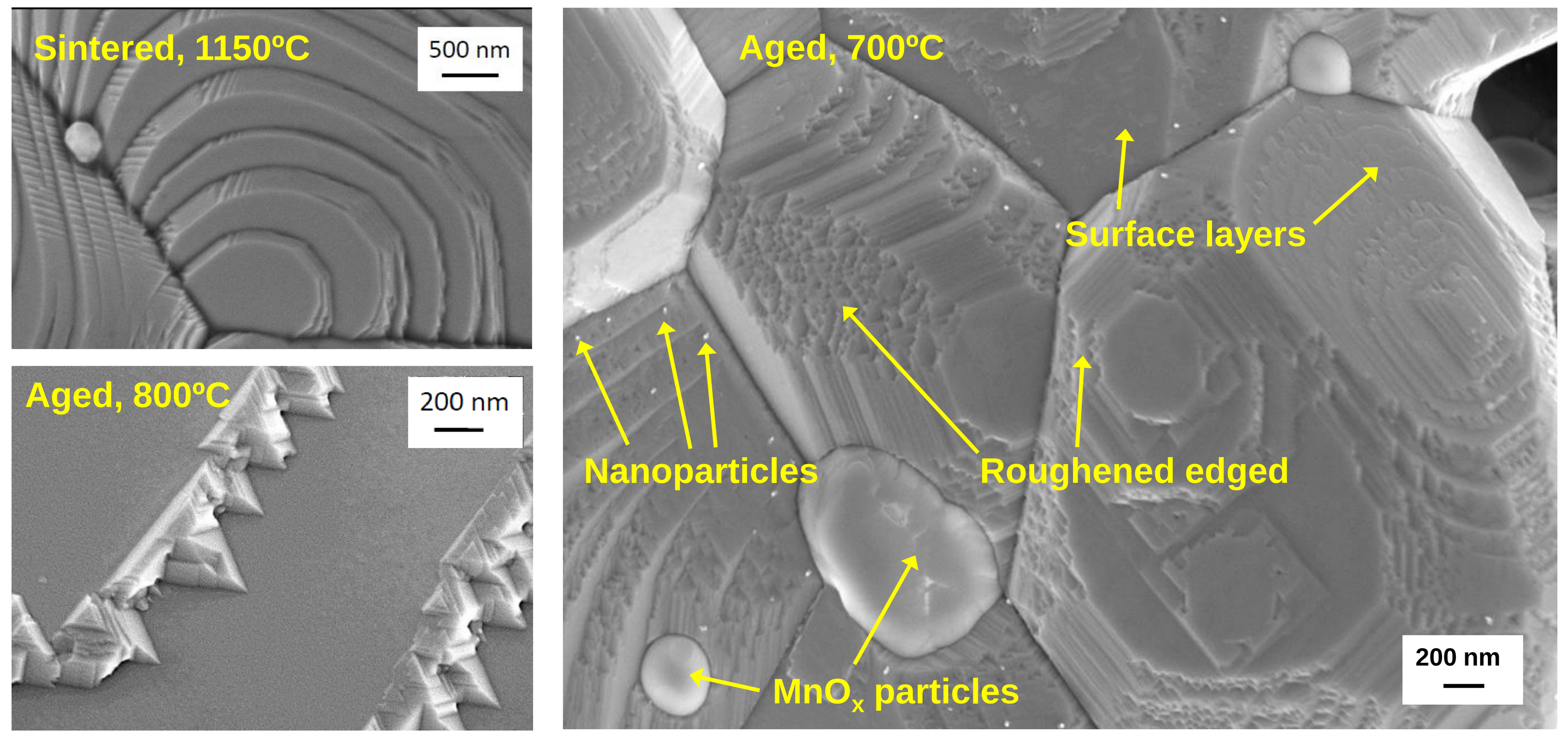
Isolation of the aging mechanism by varying the cathode/electrolyte and the cathode/air interface. The aging behavior of LSM was independent of electrolyte and different from that of LSCF



