Probing LSCF cathodes exposed to contaminants (H_2O, CO_2 & Cr) using surface enhanced Raman spectroscopy (SERS) and synchrotron-based X-ray analyses

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Introduction

- Cathode durability is crucial to long term SOFC performance of commercial development while The contaminants commonly encountered in air (e.g., H_2O and CO_2) and/or Cr-containing interconnect materials may activate or accelerate the degradation of LSCF cathodes.
- It is of importance to understand the effect of contaminants on LSCF cathode performance under realistic operating conditions.
- Well-designed electrochemical characterization is an effective approach to monitor the performance change of the LSCF cathode exposed to contaminants, ruling out the variation in the performance from cell to cell as well as the variation caused by other time-dependent degradation modes.
- SERS is very flexible in terms of having the largest tolerance under various measurement conditions and the greatest range of surface species of the LSCF cathode, such as hydroxide, carbonate, chromate that can be probed and mapped upon exposure to a variety of contaminants.
- *In situ* synchrotron-based XAS is powerful in probing the local atomistic and electronic structure under typical operating conditions, and it enables careful and definitive study of individual elements in an electrode in electrochemical systems.
- These characterization techniques may help us to unravel the degradation mechanism of the LSCF cathode, thus providing scientific basis for rational design of more efficient electrode materials and structures to mitigate the effect of contaminants.

Experimental

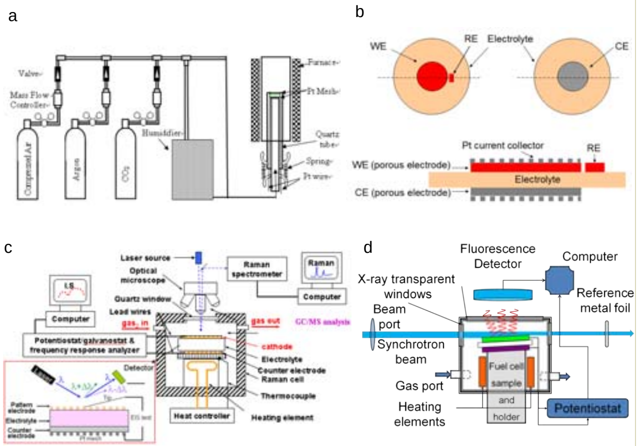

Figure 1. (a) A schematic of the electrochemical testing stand for symmetrical or asymmetrical cells exposed to H_2O and CO_2; **(b)** A LSCF-based symmetrical cell on YSZ electrolyte with three-electrode configuration; **(c)** An *in situ* configuration of Raman spectroscopy for the SOFC pattern electrode; **(d)** The design schematic of the *operando* testing assembly for X-ray analysis. The sample is slightly slanted so that the beam is close to a grazing angle. As a result, its information depth is limited and the beam can also be used for reference metal foil energy calibration;

