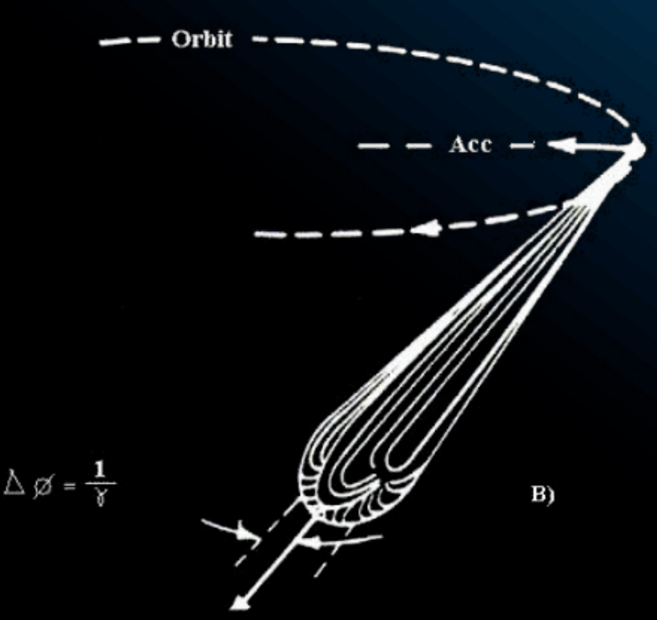

Studying Solid Oxide Fuel Cell Degradation:

An X-ray Absorption Spectroscopy Technique for Operating Conditions

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Why Solid Oxide Fuel Cells (SOFCs)?

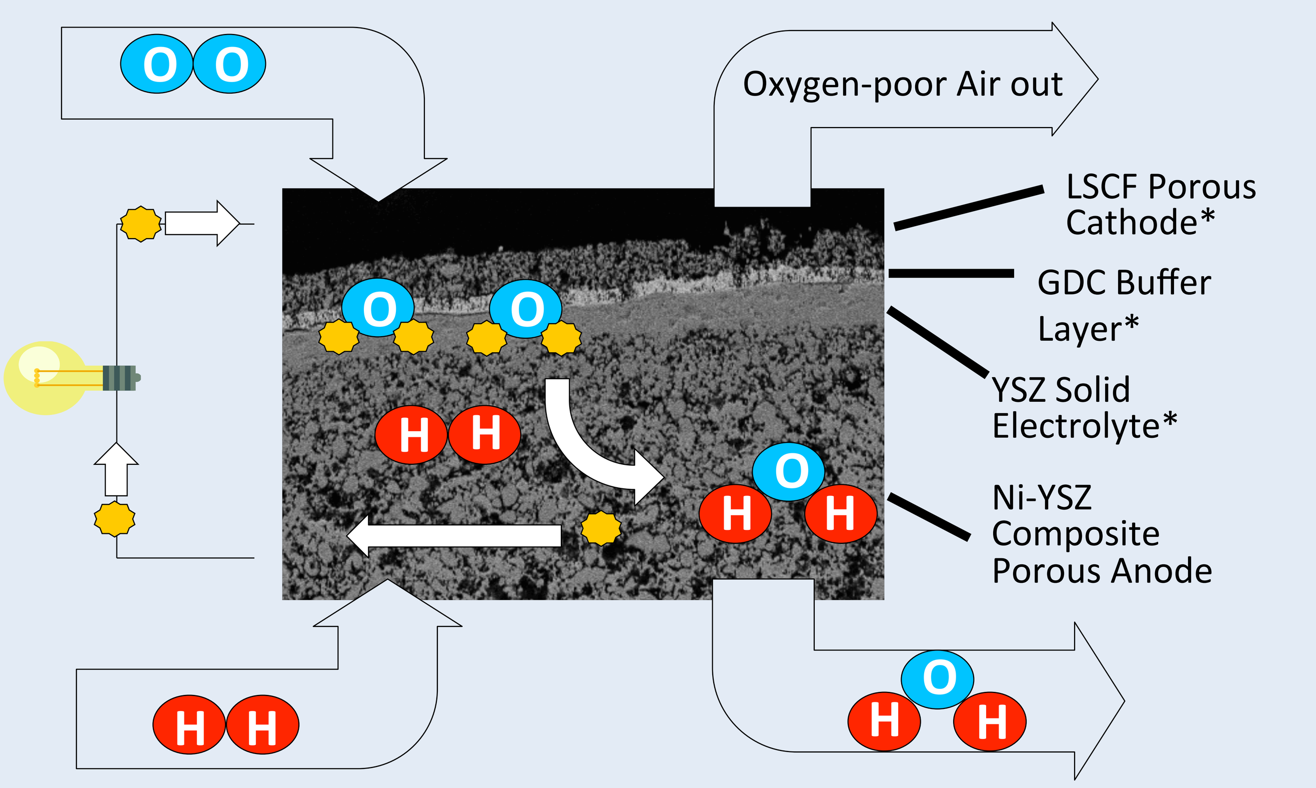
Advantages
- Powered by readily available fuels
- Superior efficiency to power plants
- Fuel-flexible with hydrogen

