In situ X-ray studies of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ epitaxial thin films as model solid oxide fuel cell cathodes

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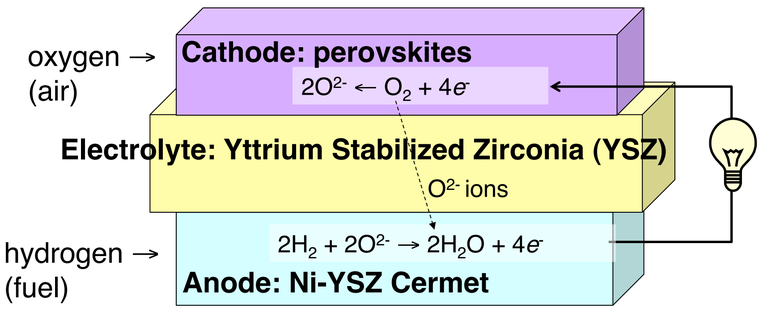
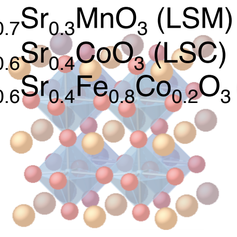
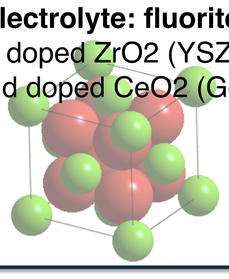
Solid Oxide Fuel Cells



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)

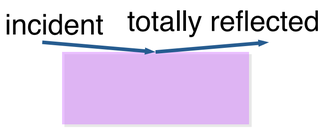


Grazing Incidence X-rays

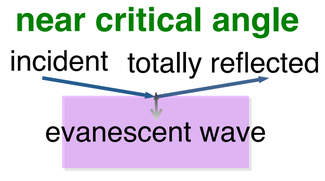
surface sensitivity with X-rays

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

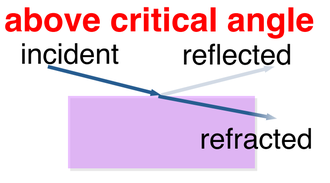
below critical angle

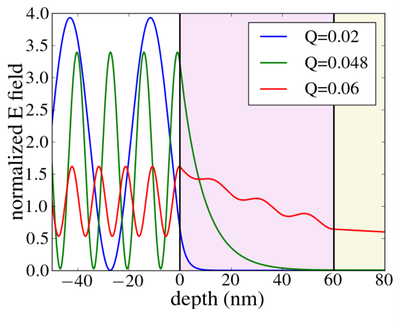


near critical angle



above critical angle

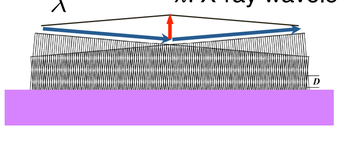


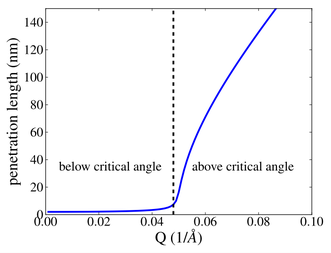


measure XAS and fluorescence at different incident angles for surface sensitivity