Results and Discussion

1. Electrochemical behavior of the LSCF cathode exposed to H_2O, CO_2 and Cr

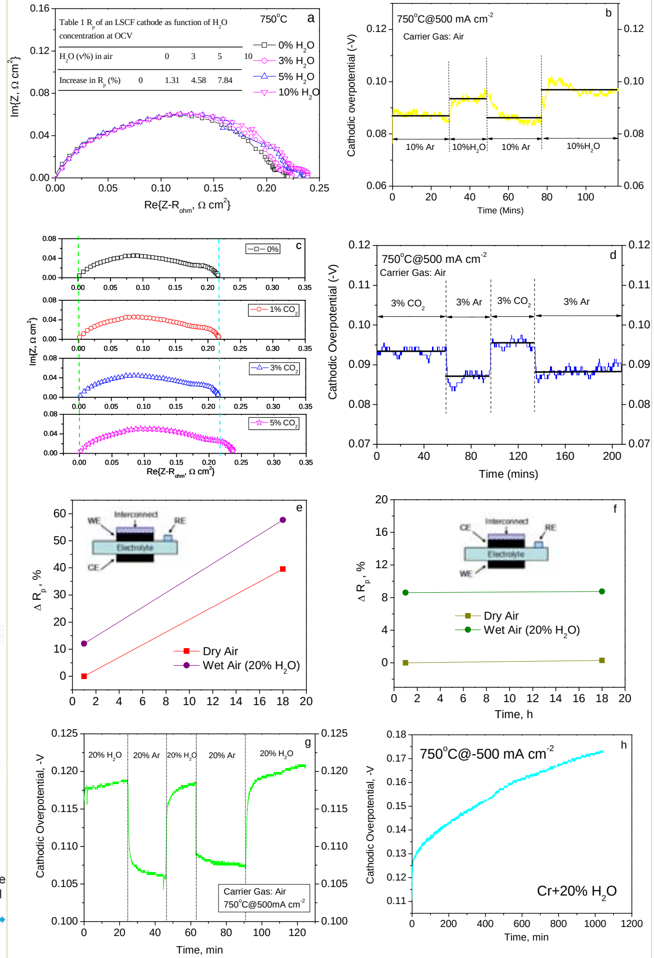

Figure 2. (a) The impedance spectra of the LSCF cathode in humidified air with different concentrations of water vapor (0, 3, 5, and 10%) under OCV; **(b)** Overpotential of the LSCF cathode in air with 10% of argon and H_2O at a constant current density of 500 mA cm^{-2}; **(c)** The impedance spectra of the LSCF cathode in humidified air with different concentrations of water vapor (0, 1, 3, and 5%) under OCV; **(d)** Overpotential of the LSCF cathode in air with 3% of argon and CO_2 at a constant current density of 500 mA cm^{-2}; Variation in Rp of an LSCF cathode in dry air and wet air (20% H_2O) with time under OCV condition for the electrode: **(e)** in direct contact with the interconnect and **(f)** away from the interconnect; Overpotential of the LSCF cathode in direct contact with the interconnect in: **(g)** air with 20% of argon and H_2O and **(h)** air with 20% H_2O at a constant current density of 500 mA cm^{-2}. All measurements were performed at 750^{o}C

2. SERS for the LSCF cathodes exposed to H_2O, CO_2 and Cr

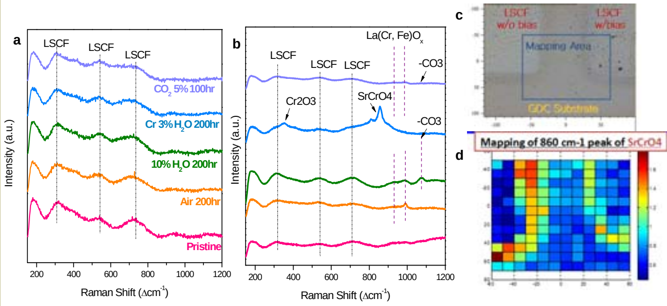

Figure 5. (a) Raman and **(b)** SERS analysis of the LSCF pellets annealed with a variety of contaminants. **(c)** and **(d)** The SERS mapping of the LSCF pattern electrode after Cr poisoning which showed the $SrCrO_4$ peak at 890 cm-1 concentrated on the LSCF-GDC boundaries.

3. synchrotron-based *operando* XAS for the LSCF cathodes exposed to H_2O and CO_2

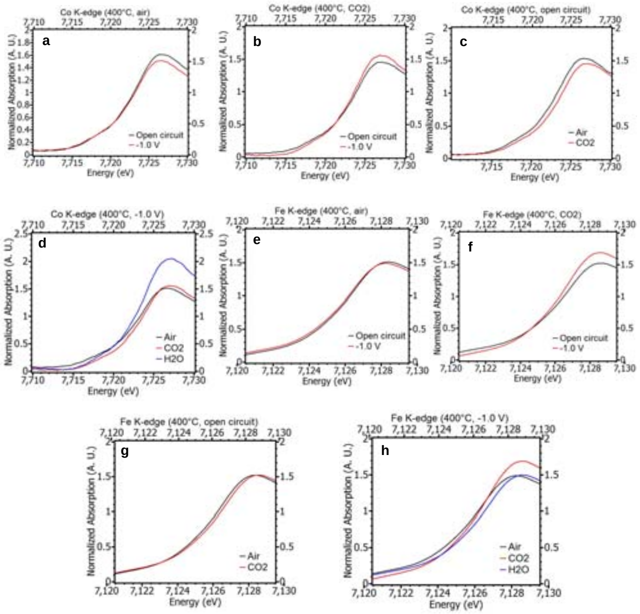

Figure 6. Co K-edge of the LSCF electrode under different atmospheres with different operational conditions at 400^{o}C: **(a)** in air; **(b)** in CO_2; **(c)** OCV; **(d)** -1.0 V. Fe K-edge of the LSCF electrode under different atmospheres with different operational conditions at 400^{o}C: **(e)** in air; **(f)** in CO_2;(g) OCV; **(h)** -1.0 V.

Acknowledgement

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