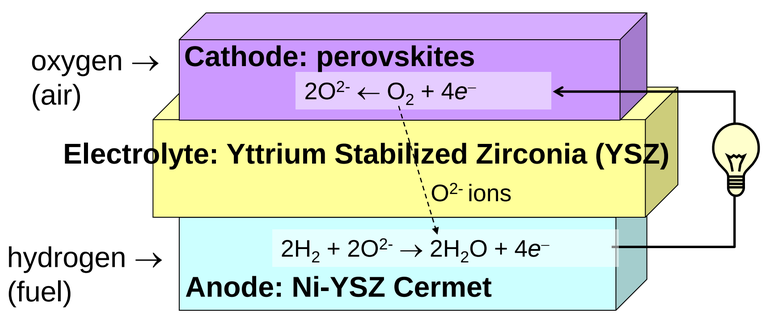
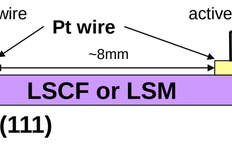
In situ Synchrotron X-ray Characterization of Potential-dependent Cation Segregation and B-site Surface Oxidation State in Model Thin-film Perovskite Cathodes

Kee-Chul Chang[1], Brian Ingram[2], Lu Yan[3], Paul Salvador[3], and Hoydoo You[1]
[1]Materials Science and [2]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439
[3]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

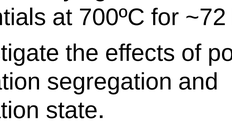
Solid Oxide Fuel Cells



Cathode: perovskites
$La_{0.7}Sr_{0.3}MnO_3$ (LSM)
$La_{0.6}Sr_{0.4}CoO_3$ (LSC)
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSCF)



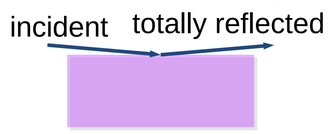
Electrolyte: fluorites
Y doped ZrO2 (YSZ)
Gd doped CeO2 (GdC)



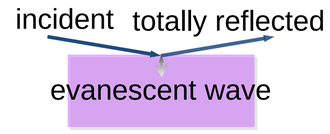
Grazing Incidence X-rays – surface sensitivity

Index of refraction of X-rays in matter is less than 1

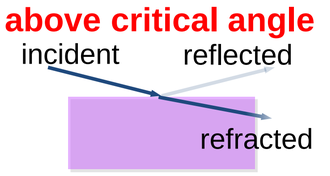
below critical angle

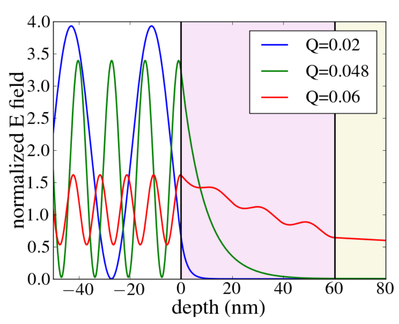


near critical angle



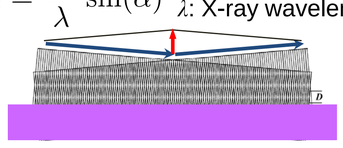
above critical angle



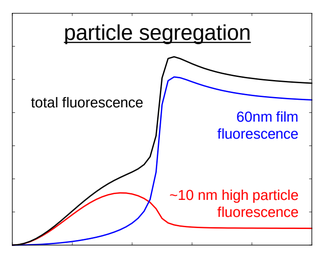


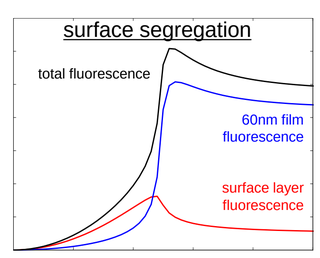
$$Q = \frac{4\pi}{\lambda}\sin(\alpha)$$

α: incidence angle
λ: X-ray wavelengt

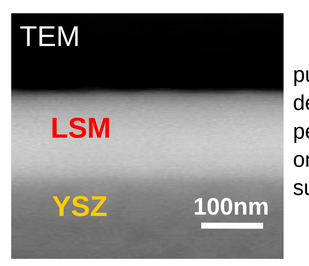


segregation can be determined by incidence angle scans…





…but we need to use thin film cathode on a single crystal substrate to get the required surface smoothness