Barriers
- Degradation
- High cost of materials
- Harsh operating conditions

Design improvements necessary to improve performance and lower cost
- **Hampered by inability to observe SOFCs under operating conditions**

Solution: **a novel experimental apparatus to enable the monitoring of SOFC chemistry *during* the cell's operation.**

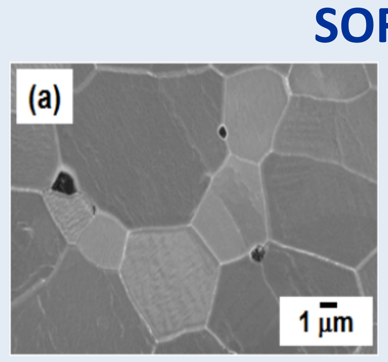
Solid Oxide Fuel Cells



SOFCs use porous, solid-state electrodes and electrolytes. Oxygen-rich air flows through the porous cathode, and hydrogen-rich fuel flows through the porous anode. Oxygen and hydrogen combine to form water and release electrons, which are used to power an external load.

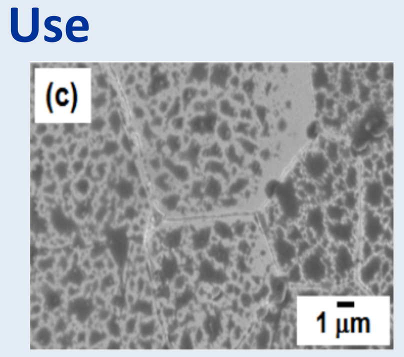
*LSCF = $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\pm\delta}$, YSZ = yttria-stabilized zirconia, GDC = gadolinium-doped ceria.

SOFC Degradation Under Use



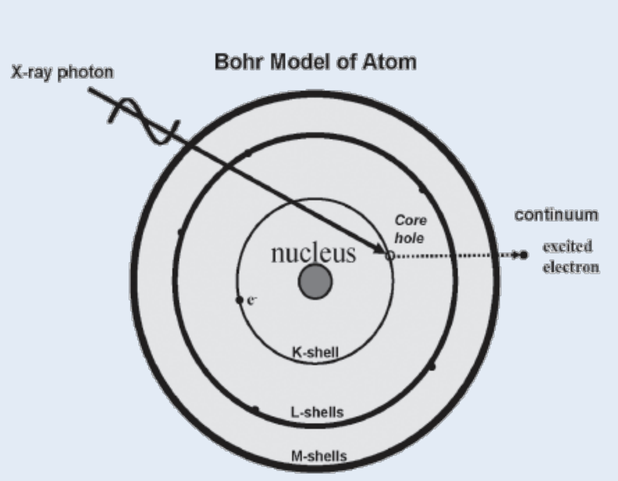
LSCF dense cathode before long-term annealing at 850°C.[1]

Degradation is a key, persistent barrier to SOFC feasibility and commercialization but it is difficult to understand the underlying mechanisms that dictate its processes.