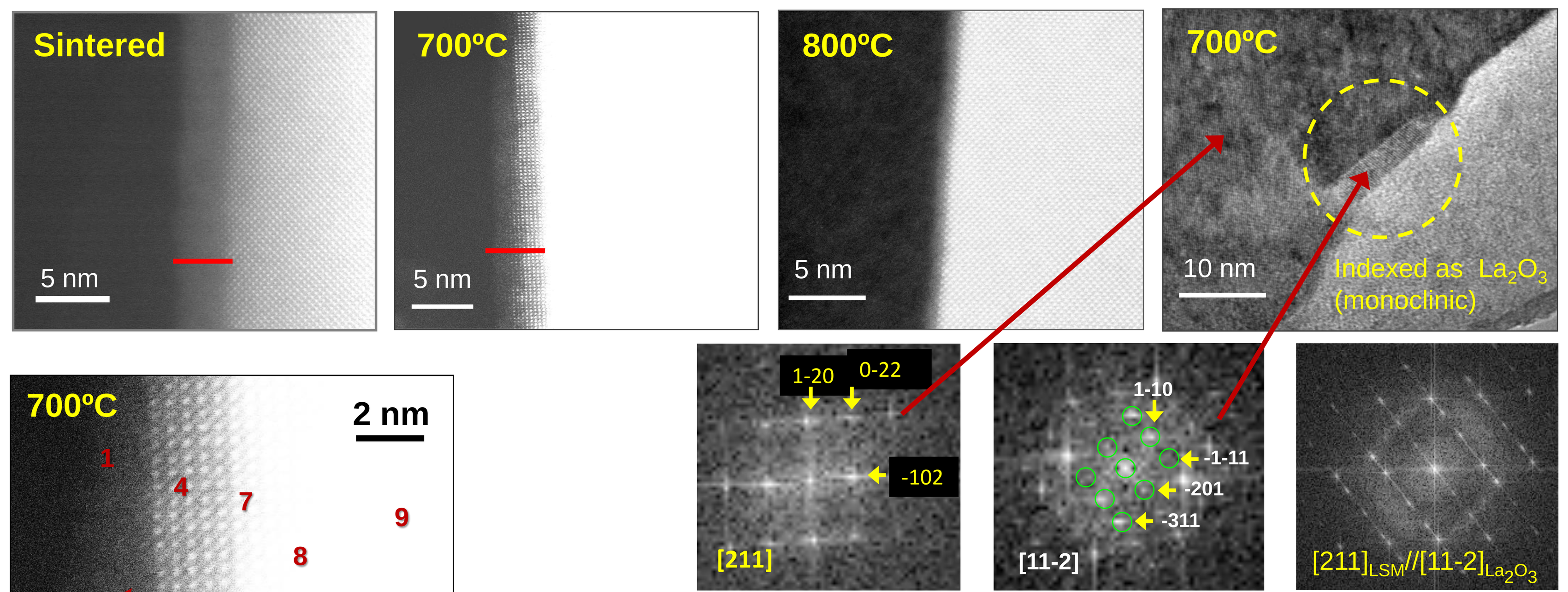
Deconvolution of the impedance spectra of an LSM/YSZ symmetrical cell aged at 800ºC. Multiple peaks could be used to fit the spectra, but a peak around 10 Hz contributes to the majority of the aging behavior

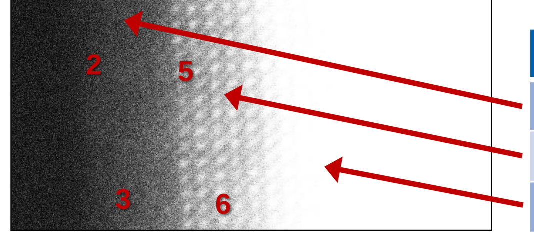
Dense LSM Pellet Studies

Pellets of LSM powder were sintered at 1150ºC and cooled to room temperatures. Pellets were then aged for 72 hrs at either 700ºC and 800º and quenched in liquid nitrogen to preserve the surface. In situ X-ray diffraction studies revealed no bulk phase changes for pellets sintered at 1150ºC and then aged at 700ºC, 800ºC, or 850ºC.



Sintering the LSM creates manganese oxide particles on the surface, but leaves smooth terraces and clean edges on the LSM grains. Depending on the thermal treatment, roughening of LSM can occur, along with the formation of various nanoparticles.





	(La + Sr) : Mn	La : Mn	Sr : (La + Sr)
Outer Layer	2.86 ± 0.02	2.86 ± 0.02	0
Inner Layer 1	2.41 ± 0.45	2.41 ± 0.45	0
Inner Layer 2	2.00 ± 0.08	1.73 ± 0.05	0.14 ± 0.01

TEM analysis confirms that the thermal treatments alter the thickness, composition, and structure of the LSM surface layer, changing the A:B ratio at the LSM surface and forming secondary phases.

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