Synchrotron X-Ray Studies of Environmental Effects on the Oxygen Reduction Reaction on SOFC Cathodes

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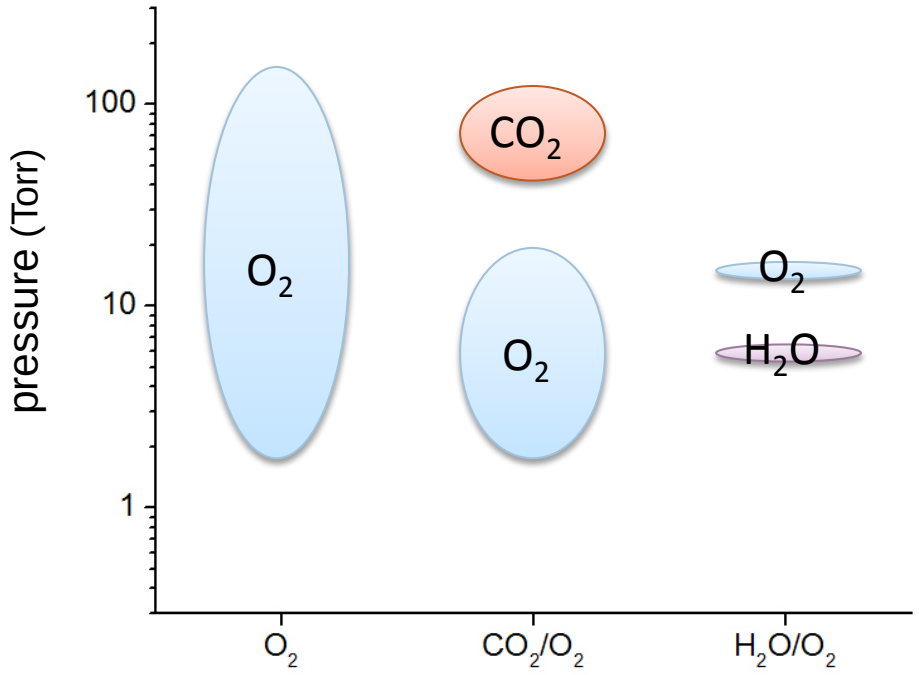
Results summary

Utilized synchrotron x-ray to established understanding of SOFC cathode performance in several areas

- Strontium segregation is apparent in all SOFC cathodes
- Measurements of lattice parameter shifts are related to changes in oxygen vacancy concentrations
- Established changes in $[V_O^{\bullet\bullet}]$ with applied potential are related to the kinetics of the oxygen reduction reaction (ORR)
- Established the gas phase composition directly affects the ORR
- Depth profiling of the vacancy concentration through the film may yield new insight into the conduction mechanisms.

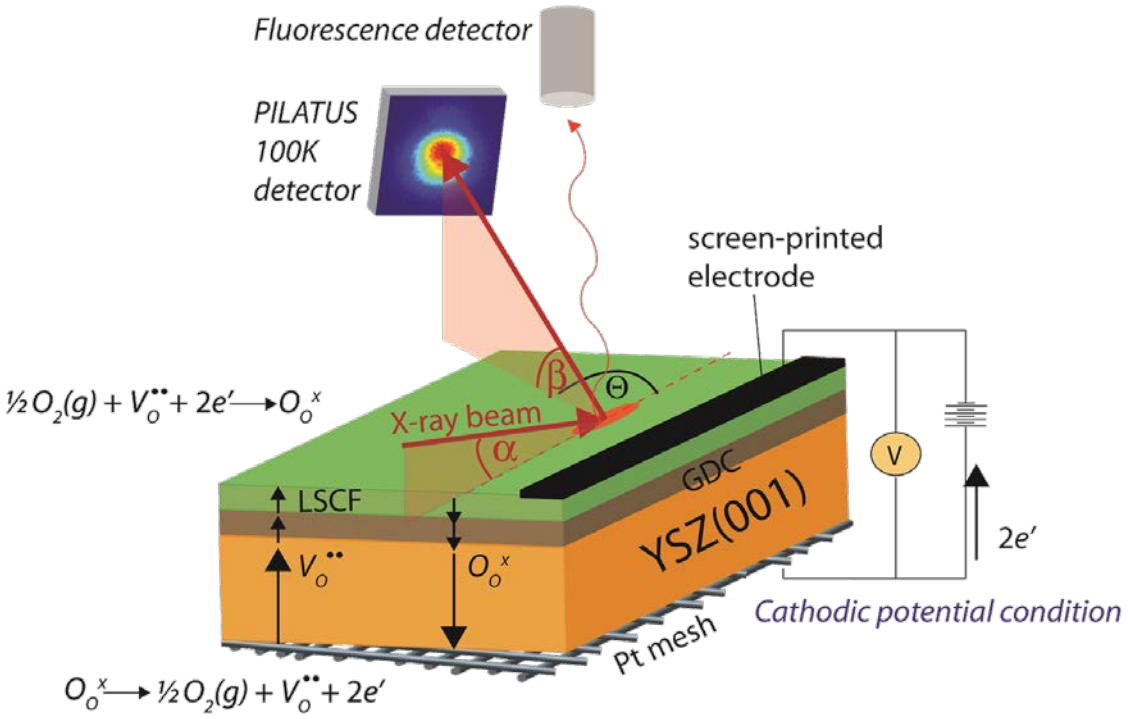
Experimental details: sample parameters

- SECA industrial teams proposed deleterious effect of gas impurities on SOFC performance
- Epitaxial 60nm LSCF/60nm GDC/YSZ(001) grown by PLD by the Salvador group at Carnegie Mellon
- Vary environment (pCO_2, pH_2O as well as T, pO_2)



All measurements were completed at a total pressure of 150 Torr with the balance being helium