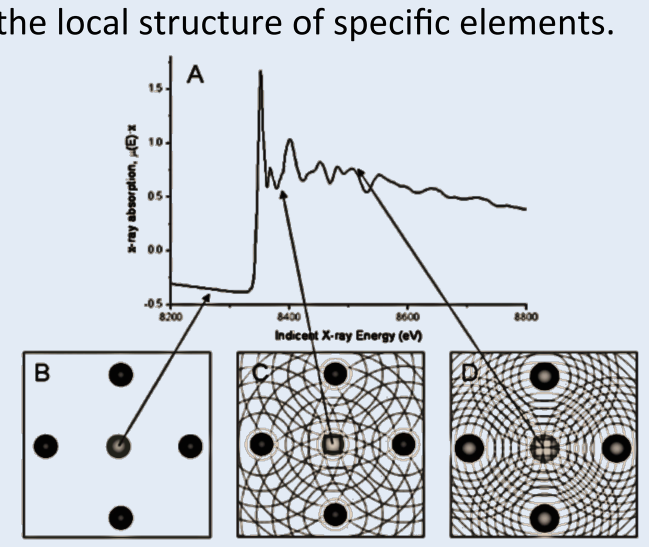
Degraded LSCF dense cathode after long-term annealing.[1]

X-ray Absorption Spectroscopy Fundamentals[2]

