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

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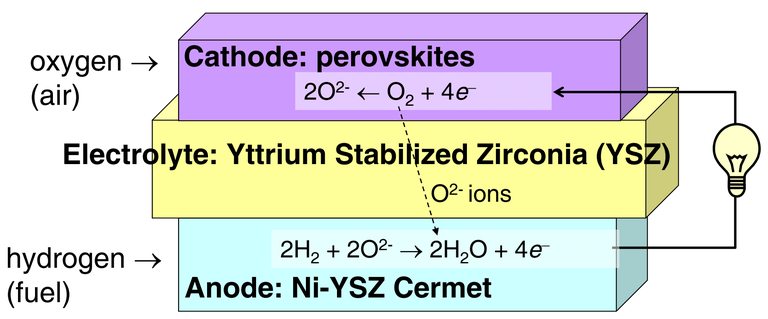
Solid Oxide Fuel Cells

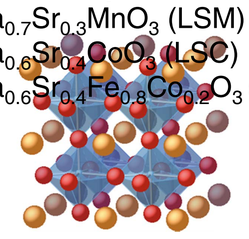


Cathode: perovskites

$La_{0.7}Sr_{0.3}MnO_3$ (LSM)

$La_{0.6}Sr_{0.4}CoO_3$ (LSC)

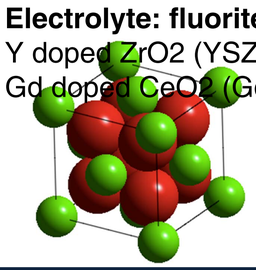
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSCF)



Electrolyte: fluorites

Y doped ZrO2 (YSZ)

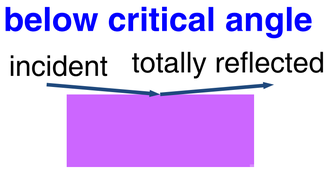
Gd doped CeO2 (GdC)



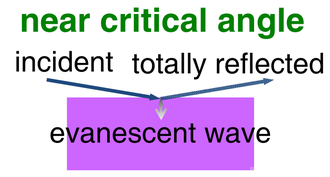
Grazing Incidence X-rays – surface sensitivity

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

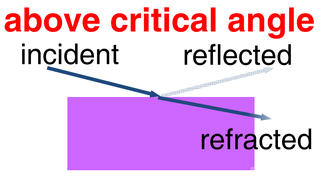
below critical angle

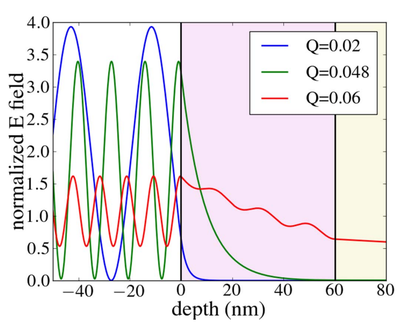


near critical angle



above critical angle

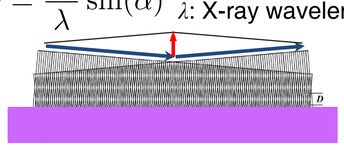




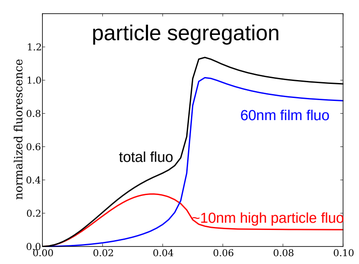
$$Q = \frac{4\pi}{\lambda}\sin(\alpha)$$