Experimental details: in situ synchrotron studies

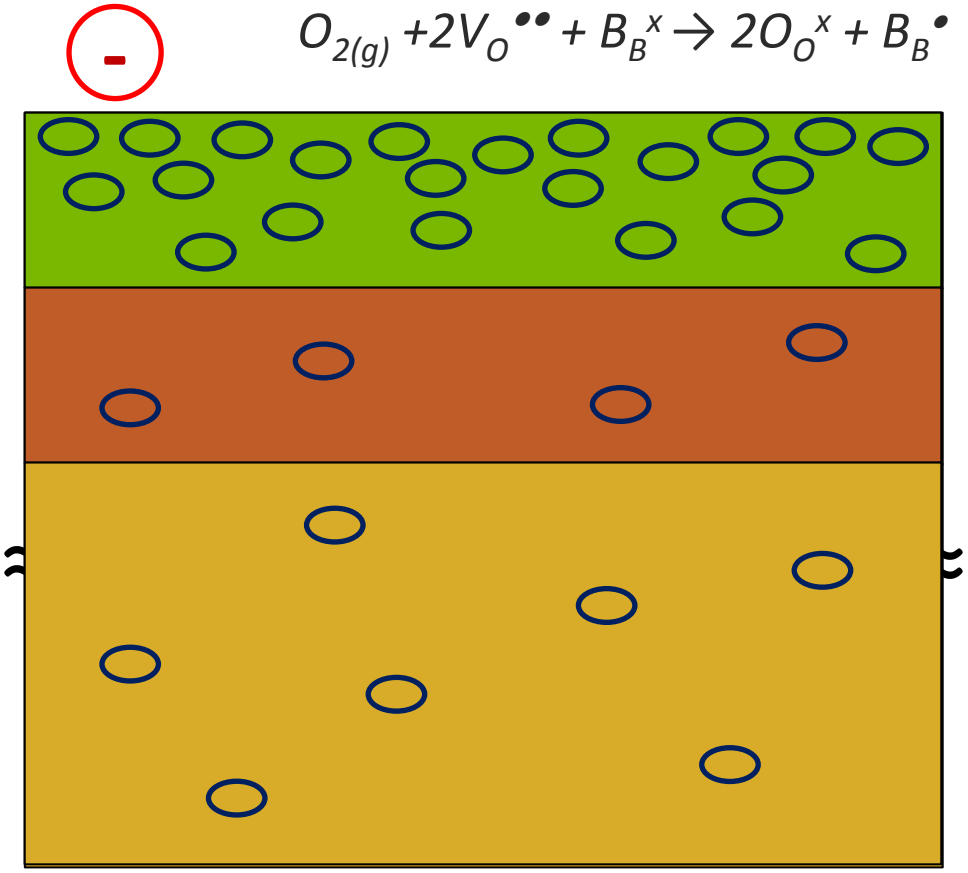


~20 µm wide incident X-ray beam

- Applied dc potential
- Monitored rapid changes
  - current (conduction)
  - lattice parameter
- Investigated ionic component of LSCF conductivity
- Lattice parameter changes directly correlate to $\Delta[V_O^{\bullet\bullet}]$
- Only observe c-lattice changes (out of plane) in the LSCF

Effect of applied potential on oxygen stoichiometry

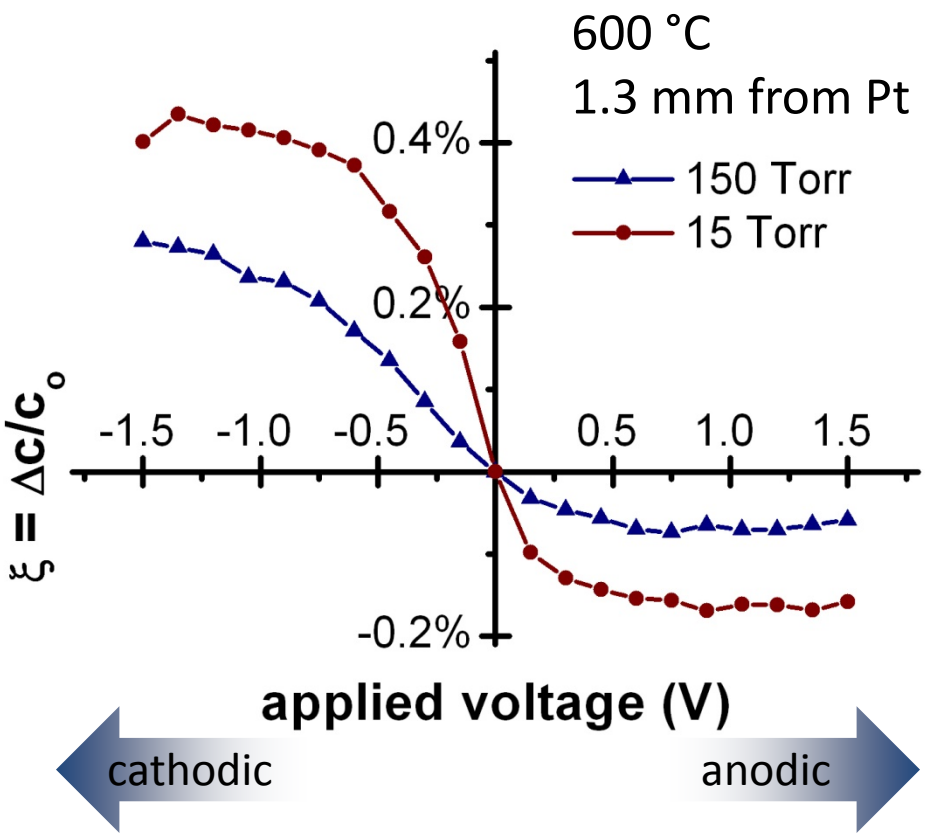
- Applying a cathodic potential drives oxygen into the LSCF film at the LSCF/gas interface
- If changes in lattice parameter and conduction are observed, we can determine which interface is rate limiting
- Assume buried interface remains constant, role of gas composition on ORR can be determined



Cathodic potential condition

LSCF lattice parameter shift vs applied potential

- Oxygen transport across the LSCF/gas interface is rate-limiting under both anodic and cathodic conditions
- Cathodic potentials result in larger $\Delta\delta$ than anodic potentials
  - Propensity for oxygen substoichiometry vs superstoichiometry in perovskites
- Stoichiometry changes increase with decreasing pO_2
  - O_2 reduction barrier increases with decreasing pO_2



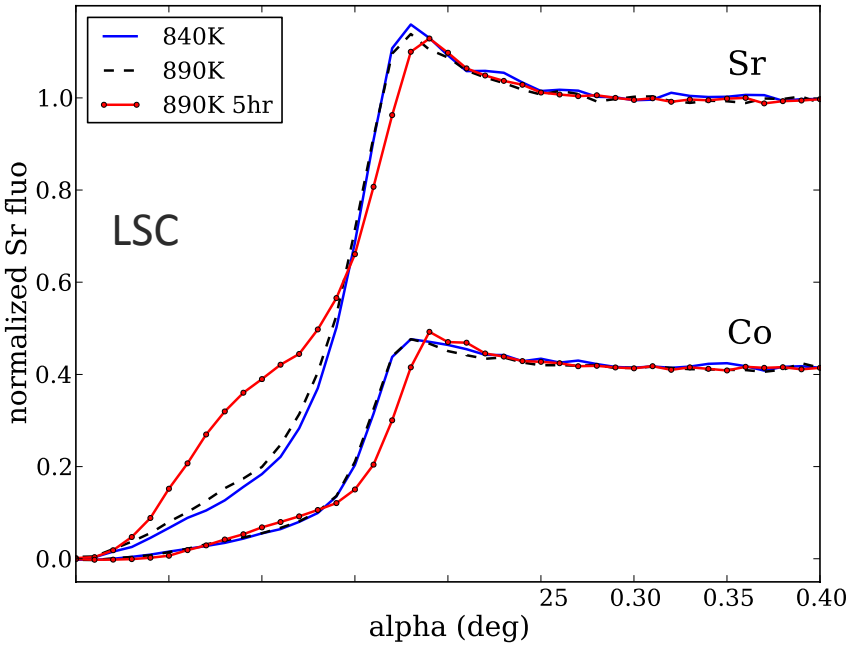
Ingram et al., APL. **101**, 051603 (2012)