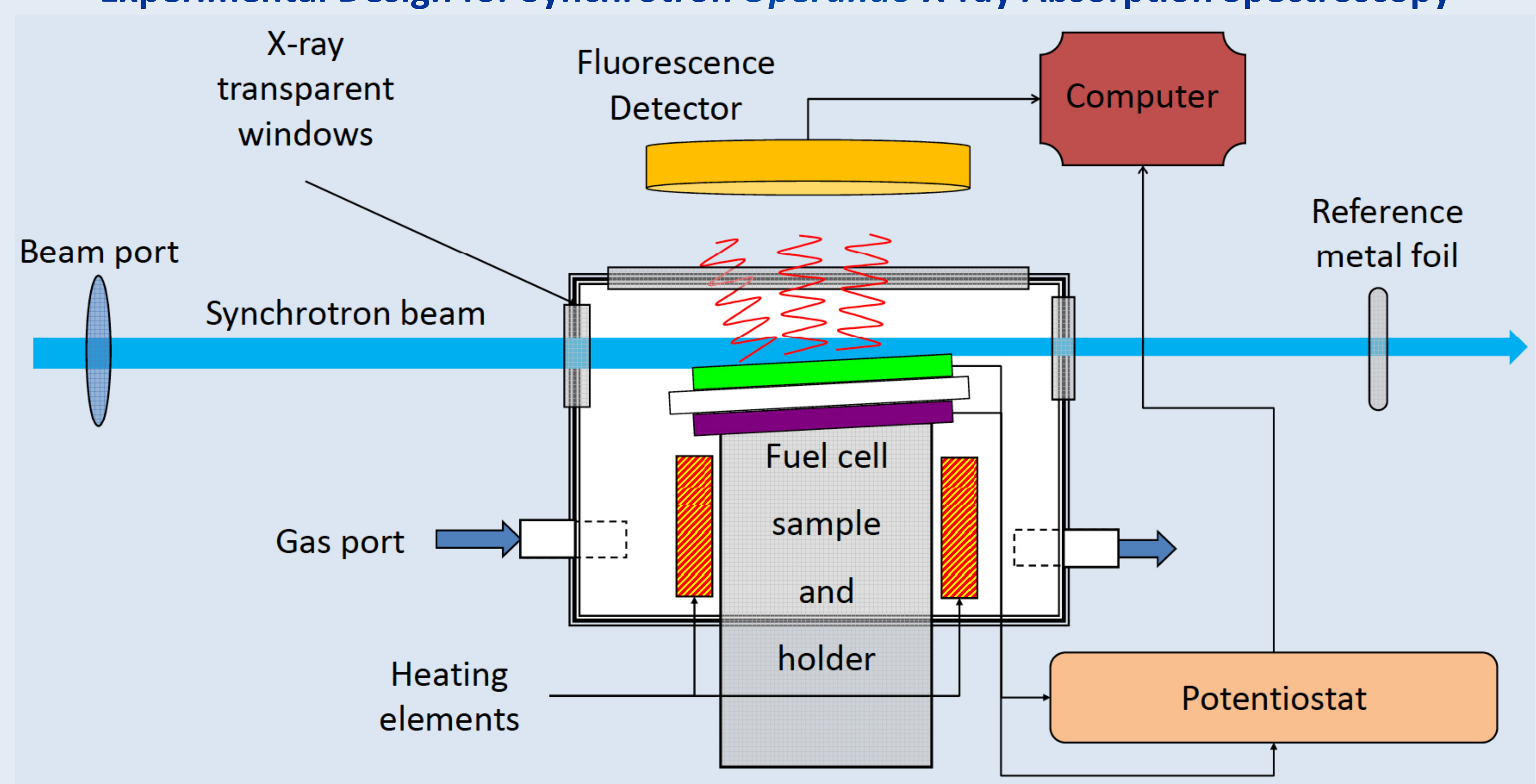


X-rays of varying energy excite core and valence shell electrons, causing X-ray absorption and fluorescence. The absorption energy reflects chemical and bonding effects on electrons.

Above the absorption energy, emitted photoelectron waves impinge on neighboring atoms and interfere to form standing waves that show differences in the local structure of specific elements.

