X-ray, AFM, and Electrochemical Studies of Cation Segregation in Thin-Film Perovskite Cathode materials for solid oxide fuel cells

K.-C. Chang[1], B. Yildiz[2], B. Ingram[3], D. Hennessy[1], K. Balasubramaniam[4], P. Salvador[4], and H. You[1]

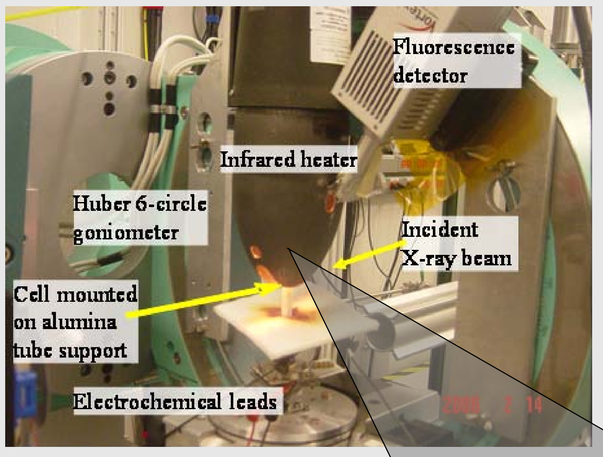
[1]Materials Science Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439

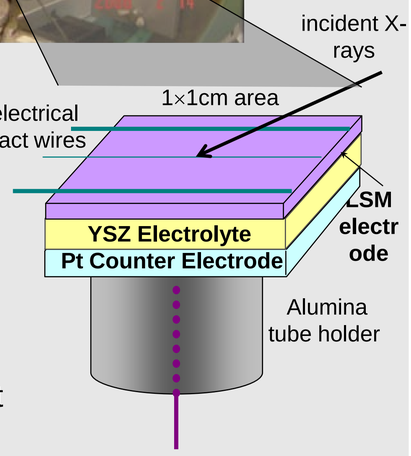
[2]Department of Nuclear Science and Engineering, MIT, 77 Massachusetts Ave., Cambridge, MA 02139

[3]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439

[4]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Experimental Setup





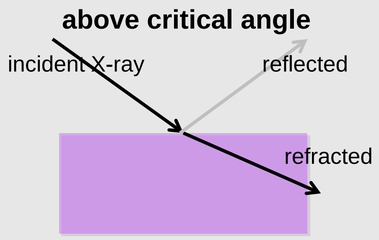
In situ **electrochemical cell**

operates as a oxygen pump in the half-cell mode

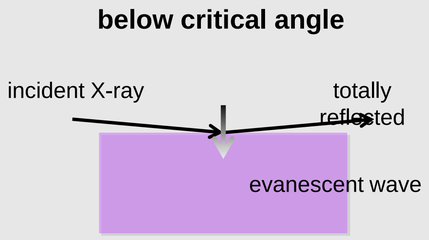
We need to prepare the sample with electrical contacts which subjects it to one or more annealing steps.

Grazing Incidence X-rays

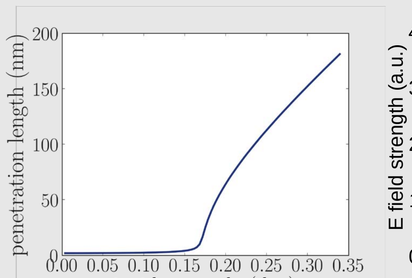
Surface sensitivity with X-rays

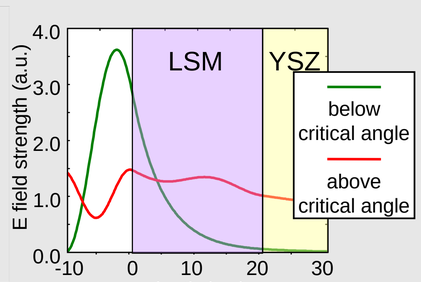


variation of penetration length with incident angle



E field strength below and above critical angle

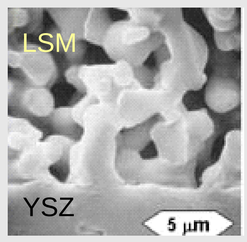




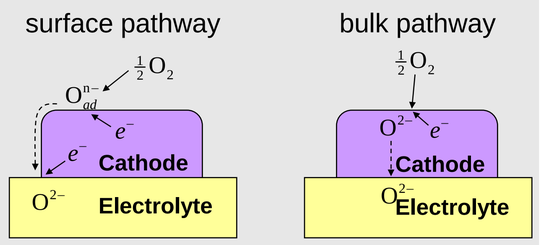
We measure X-ray absorption spectroscopy and fluorescence at different incident angles for surface sensitivity