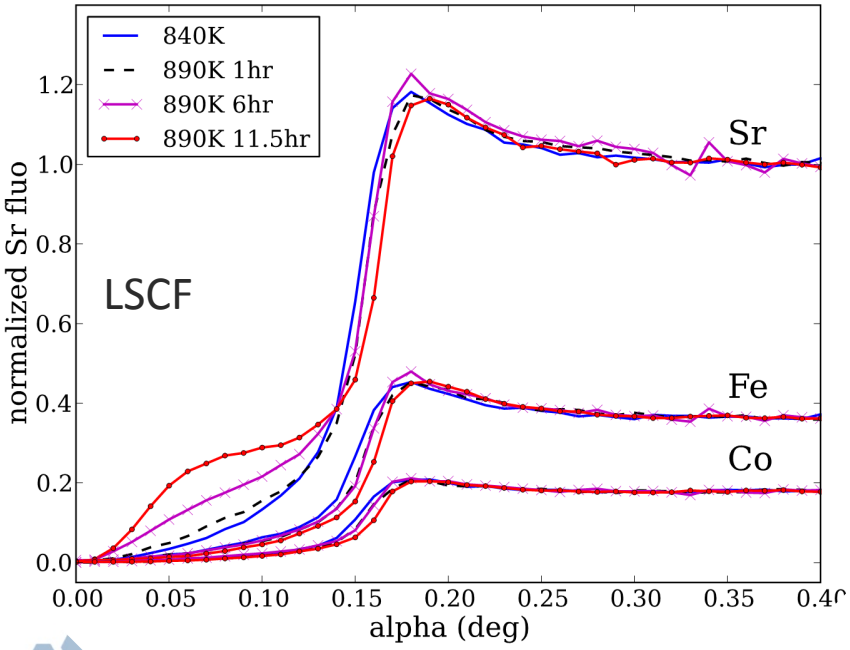
Outline

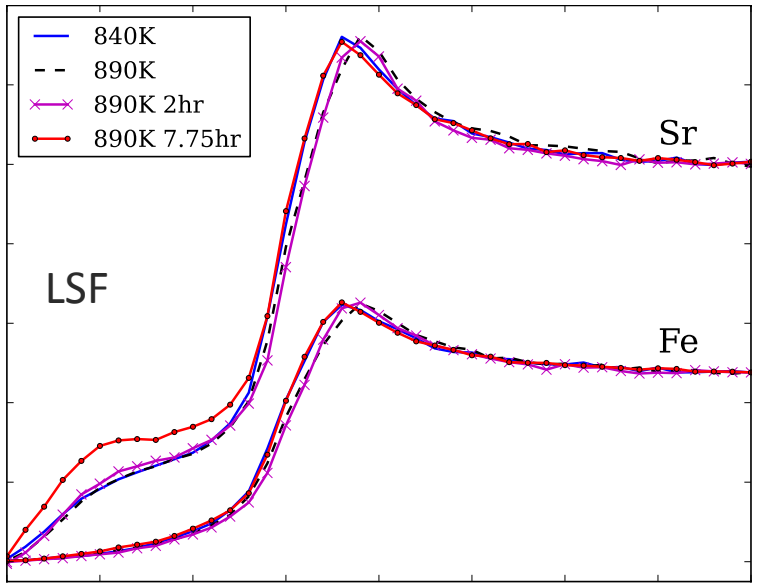
- Background and previous results
- Strontium segregation
  - Comparison of perovskite composition
  - Effect on performance
- Gas composition effects on LSCF performance
- Oxygen vacancy concentration depth profiling

Sr segregation

- Sr segregation is universal (thermal)
- $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ powder sample seems to be segregated at 570°C
- Sr segregation LSC and LSCF samples

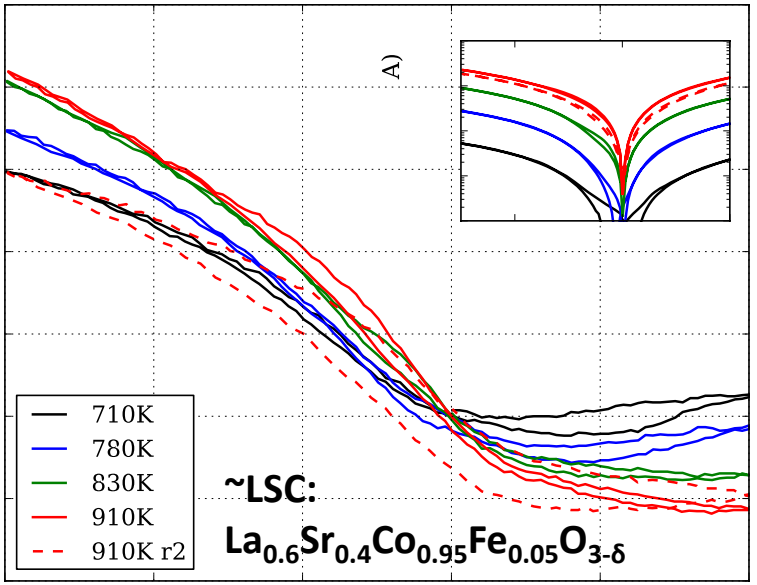




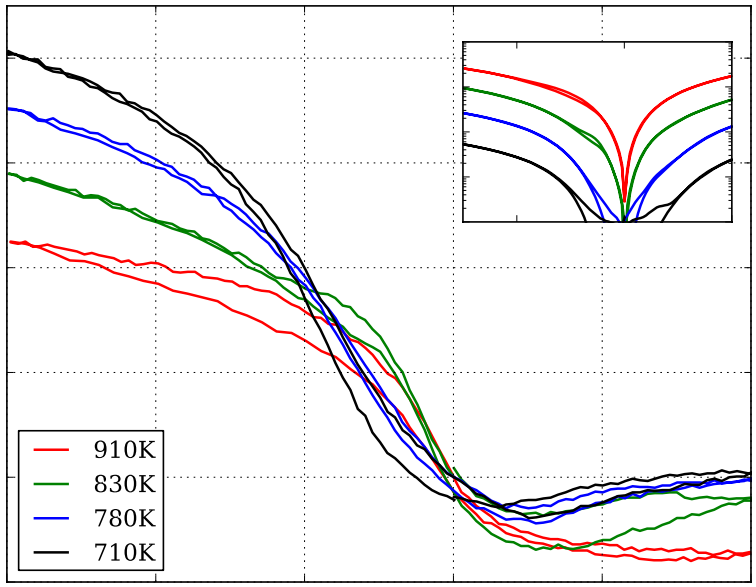


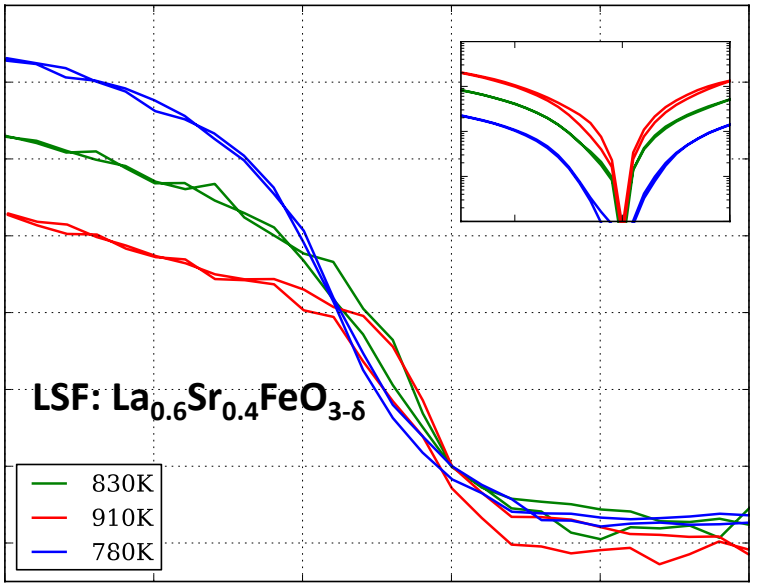
Chemical expansion after Sr segregation

- $La_{0.6}Sr_{0.4}Co_{0.95}Fe_{0.05}O_{3-\delta}$ chemical expansion is much smaller compared with other samples
- $La_{0.6}Sr_{0.4}Co_{0.95}Fe_{0.05}O_{3-\delta}$ also has opposite trend with temperature

