

## Introduction

- The contaminants commonly encountered in air (e.g., H<sub>2</sub>O and CO<sub>2</sub>) and/or Cr-containing interconnect materials may activate or accelerate the degradation of LSCF cathodes, thus degrading durability of SOFCs.
- Model cells with well-designed electrodes characterized using powerful surface analysis techniques such as surface enhanced Raman spectroscopy, and *in situ/operando* synchrotron-enabled X-ray adsorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) provided us with critical insights into the degradation mechanisms of the LSCF cathode, offering scientific basis for rational design of more efficient electrode materials and structures to mitigate the effect of contaminants.
- Proper surface modifications of LSCF cathodes through solution infiltrations are the most effective approaches to achieving durable and high-performing cathode at reasonable cost.

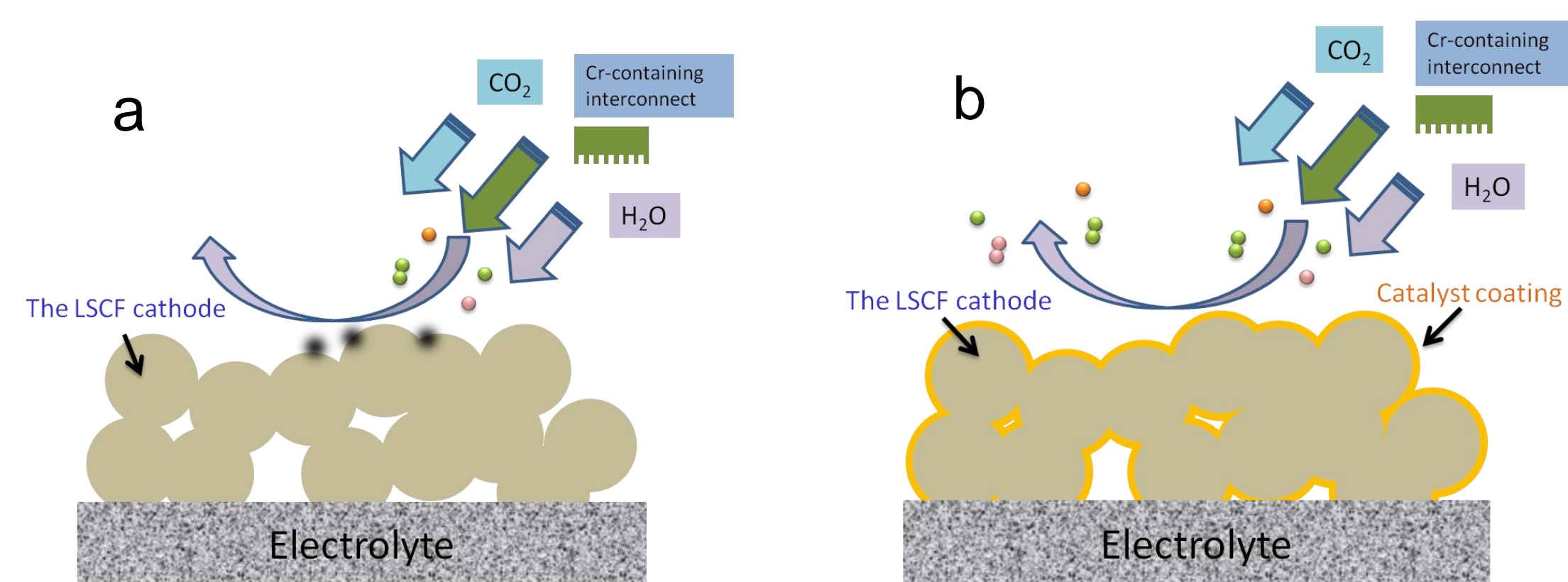


Figure 1. Schematic of (a) an LSCF cathode exposed to H<sub>2</sub>O, CO<sub>2</sub> and Cr-sources and (b) a surface-modified LSCF cathode exposed to H<sub>2</sub>O, CO<sub>2</sub> and Cr-sources.