LSM and LSC PLDfilms/YSZ

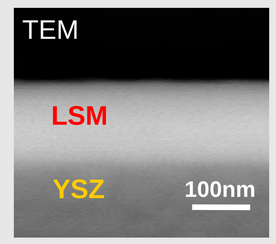
complex interfaces



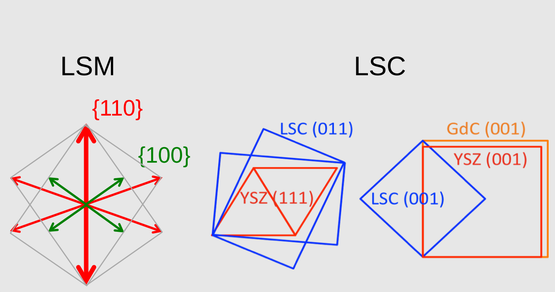
Multiple reaction paths



Our sample, PLD perovskite film on YSZ substrate, limits to the bulk pathway.

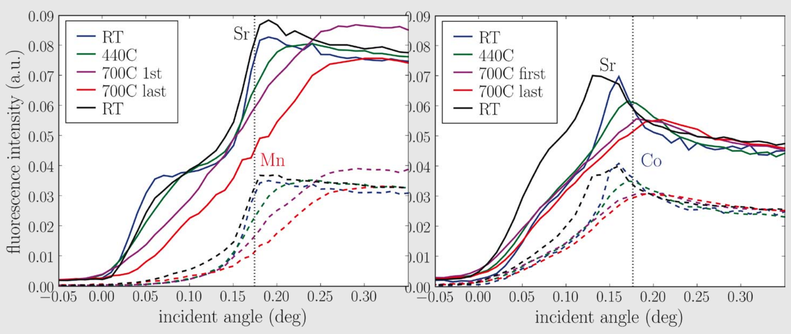


Both films grow in the (110) orientation on YSZ(111) and show 6 domains associated with this epitaxy



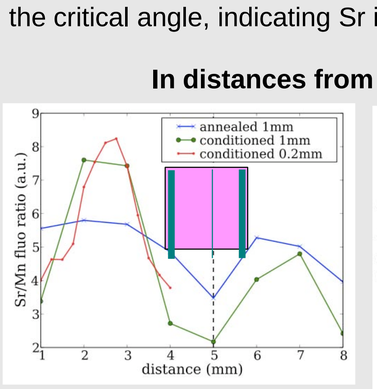
Cation Segregation

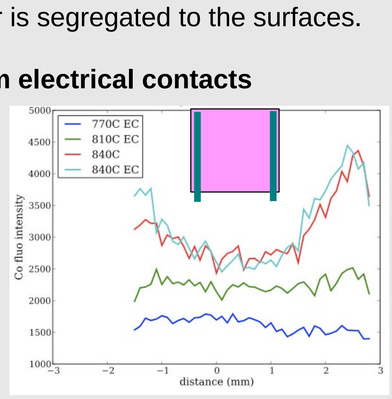
Surface-sensitive Fluorescence Yield



The fluorescence yield of Sr is dramatically enhanced below the critical angle, indicating Sr is segregated to the surfaces.

In distances from electrical contacts

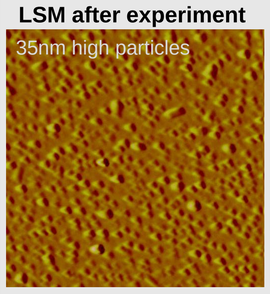




Fluorescence signals sensitively vary across the samples indicating electrochemistry affects the cation profile.