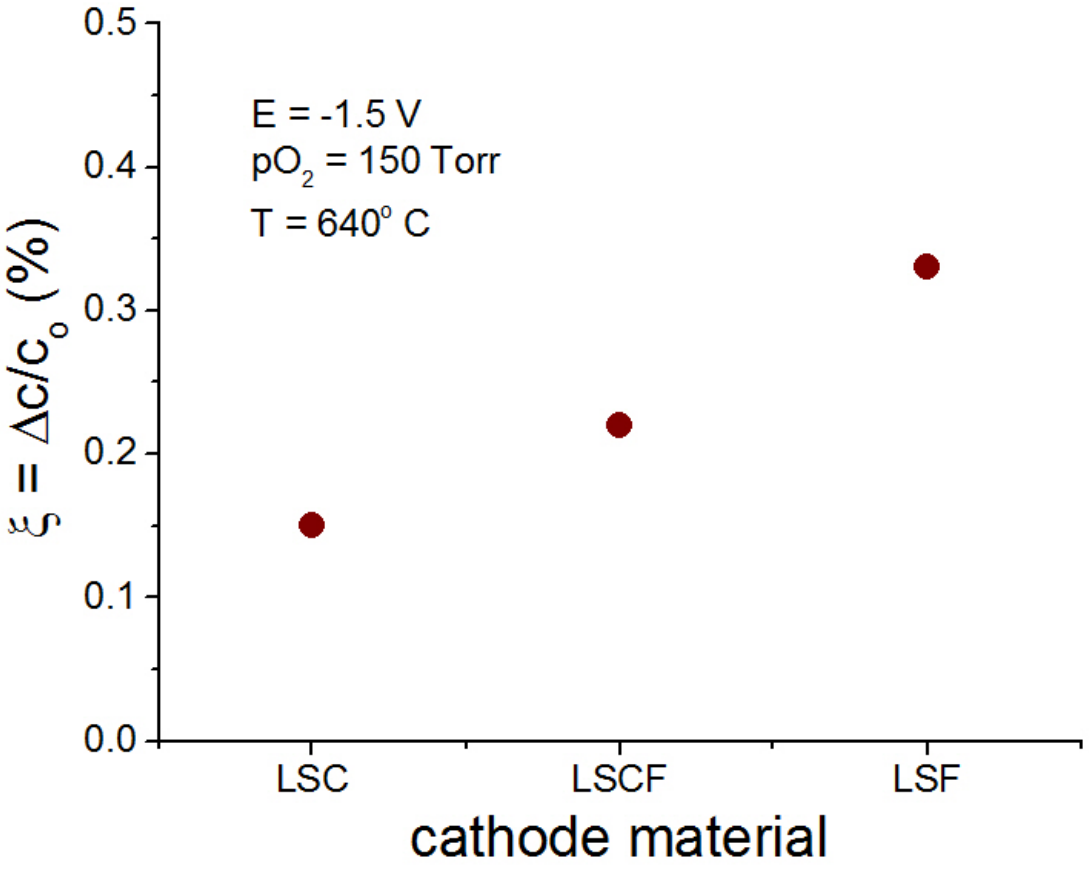


LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$





Perovskite comparison: ORR rates



- Post Sr segregation
- LSC (5% Fe) has facile ORR rate
- Stability concerns not considered

Outline

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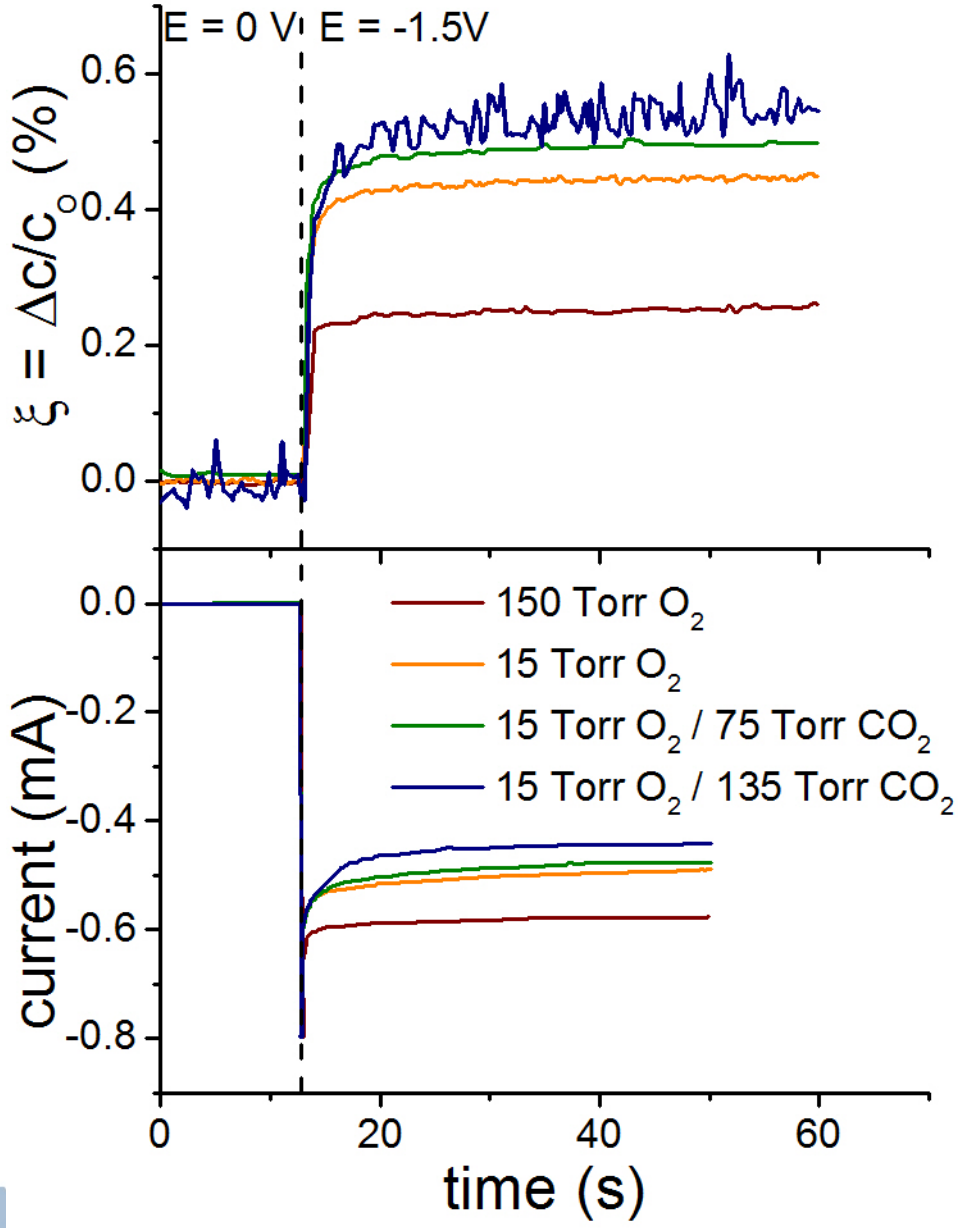
- Gas composition effects on LSCF performance
- Oxygen vacancy concentration depth profiling