pulsed laser deposited (PLD) perovskite film on YSZ substrate

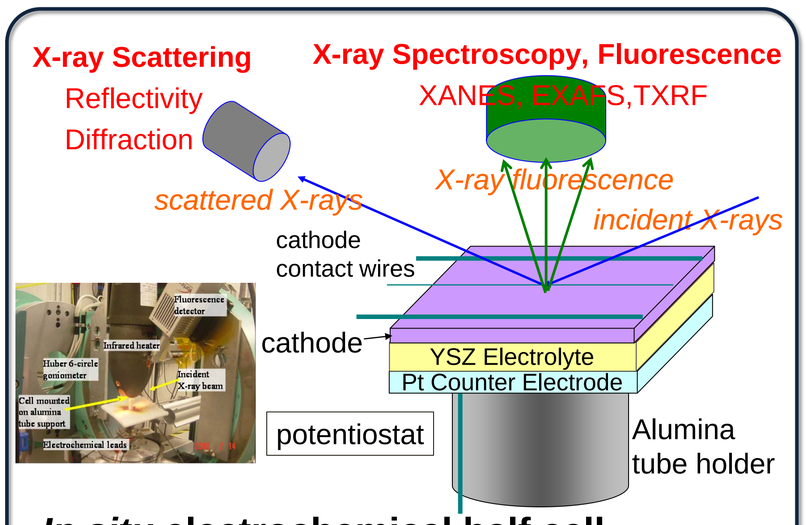
Epitaxial relationship:
perovskite (011) // YSZ(111) with 6 fold rotational domains

perovskite (001) // GdC(001) // YSZ(001)

Experimental Setup

X-ray Scattering
Reflectivity
Diffraction

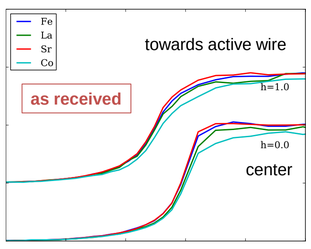
X-ray Spectroscopy, Fluorescence
XANES, EXAFS,TXRF



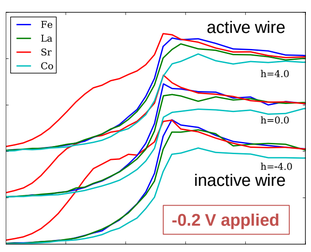
***In situ* electrochemical half cell**
operates as an oxygen pump

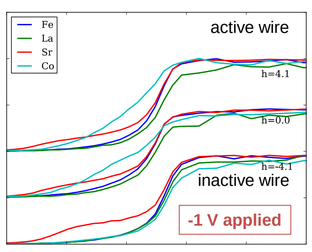
Ex-situ measurements

- Applied varying electrochemical potentials at 700ºC for ~72 hours
- Investigate the effects of potential on cation segregation and oxidation state.
- Removable Pt-wires were pressure contacted to film surface
- Inactive wire was used as a control
- Surface potential expected to decrease as a function of distance from the active wire.

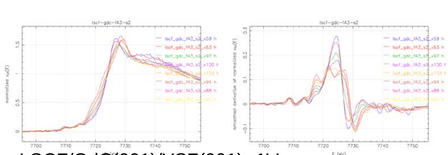


Sr segregation is evenly spread around the surface but Co segregation is confined near the active wire at -1 V.

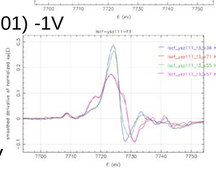




Surface Co oxidation state changes into 'spinel' state after annealing, regardless of orientation. Degree of Co surface oxidation state change is also correlated with the Co segregation



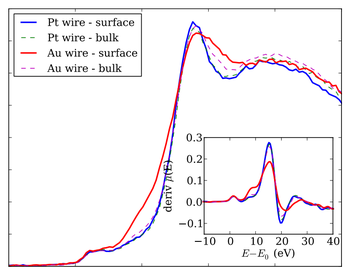
LSCF/GdC(001)/YSZ(001) -1V

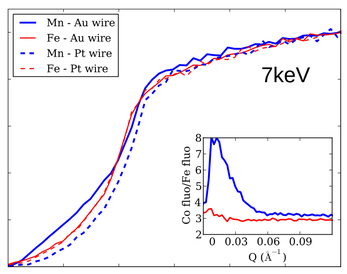


LSCF/YSZ(111) -1V

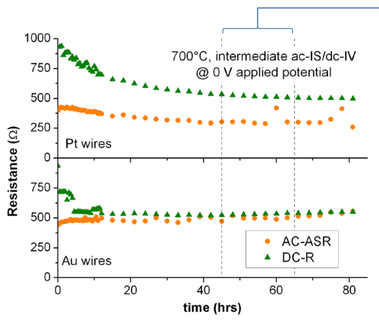
LSM/YSZ(111) results

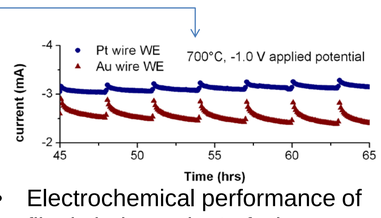
Influence of Au vs Pt wires, 1 V at 700ºC for 81 hours