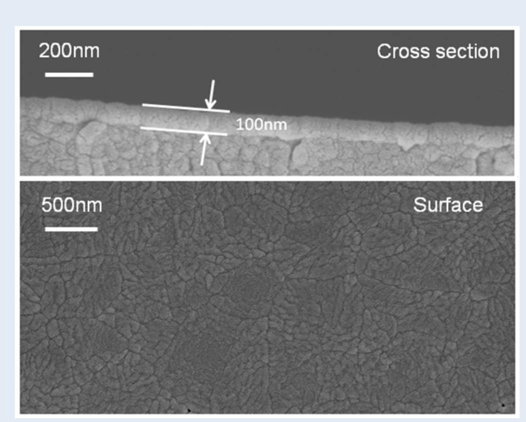


Experimental Design for Synchrotron *Operando* X-ray Absorption Spectroscopy



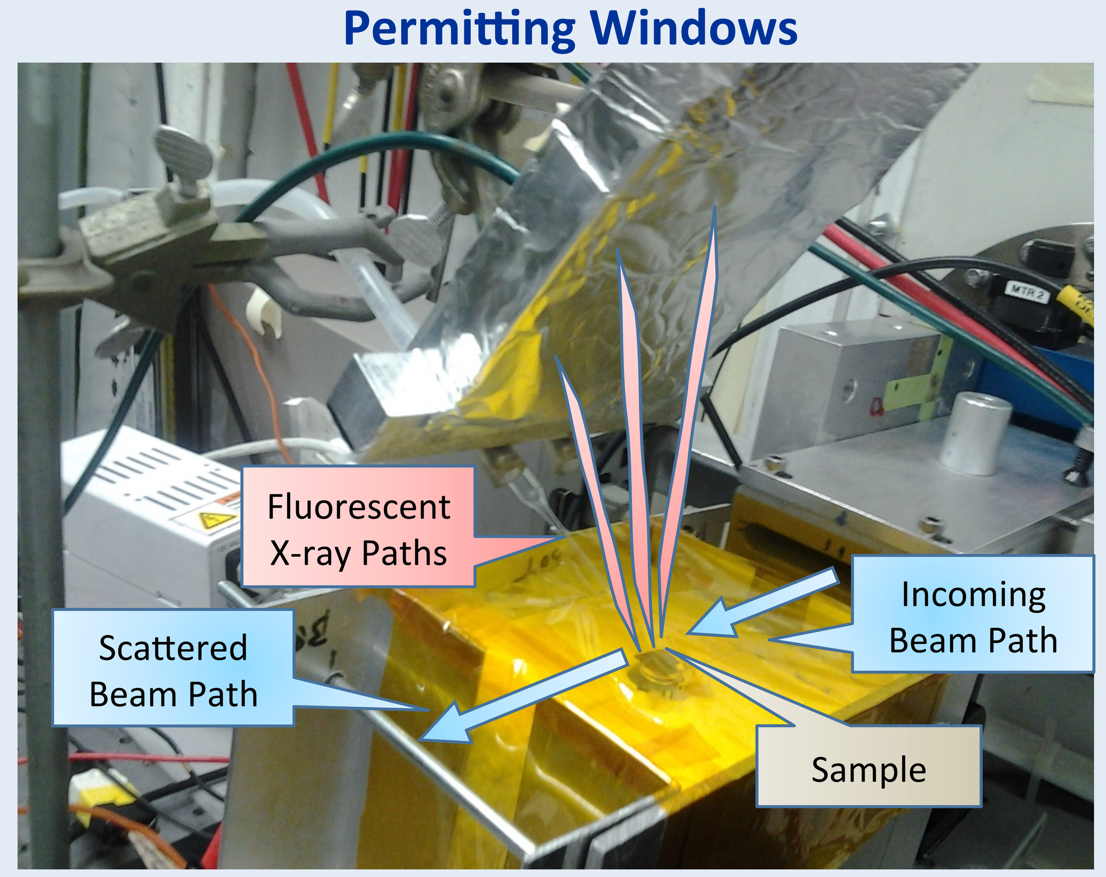
A unique, homemade, custom-designed testing assembly combined high temperature, gas atmosphere, and electrical polarization controls with X-ray characterization capabilities. The glancing angle limits the information depth to the top, near-surface and also allows energy referencing via measuring the X-ray transmission through the metal foil.

Example Cross-Section of Fuel Cell



An asymmetrical LSCF cathode cell was fabricated on a YSZ single crystal. The working electrode was a thin film of LSCF that was sputter-deposited and annealed at 500°C to form dense, uniform 100-nm layers. A thin film limits the gaseous reactions to the surface for more robust X-ray analysis.

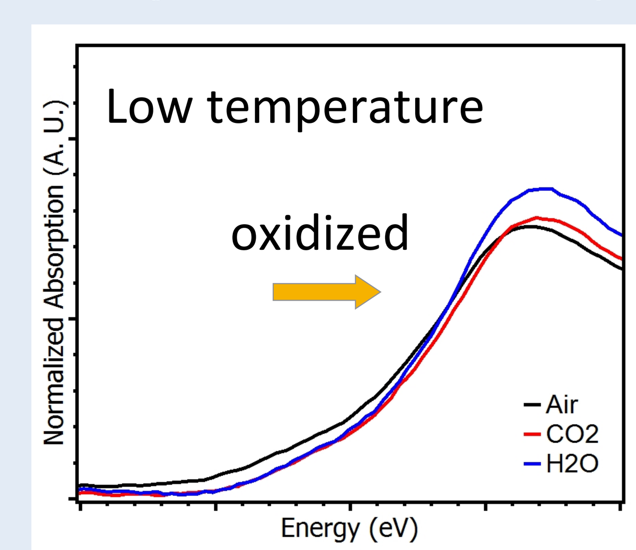
Custom-built Fuel Cell Furnace with X-Ray Permitting Windows