Effect of CO_2 on lattice strain / current (500°C)



Introduction of CO_2 decreases the ORR rate

- electrochemical current decreases
- lattice shift increases (excess $V_O^{\bullet\bullet}$)

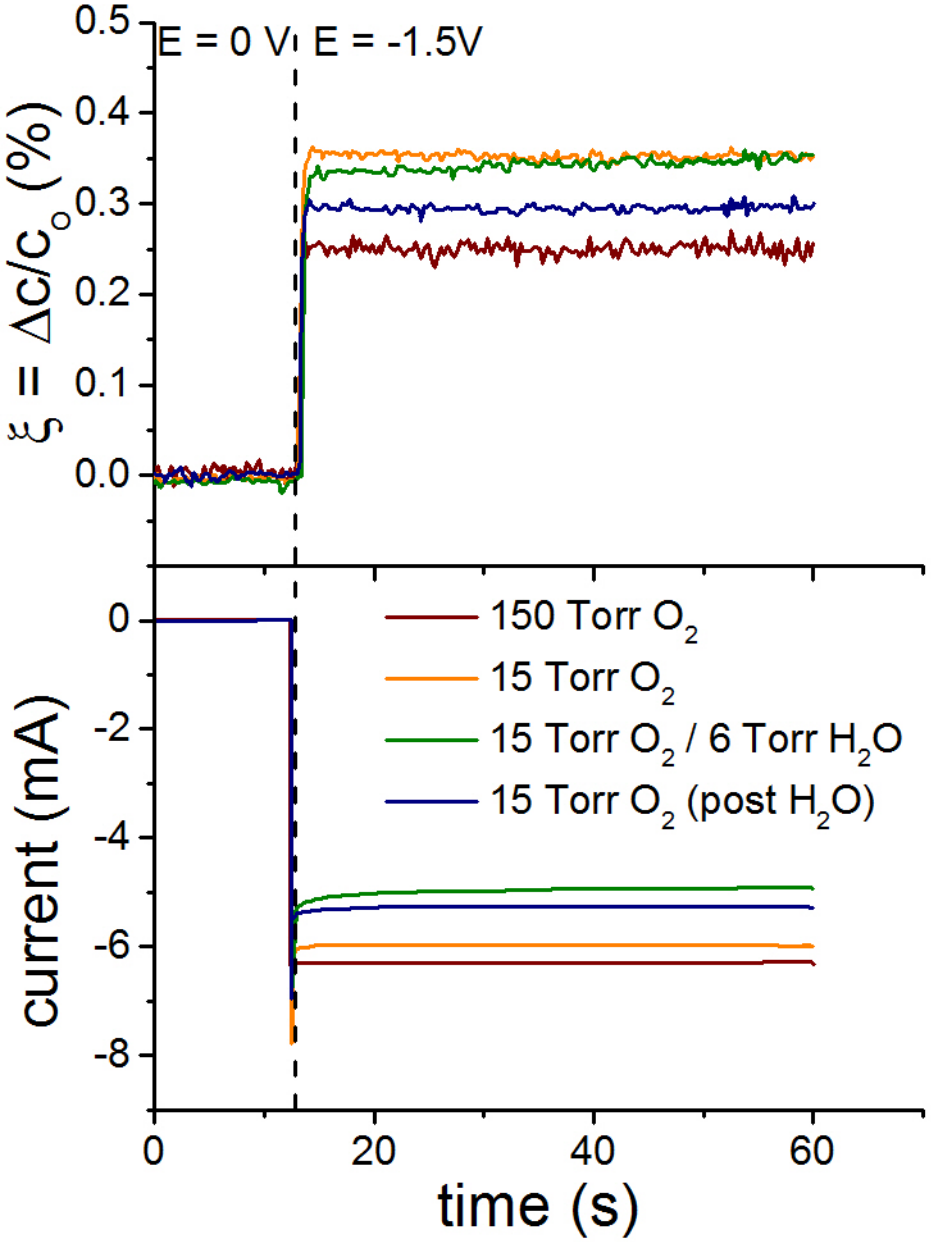
O_2 ↓ current ↓ c-shift ↑

CO_2 ↑ current ↓ c-shift ↑

CO_2 permanently poisons the surface

Carbonate formation is possible, including strontium segregation

Effect of H_2O on lattice strain / current (650°C)



The ORR behavior after introduction of H_2O is less clear than CO_2 environments

- electrochemical current decreases
- lattice shifts are less affected

O_2 ↓ current ↓ c-shift ↑

H_2O ↑ current ↓ c-shift ↔

Effects on ξ and electrochemical current are reversible (partially)