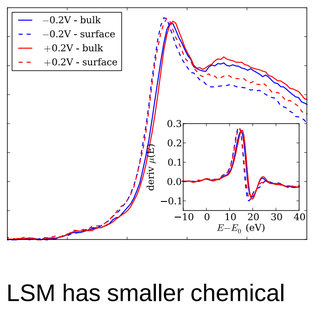
Mn segregation and surface oxidation state change was not observed for Pt-electrodes but occurs near Au-electrodes under cathodic potential





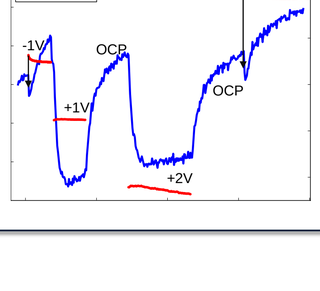
- Electrochemical performance of film is independent of wire
- Apparent increase in film polarization with Au wires relative to Pt wires

Effect of thin layer of LSM on LSCF/YSZ(111)



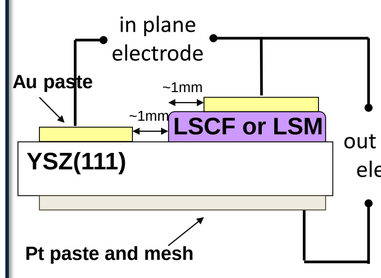
- LSM has smaller chemical expansion and slower kinetics compared to LSCF
- Transient effects are observed under applied cathodic potential

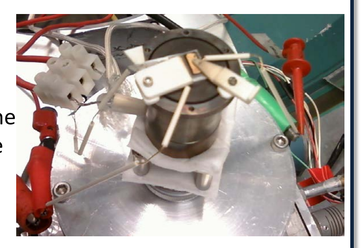
- Surface LSM with Pt contact wires prevents the Co oxidation state from changing into a spinel-like state
- The surface Co K XANES edge shifts while bulk which remains constant - implying a Co oxidation state change only at the surface



LSCF/YSZ(111) results

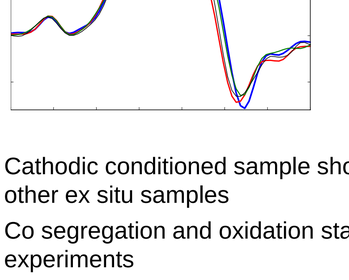
Modified experimental setup

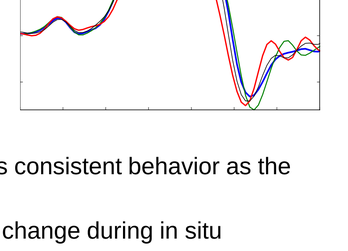




- Switching connections allows the applied potential to be either in-plane or out-of-plane with respect to the YSZ surface
- Samples were annealed at 700ºC under -1 V potential over 72 hours before in situ APS experiments

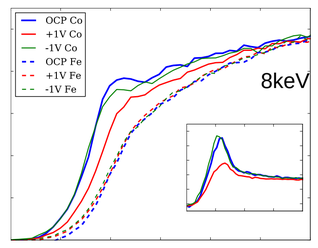
Chemical expansion of specular LSCF(011) on YSZ(111)

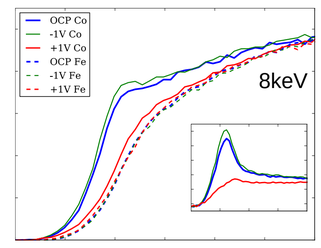


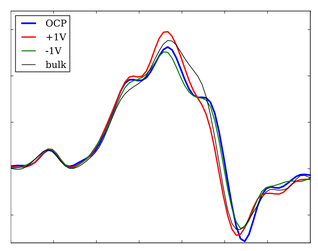


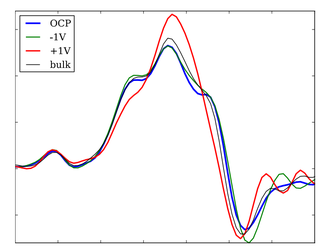
- LSCF shows fast chemical expansion kinetics (due to oxygen vacancies)
- Measurement time scale ≥ 1 second
- High applied out-of-plane potential induces transient chemical expansion behavior

Co segregation and surface Co oxidation state change









- Cathodic conditioned sample shows consistent behavior as the other ex situ samples
- Co segregation and oxidation state change during in situ experiments
- Electrochemical potential effects are enhanced for out-of-plane configuration

Conclusions

- B-site (i.e., Co or Mn) segregation and oxidation state changes were observed in situ at high cathodic electrochemical potentials
- B-site desegregation occurs under high anodic potential
- The oxygen vacancy concentration of the films are indirectly monitored with chemical expansion and influenced by magnitude of applied electrochemical potential
- Pt-wires limit charging on film surfaces due to active participation in oxygen reduction reaction

12th Annual SECA Workshop, July , 2011