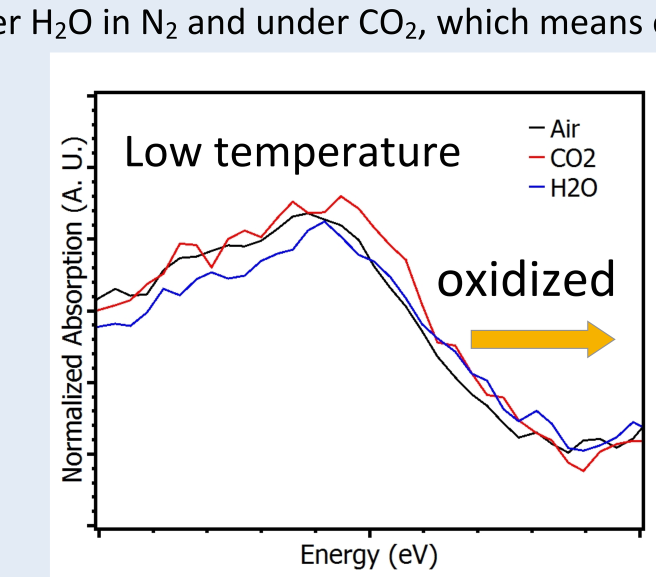
The unique, homemade, custom-designed testing assembly is shown in position for synchrotron X-ray analysis. The window material is Kapton, a polyimide film that is thermally stable and mechanically strong yet largely X-ray transparent. It also helps maintain a semi-controlled atmosphere above the sample.

Preliminary Key Results*

The combined effects of temperature, gas, and polarization to oxidize doped cations were only observed under *operando* conditions and were absent when individual parameters were tested, validating the need for this technique.



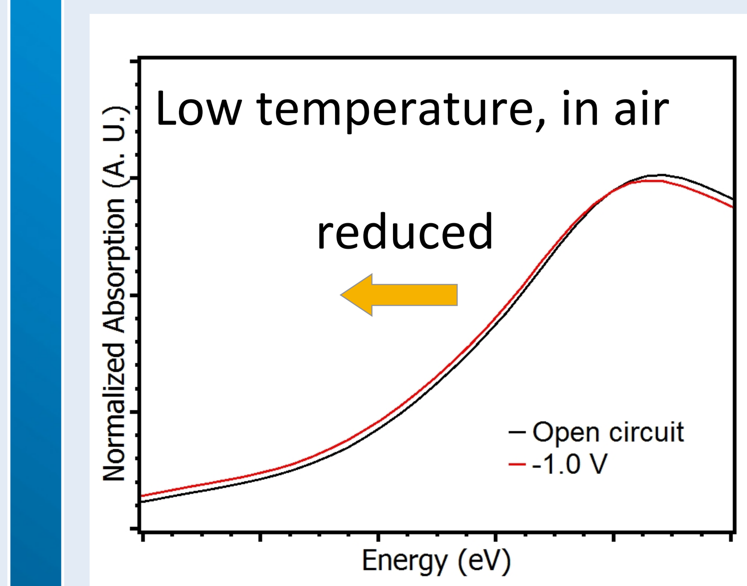
The cation absorption edge shifts to higher energy under H_2O in N_2 and under CO_2, which means oxidation.