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

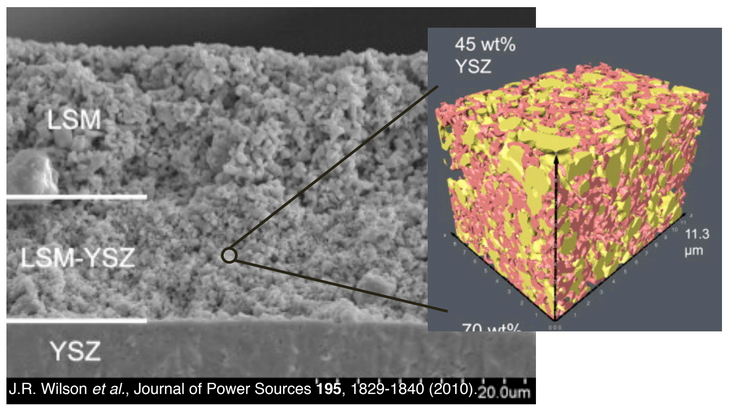
α: incidence angle
λ: X-ray wavelength



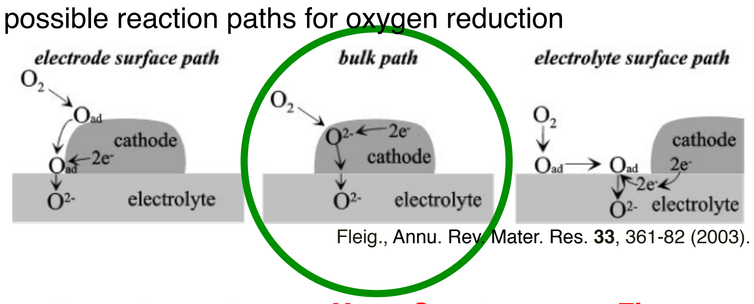


Model Cathodes and Experimental Setup

Real SOCF interfaces are complex with multiple reaction paths

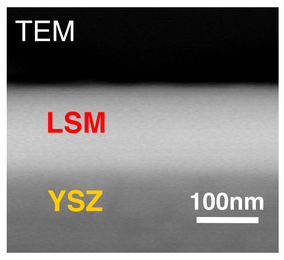


possible reaction paths for oxygen reduction

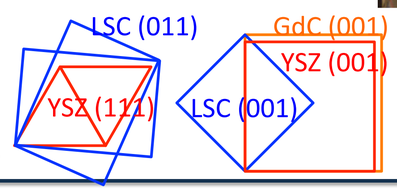


Fleig., Annu. Rev. Mater. Res. **33**, 361-82 (2003).

Our approach: Simplify the system and reaction paths by using thin film electrodes



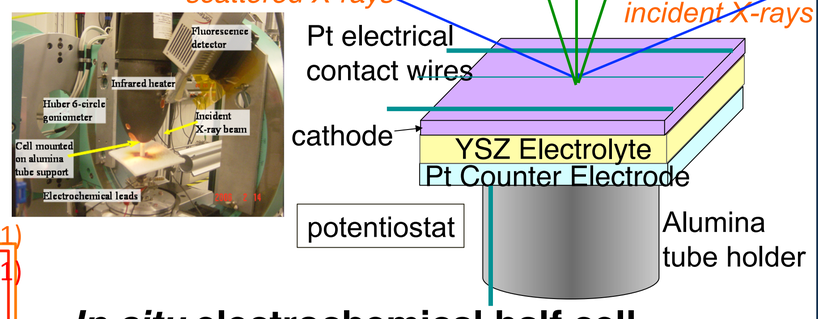
Epitaxy:
perovskite (011) // YSZ(111) with 6 fold rotational domains
perovskite(001) // GdC(001) //YSZ (001)



pulsed laser deposited (PLD) perovskite film on YSZ substrate

X-ray Scattering
Reflectivity
Diffraction

X-ray Spectroscopy, Fluorescence
XANES, EXAFS,TXRF

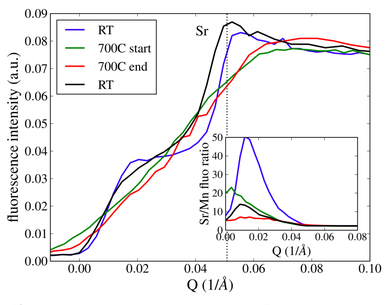


***In situ* electrochemical half cell**
operates as an oxygen pump

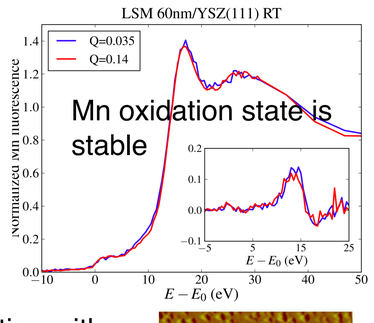
Previous LSM and LSC results

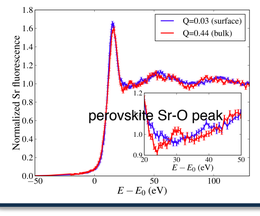
LSM(011)/YSZ(111)

TXRF

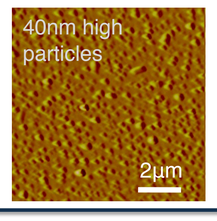


Mn K XAS



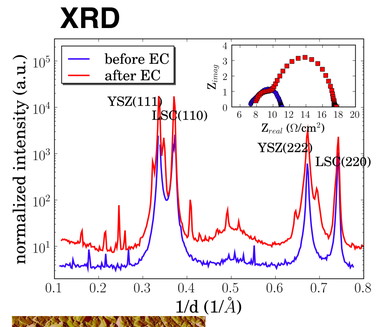


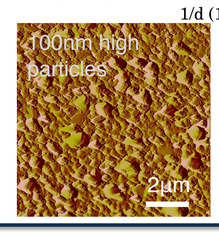
Sr segregation with surface Sr phases of different crystal structure



LSC(011)/YSZ(111)

XRD

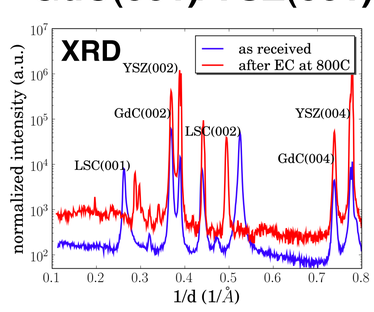




interfacial LSC/ YSZ reactions

LSC(001)/ GdC(001)/YSZ(001)