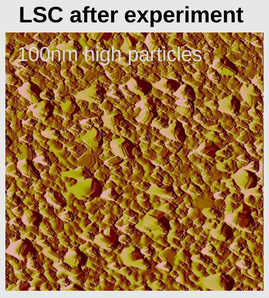
AFM Measurements

LSM after experiment



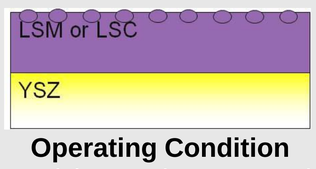
as received

LSC after experiment



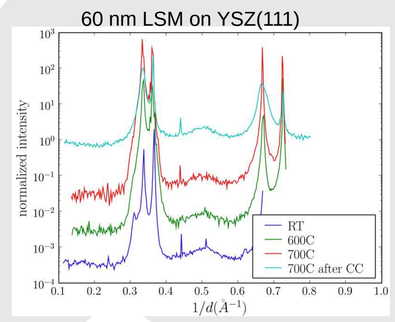
Models

Room Temperature
Cation enriched particles form on the surface

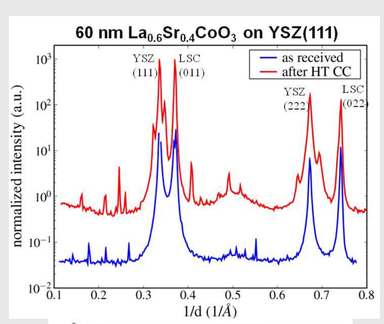


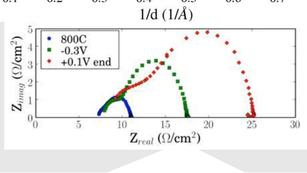
Operating Condition
particles are incorporated into the LSM/LSC film

Phase stability



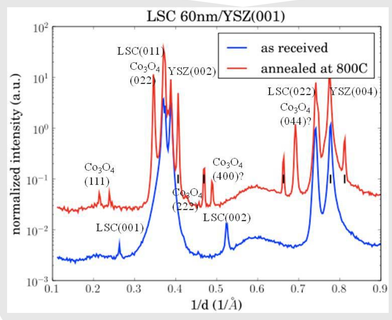
Phases of LSM film and YSZ substrates are stable in operating condition

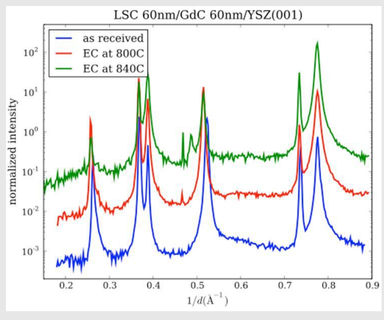




LSC/YSZ(111) forms a new tetragonal phase in operating condition: also seen in impedance measurements.

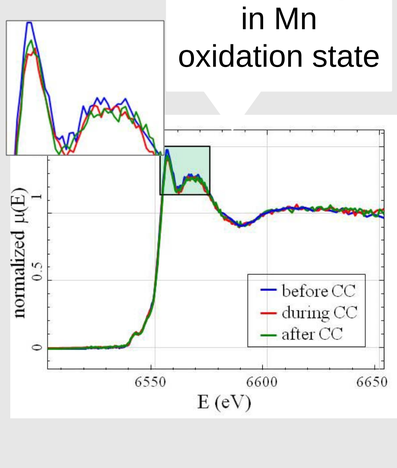
Thin GdC layers do not stop decomposition of LSC

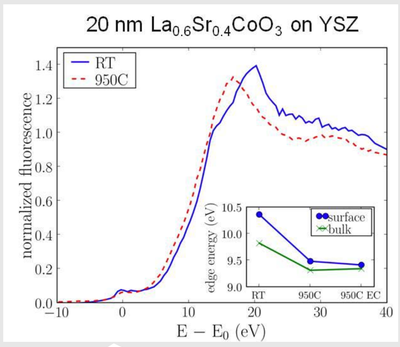




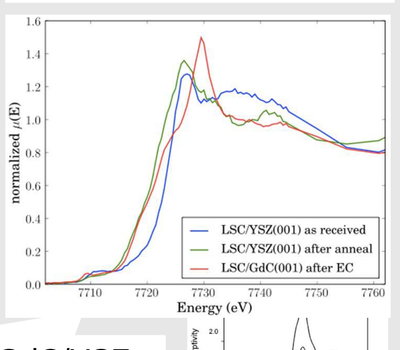
XANES: Oxidation States

Little change in Mn oxidation state

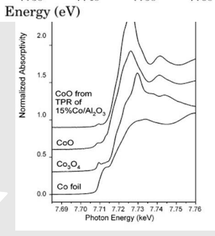




Change in Co oxidation state is easily seen in T.



Co edge XANES of LSC/GdC/YSZ after annealing turns to that of Co_3O_4



Co edge XANES standards

Summary

- Developed *in situ* synchrotron X-ray setup to study cathodes in air under half-cell (oxygen pump) or full cell (with fuels such as H_2 or CO) operating conditions.
- Found that Sr segregates to the surface of LSM and LSC films, forms Sr-rich nanoparticles at room temperature, and reincorporates into the films when heated to 700°C.
- Segregation is found dependent on the distance from the contact wires, suggesting that the electrochemistry drives the (de-)segregation.
- LSM films are stable while LSC not. – LSC(011) reacts with the YSZ(111) substrate at 800C.
- Thin (≤60nm) GdC layers do not prevent LSC(001)/YSZ(001) from reacting.
- Co first forms CoO which then transforms into Spinel ACo_2O_4.