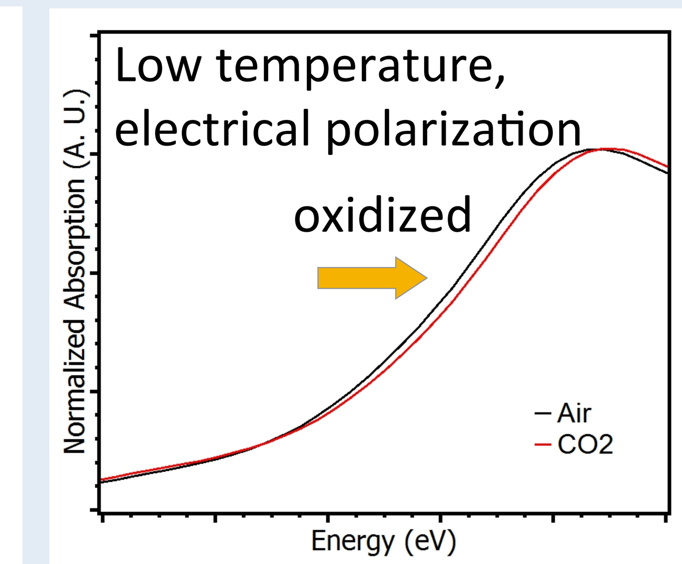
In the derivative plot, the cation absorption edge energy shift is more clearly seen, indicating oxidation under H_2O in N_2 and under CO_2.

* The results have been condensed to preserve the integrity of forthcoming publications.

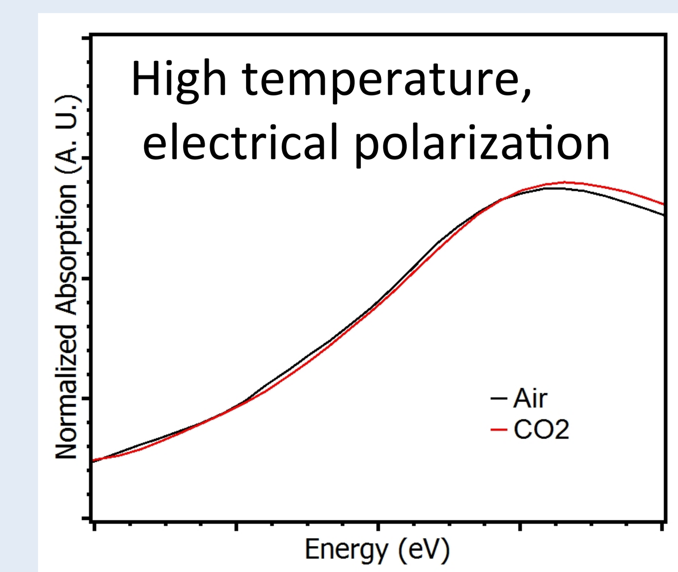
Additional Preliminary Key Results*



Negative electrical polarization causes reduction of the cation oxidation state.



The cation is oxidized by CO_2, dominating the polarization effect.



At high temperature and under -1.0 V polarization, the effects of CO_2 are neutralized, an observation only possible through *operando* spectroscopy.

Through *operando* experiments, the individual and combined effects of temperature, gas, electrical polarization, and gas contaminants can be isolated and observed.

- Carbon dioxide contamination strongly oxidizes the cations, indicating the formation of carbonates, which are suspected to be the cause of degradation.
- High temperatures provide oxygen vacancies that help neutralize CO_2's oxidative effects, but depletion of oxygen vacancies in long-term operation could lead to degradation.

Conclusions

- **Demonstrated an *operando* X-ray absorption spectroscopy test for analyses of a SOFC material under operating conditions**
- ***Operando* analysis allows for investigation of transient reactions that only occur under operating conditions, particularly those related to degradation by thermal aging and/or by contamination**

This technique will prove useful for future elucidation of SOFC chemistry, from which design principles can be derived, leading to better-performing, cost-effective SOFCs.

Future Work

- Analyze the extended X-ray absorption fine structure to identify changes to the cations' local structures as a function of contaminating gas, such as CO_2 and H_2O.
- Make use of synchrotron-generated soft X-rays to study the desorption temperatures of CO_2 and H_2O from LSCF.
- Apply *operando* technique to other types of novel SOFC electrodes.

Acknowledgements

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