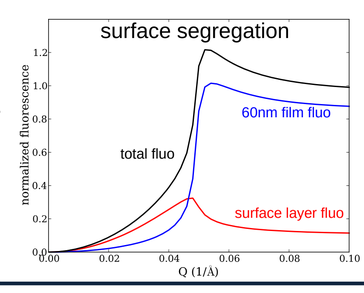
α: incidence angle

λ: X-ray wavelengt

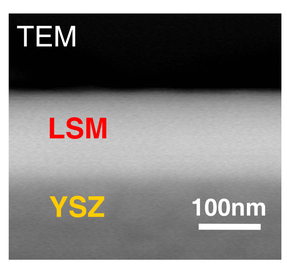


segregation can be determined by incidence angle scans





…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

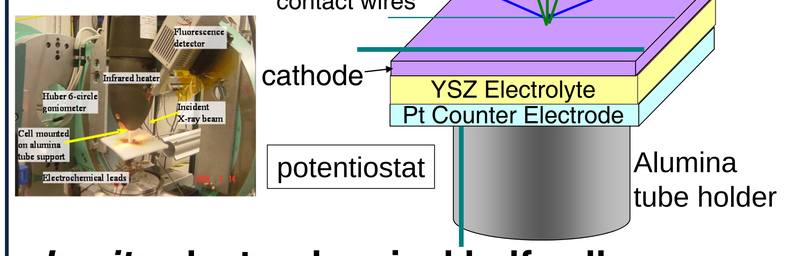
X-ray Scattering

Reflectivity

Diffraction

X-ray Spectroscopy, Fluorescence

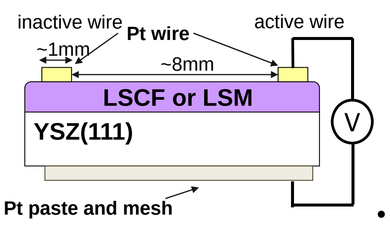
XANES, EXAFS,TXRF



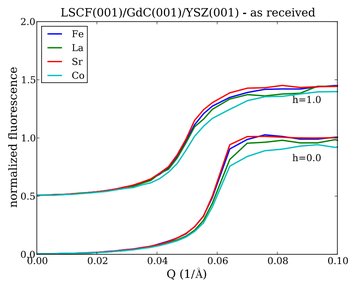
***In situ* electrochemical half cell**

operates as an oxygen pump

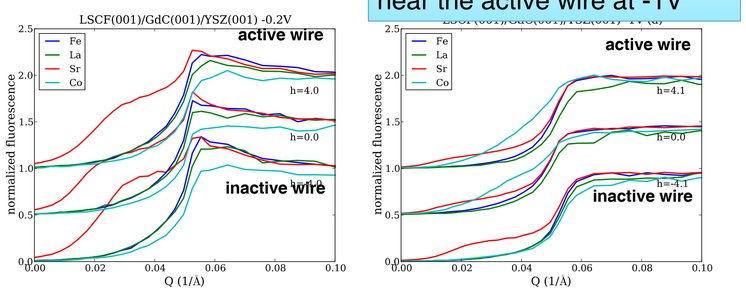
Ex-situ measurements

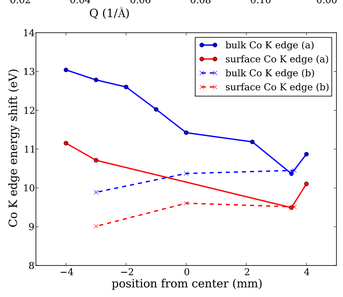


- Thin film cathodes were electrochemically conditioned at 700° C for 72 hrs under different potentials to investigate the effects of potential on cation segregation and oxidation state.
- We used flattened wires with pressure contacts to look at the surface underneath the wire.
- Inactive wire was used to separate the effects of wire covering the surface.
- potential drops away from the active wire.



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

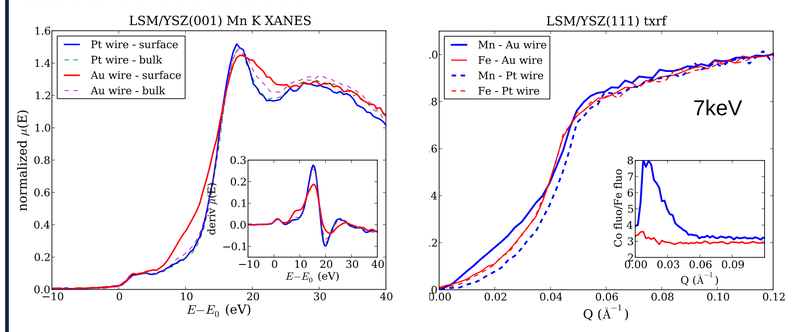




Surface Co oxidation state is also correlated with the Co segregation

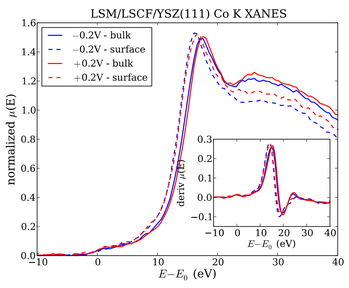
LSM/YSZ(111) results

Influence of Au wires



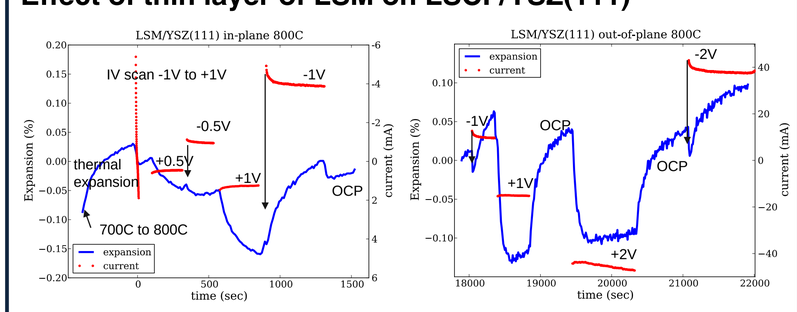
2 samples with different wires, -1V at 700° C for ~72 hours: Mn segregation and surface oxidation state change was not observed for Pt electrodes but occurs near Au electrodes under cathodic potential.