On going effort is underway to establish enhanced analytical approaches

Consider assumption that the buried interface is unchanged

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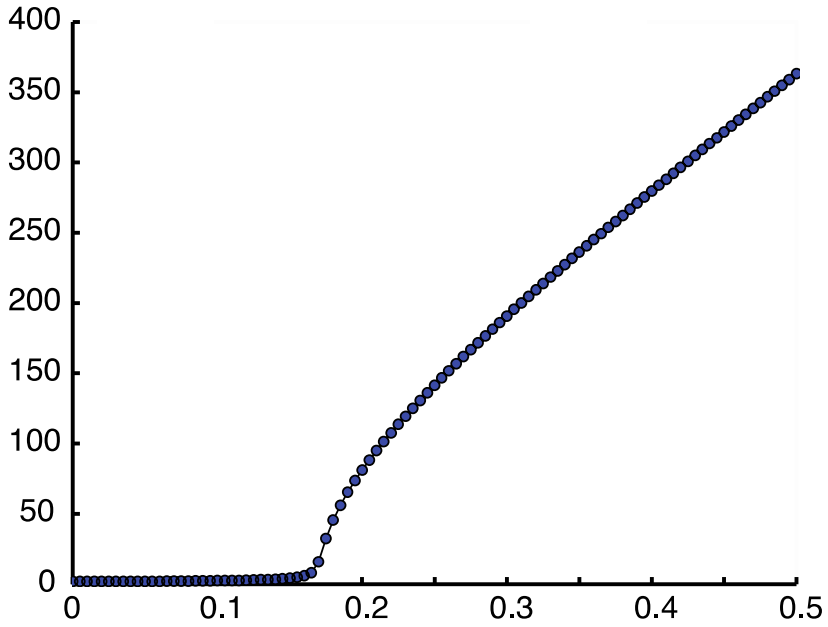
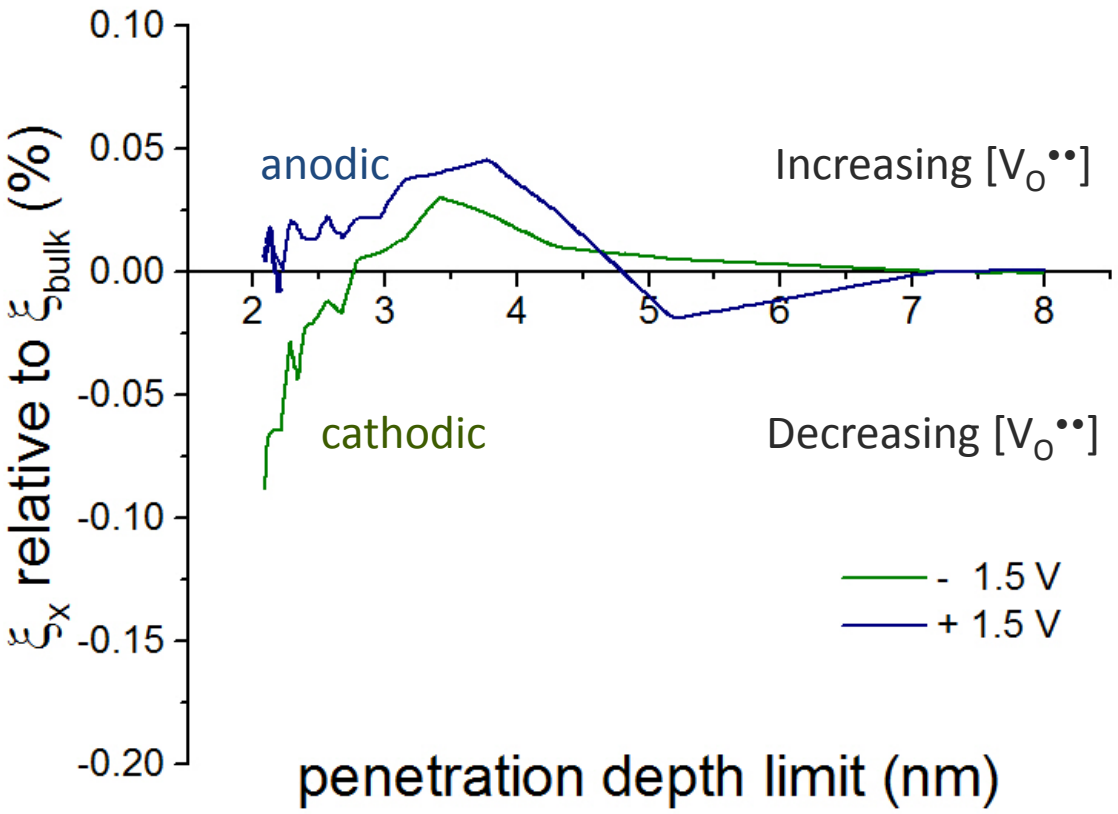
Depth Resolved Lattice Parameter (O_2 Vacancies)

By varying the x-ray angle of incidence, the lattice parameter (and, indirectly, the oxygen vacancy concentration) can be determined as a function of location in the film.



Depth resolved lattice parameter: pO_2 effect



T = 500 °C

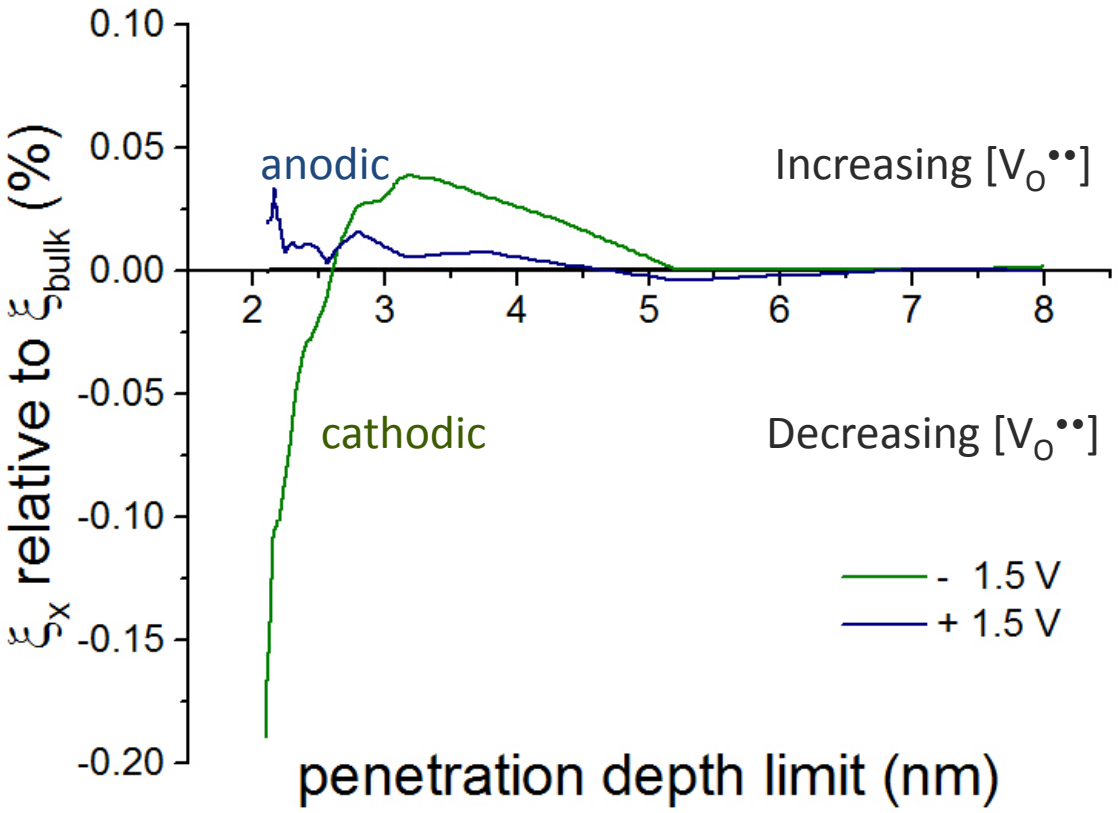
pO_2 = 150 Torr

$\xi = \Delta c/c_o$

Cathodic potential: $V_O^{\bullet\bullet}$ are annihilated at the surface → lattice contraction at the surface; increase in near surface [$V_O^{\bullet\bullet}$] relative to the bulk

Anodic potential: $V_O^{\bullet\bullet}$ created at the surface → lattice expansion at the surface