## Experimental

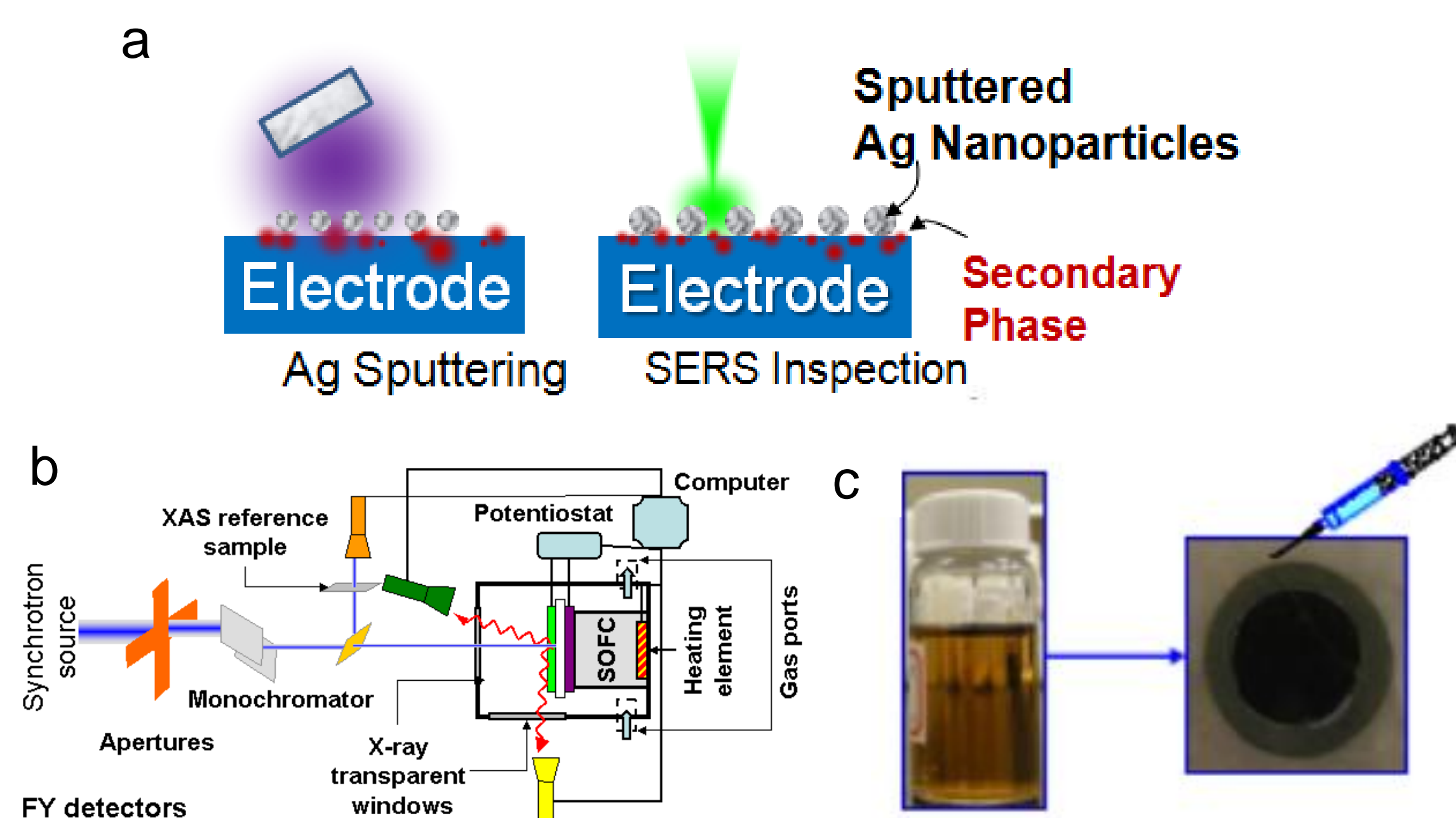


Figure 2. (a) A testing platform for surface enhanced Raman spectroscopy (SERS) to detect the species on the cathode surface exposed to a variety of contaminants; (b) *In situ* and/or *operando* synchrotron enabled X-ray technique for the present study; (c) A typical solution infiltration process to modify the surface of the cathode and mitigate the effects of the contaminants.