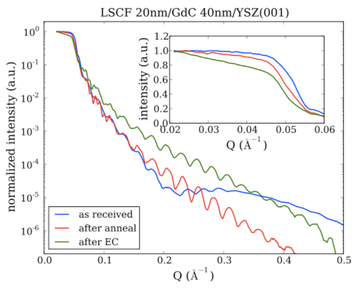
XRD



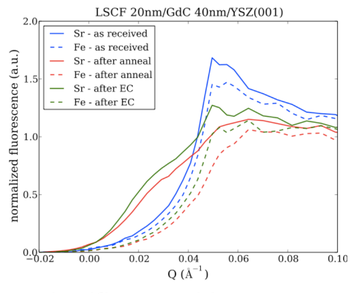
complete decomposition of LSC film if the GdC layer is less than 60nm thick

LSCF(001)/GdC/YSZ(001)

Reflectivity

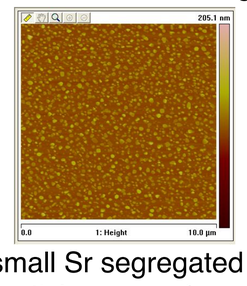


TXRF



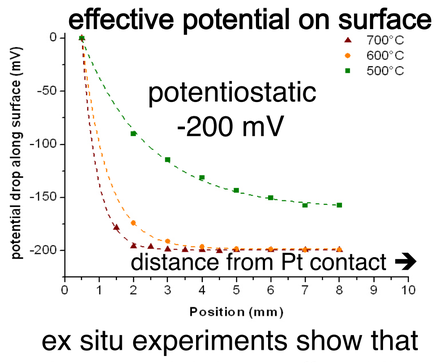
Interfaces are fairly stable with no significant critical angle change after ~3 days of annealing and ~1 day of electrochemistry

AFM after annealing/EC



small Sr segregated particles on surface after experiment

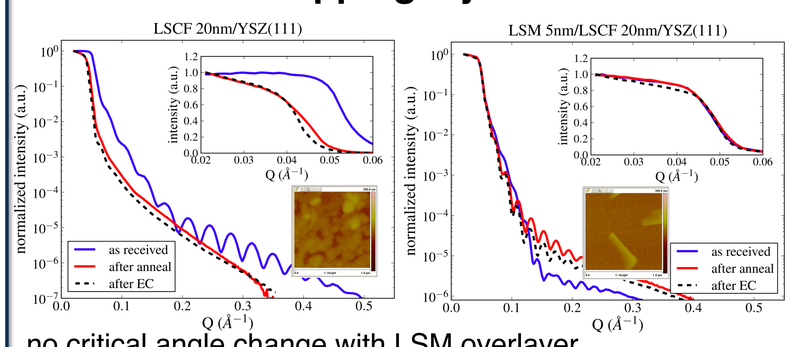
effective potential on surface



ex situ experiments show that the potential drops off rapidly away from Pt contacts

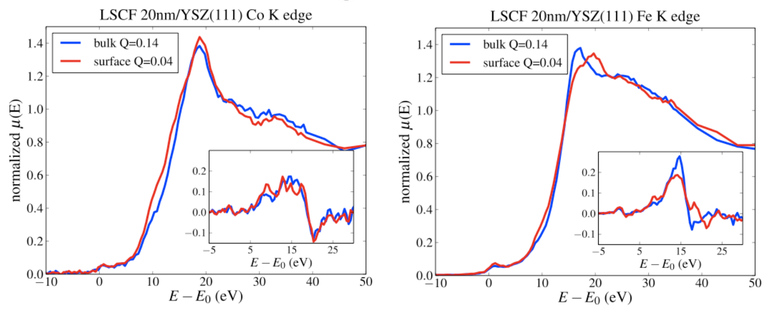
LSCF(011)/YSZ(111)

effect of LSM capping layer



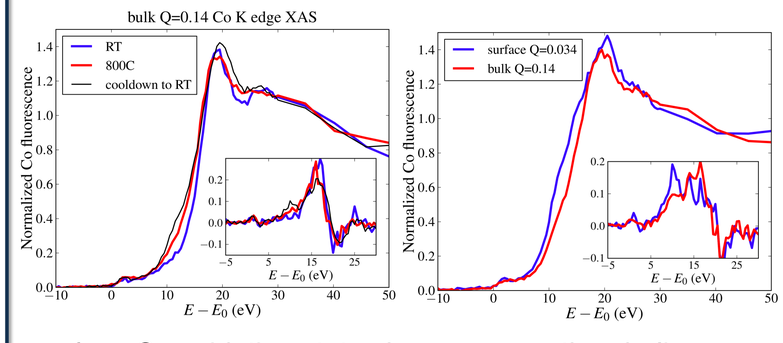
no critical angle change with LSM overlayer

Extended annealing



slight changes in Fe oxidation state

Co oxidations state with annealing



surface Co oxidation state changes more than bulk

Conclusions

Cation oxidation change: Co >> Fe > Mn
- B site cation surface oxidation state change observed for LSCF (not potential dependent but thermally activated)

cation motion at operating conditions
- Sr segregation on LSM, LSC and LSCF
- Sr segregation depends on applied potential for LSM
- LSC interface reactivity dependent on LSC/YSZ epitaxy
- LSM capping layer helps LSCF stability

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