Depth resolved lattice parameter: pO_2 effect



T = 500 °C

pO_2 = 15 Torr

$\xi = \Delta c/c_o$

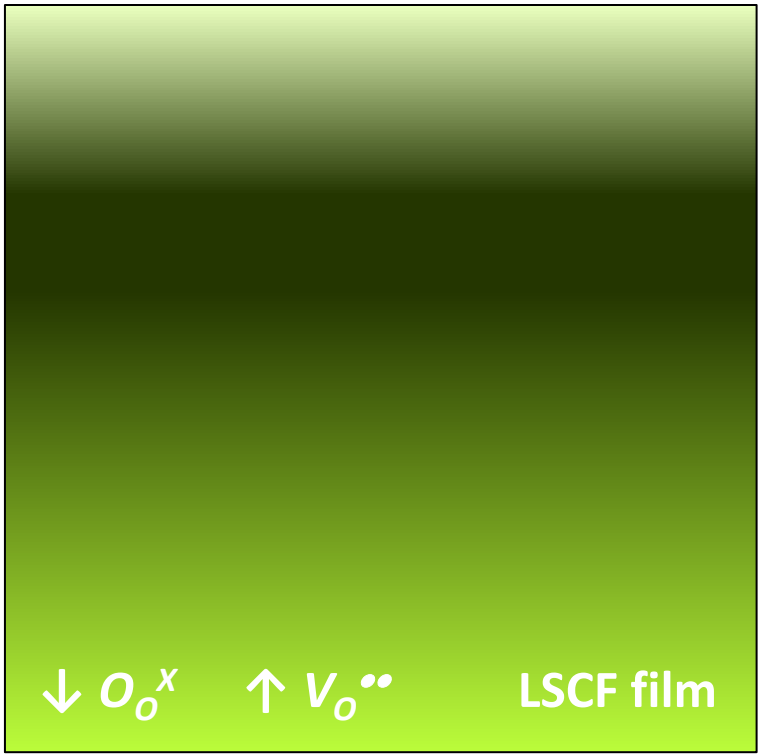
Cathodic potential: $V_O^{\bullet\bullet}$ are annihilated at the surface → lattice contraction at the surface; increase in near surface [$V_O^{\bullet\bullet}$] relative to the bulk

Anodic potential: $V_O^{\bullet\bullet}$ created at the surface → lattice expansion at the surface