## Results and Discussion

### 1. Electrochemical characterizations coupled with a variety of surface analysis (SERS, synchrotron-based XAS & XPS)

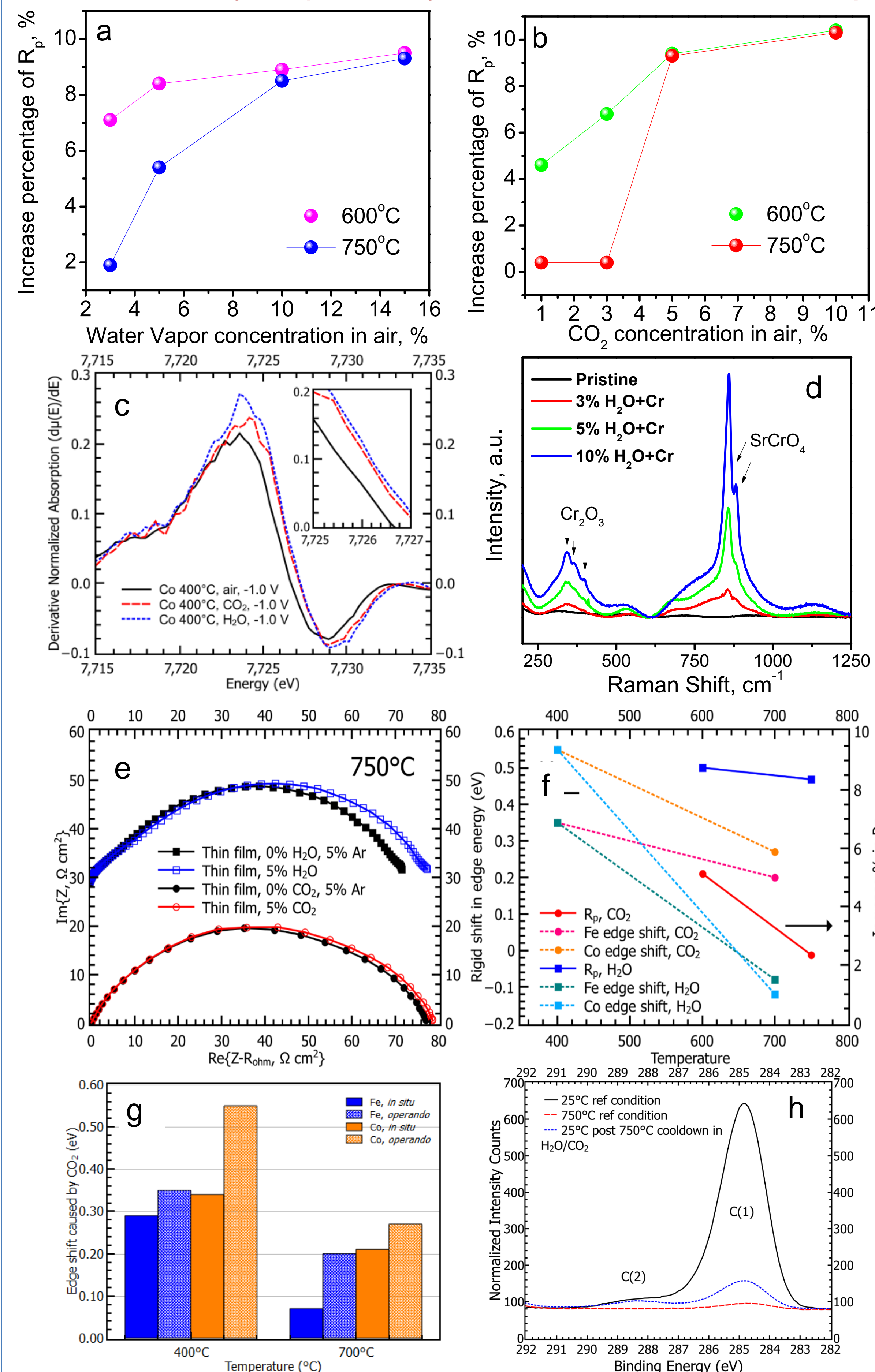


Figure 3. Increase in interfacial polarization resistance of the LSCF cathodes at 600 and 750°C, as measured under OCV conditions with different concentrations of contaminants: (a) H<sub>2</sub>O and (b) CO<sub>2</sub>; (c) Derivative of the near-edge absorption of Co at 700°C under cathodic bias while exposed to H<sub>2</sub>O and CO<sub>2</sub>; (d) post-SERS analysis of the LSCF electrode tested in contact with the Cr alloy at different H<sub>2</sub>O concentrations; (e) Impedance spectra of a thin film LSCF cathode show the increase in polarization resistance caused by H<sub>2</sub>O and CO<sub>2</sub>; (f) The correlation between performance, operating conditions, and rigid shifts in absorption edge energy; (g) Absorption edge shift in energy in both Fe and Co caused by the presence of CO<sub>2</sub> at 400°C and 700°C; (h) XPS of the as-prepared LSCF thin film at 25°C, and 750°C after cooling in an equal mixture of H<sub>2</sub>O & CO<sub>2</sub>.

### 2. Hypotheses about the degradation mechanism of the LSCF cathode exposed to contaminants

- H<sub>2</sub>O or CO<sub>2</sub> molecules may adsorb on the surface of the LSCF, which is more favorable at low temperatures while the total adsorption capacity of the LSCF cathode surface is independent of the temperature.
- The adsorbed species may bond to Co and Fe, and thus affect the valence of Co and Fe (especially Co). The bonding of H<sub>2</sub>O and CO<sub>2</sub> with Co in the LSCF cathode may reduce the surface oxygen vacancy concentration, and also impede the transport of oxygen species from the adsorption/dissociation sites to other active sites. These might be the main reasons for the observed reversible change in performance.
- The adsorbed species may react with segregated/enriched Sr to form hydroxide and then carbonate. At the same time, the carbonate may be more stable thermodynamically so that segregation is exacerbated at the presence of H<sub>2</sub>O and CO<sub>2</sub>. This could be the main reason for long term degradation.
- The degradation in performance is accelerated by Cr-poisoning due to the presence of Cr-containing materials in the testing apparatus. Our results indicated that the presence of H<sub>2</sub>O significantly exacerbated the degradation rate of the LSCF cathode in direct contact with a Cr-alloy, which may be associated with the following two causes: a) both H<sub>2</sub>O and CO<sub>2</sub> promote the formation of A-site deficiency which is very likely to accelerate the enrichment of Sr in LSCF (intrinsic degradation mechanism); b) the increased formation of Cr-containing surface species (e.g. SrCrO<sub>4</sub>) (extrinsic degradation mechanism).