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



- ~5nm of LSM was grown on LSCF to model infiltration
- surface LSM with Pt contact wires prevents the Co oxidation state from changing into 'spinel' state
- surface Co K XANES shows edge shift compared with a bulk implying a Co oxidation state change inside the perovskite structure

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



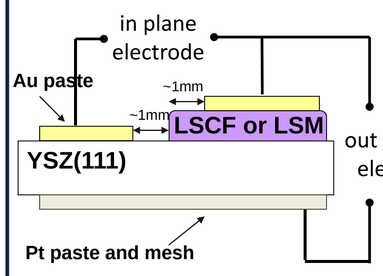
- LSM has smaller chemical expansion and slower kinetics
- Cathodic potential shows transient effects

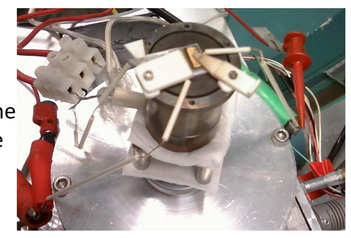
Conclusions

- B site (Co for LSCF and Mn for LSM) segregation and oxidation state change were observed in situ at high cathodic potential
- B site desegregation occurs under high anodic potential
- applied potential also changes the oxygen vacancy concentration in the cathode thin film which induces chemical expansion

LSCF/YSZ(111) results

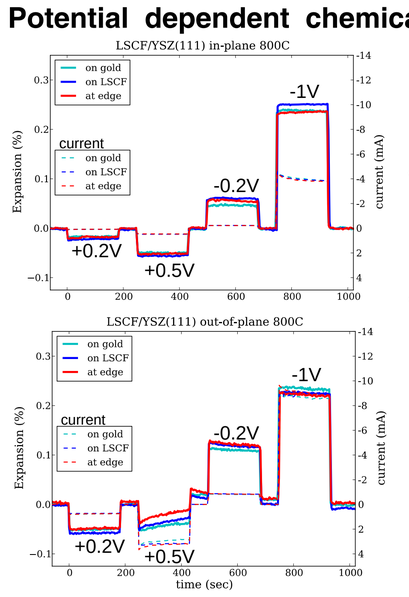
Modified half cell for in situ in-plane and out-of-plane applied potential experiment





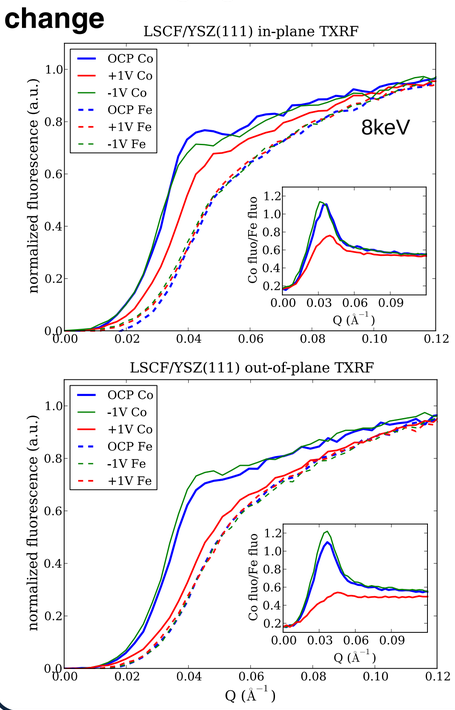
- switching connections allows the applied potential to be either in-plane or out-of-plane with respect to the YSZ surface
- samples were annealed at 700° C under -1V potential over 72hours before in situ experiments

Potential dependent chemical expansion of specular LSCF(011) on YSZ(111)



- LSCF shows fast chemical expansion kinetics (due to oxygen vacancies) which happens within 1 second
- High applied potential in the out-of-plane configuration induces transient chemical expansion behavior

In situ Co segregation and surface Co oxidation state change



- our cathodic conditioned sample shows consistent behavior as the other ex situ samples
- we were able to observe Co segregation and oxidation state change during our in situ experiments
- The order of applied potential was different between in-plane (OCP, +1V, -1V) and out-of-plane (OCP, -1V, +1V) measurements
- potential effects are enhanced for out-of-plane configuration

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