Depth resolved lattice parameter: pO_2 effect

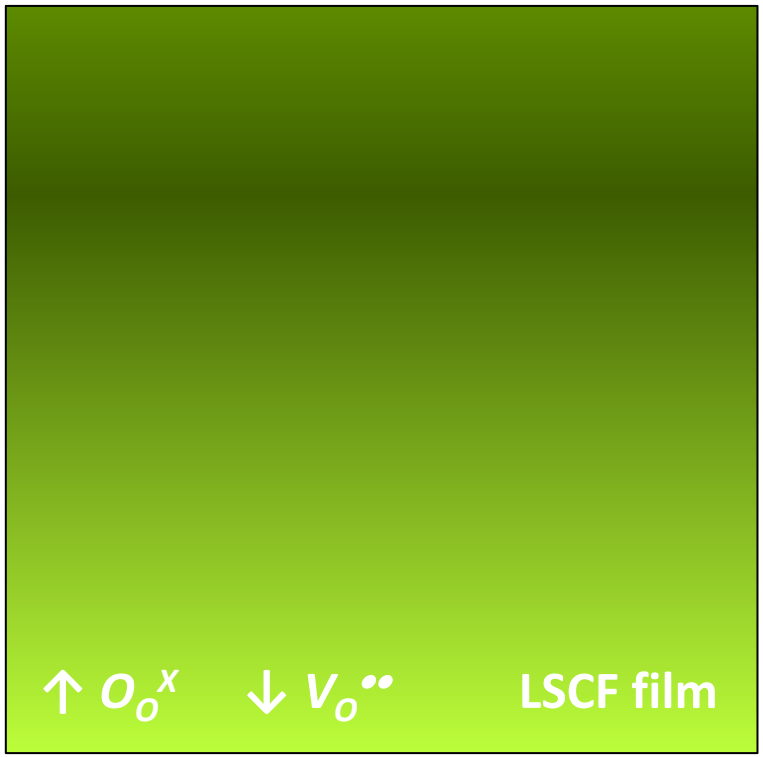
Cathodic condition

$O_{2(g)} + 2V_O^{\bullet\bullet} \rightarrow 2O_O^x$

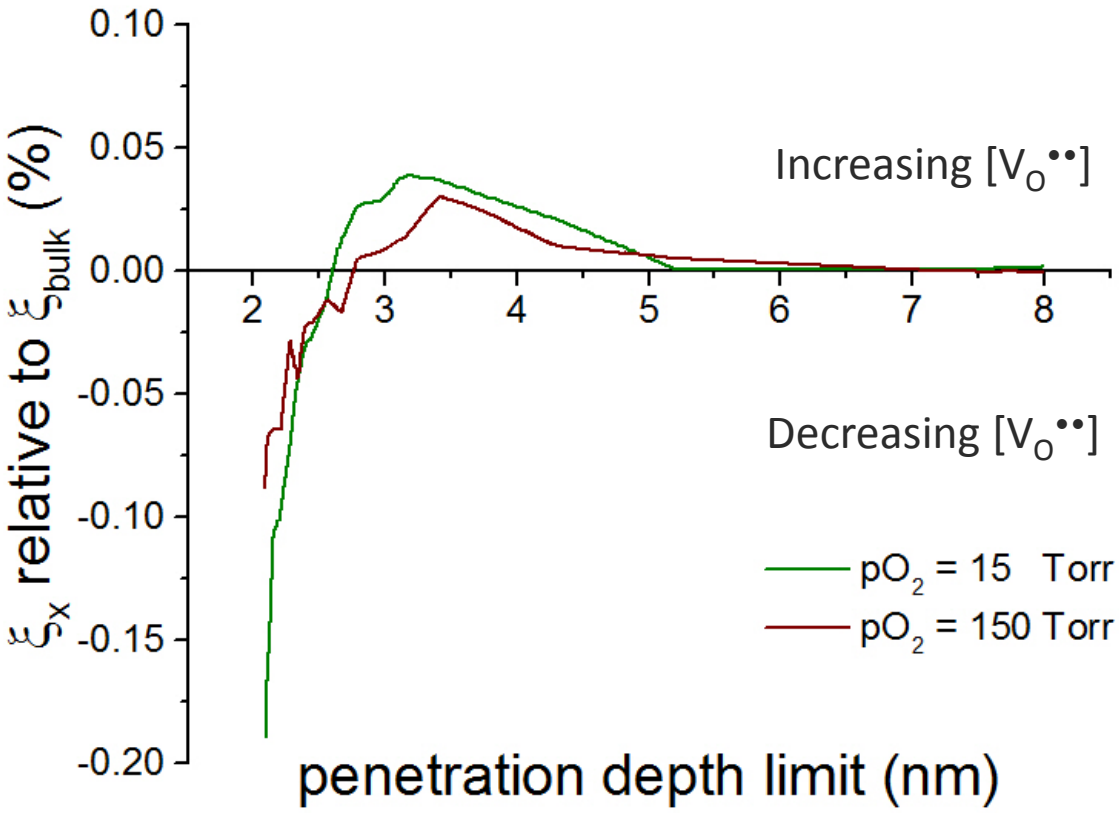


Anodic condition

$2O_O^x \rightarrow O_{2(g)} + 2V_O^{\bullet\bullet}$



Depth resolved lattice parameter: pO_2 effect



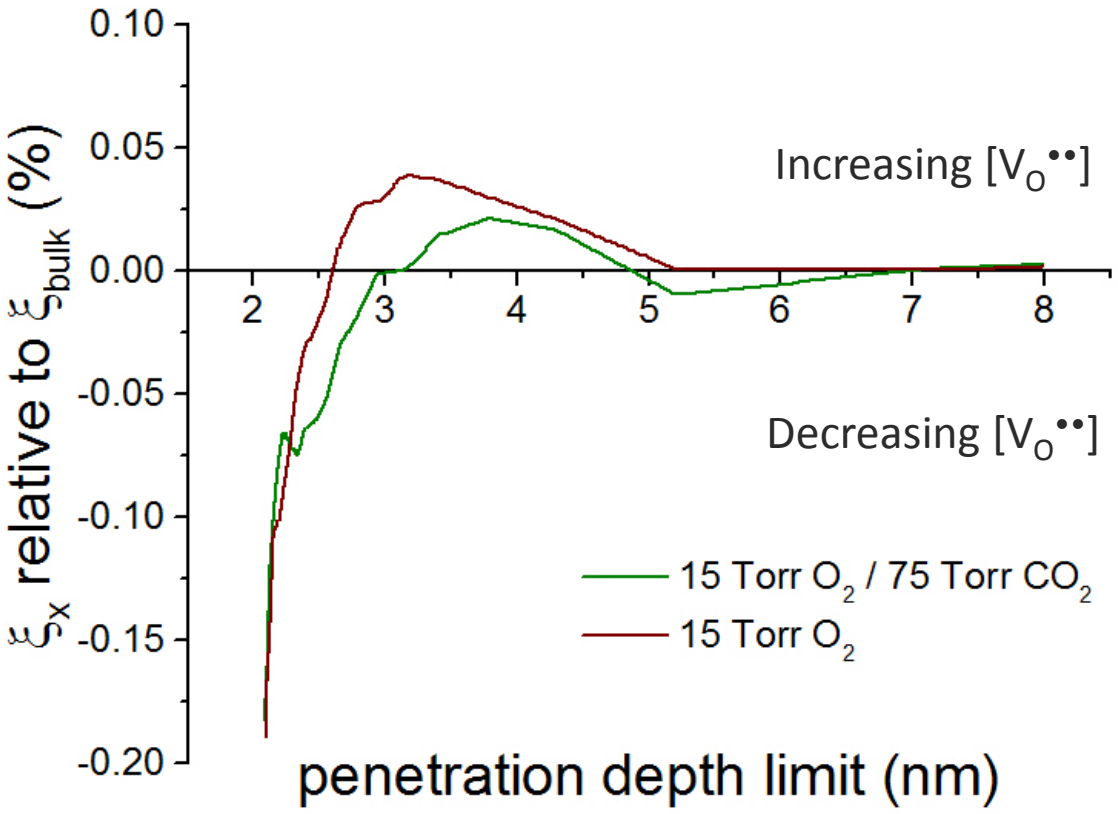
T = 500 °C
E = -1.5 V (cathodic)

$\xi = \Delta c/c_o$

As previously reported, reducing atmospheres (low pO_2) results in higher increases in bulk $[V_O^{\bullet\bullet}]$, i.e., limit the ORR.

General $[V_O^{\bullet\bullet}]$ distribution with applied cathodic potential is similar at pO_2 conditions.

Depth resolved lattice parameter: CO_2 effect



T = 500 °C

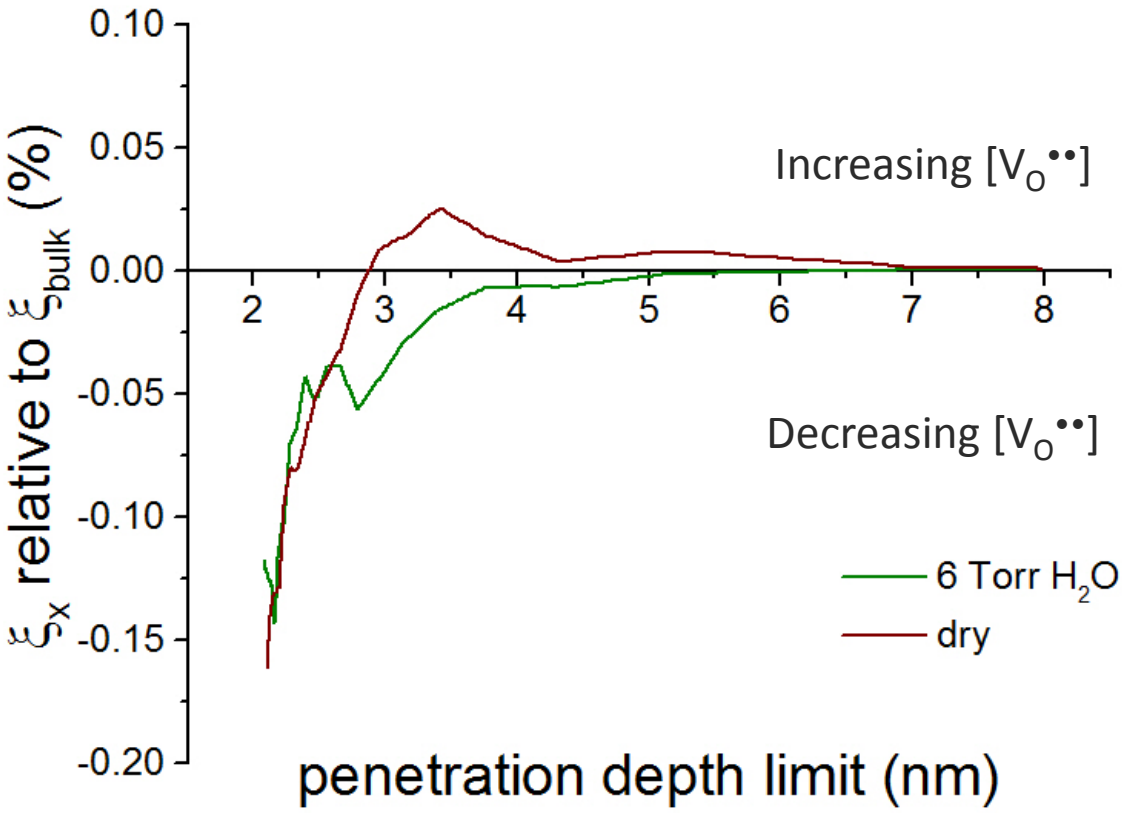
E = -1.5 V (cathodic)

$\xi = \Delta c/c_o$

As previously established, CO_2 degrades the ORR performance, increased bulk [$V_O^{\bullet\bullet}$]

Distribution of $V_O^{\bullet\bullet}$ is similar between CO_2 and pure O_2 conditions, suggesting the conduction mechanism is similar to pure O_2 conditions

Depth resolved lattice parameter: humidity effect



T = 500 °C

E = -1.5 V (cathodic)

$\xi = \Delta c/c_o$

Observe $[V_O^{\bullet\bullet}]$ depletion at the surface as typical

No enhancement layer observed suggesting altered conduction mechanism relative to dry gas

Results highlights

Utilized synchrotron x-ray to established understanding of SOFC cathode performance in several areas:

- Measurements of lattice parameter shifts are related to oxygen vacancy concentrations.
- Changes in $[V_O^{\bullet\bullet}]$ are controlled by changes in the gas phase composition
  - H_2O decreases current reversibly, alternative affect on lattice parameter changes
  - CO_2 degrades ORR and current irreversibly
- Depth profiling of the vacancy concentration through the film may yield new insight into the conduction mechanisms.

Thank you

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Questions?