### 3. Approaches to mitigate the degradation of LSCF cathode

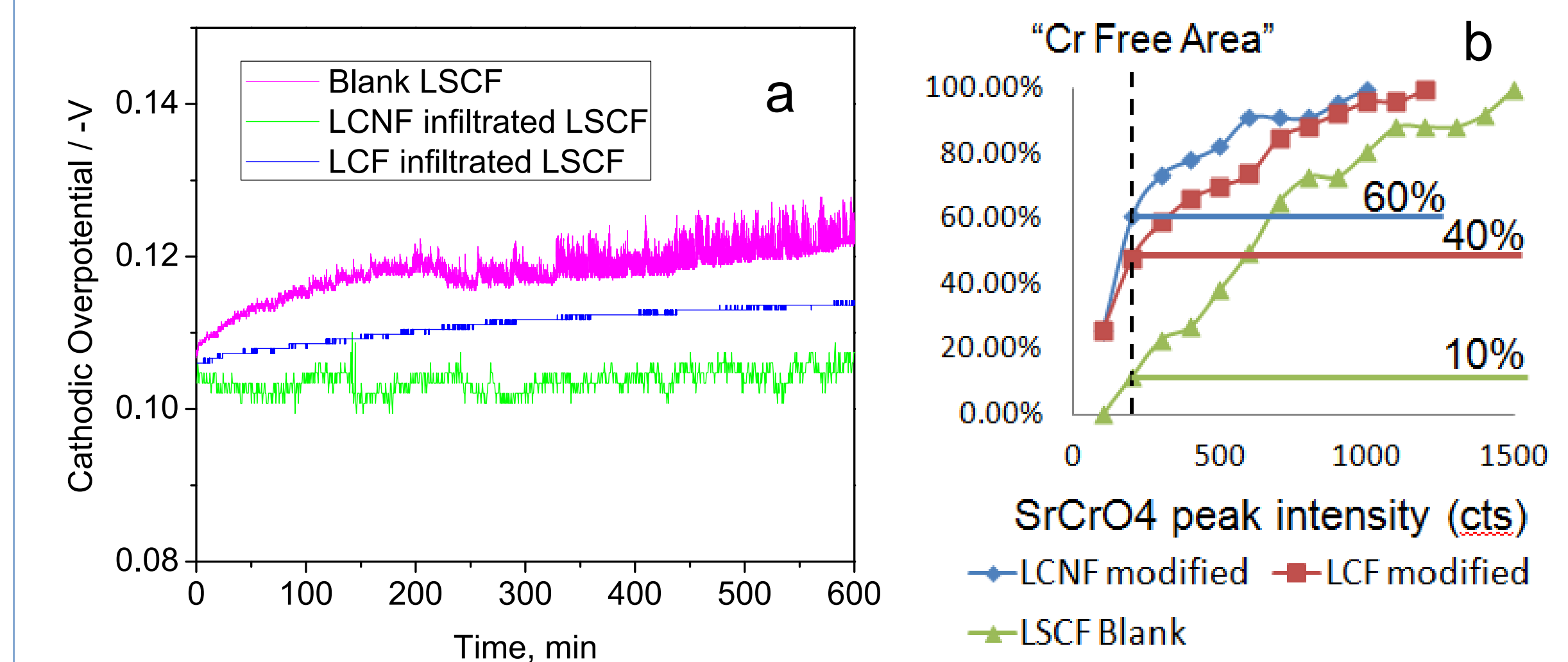


Figure 4. (a) Time dependence of cathodic overpotential of the blank LSCF and catalyst infiltrated LSCF cathodes in contact with Cr-alloy at 750°C at a constant voltage of 0.25 V when exposed to air containing 3% H<sub>2</sub>O and 1% CO<sub>2</sub>; (b) The cumulative percentage of sampled points as a function of SrCrO<sub>4</sub> band (857cm<sup>-1</sup>) intensity (in SERS) of the samples tested in (a).

## Acknowledgement

This work was supported by the US DOE SECA Core Technology Program under Grant No. FC-FE-0009652