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Invited review

ARTICLE

## Electronic Supplementary Information

# Controlling cation segregation in perovskite-based electrodes for high electro-catalytic activity and durability

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### Several *in situ* approaches for characterizing cation segregation

X-ray fluorescence spectrometry (XRF), which detects fluorescence emissions when X-rays are absorbed by atoms, is a surface-sensitive, non-destructive technique used for elemental analysis on the surface of materials.[1] The signature is irrelevant to the electronic state of an element, but rather is dependent on the relative concentration of an element.[2] Using *in situ* XRF, Fister *et al.* found evidence of reversible surface segregation in (001)-oriented $La_{0.7}Sr_{0.3}MnO_3$ thin films over a wide range of temperatures and oxygen partial pressures (Fig. S1).[3]

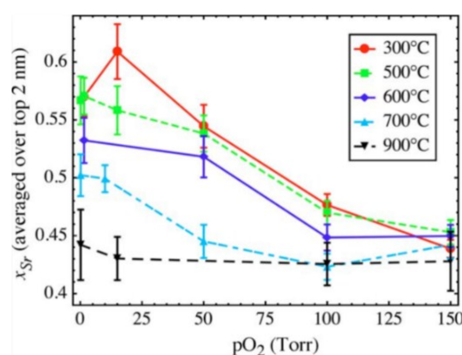


Fig. S1 Surface Sr content varies with oxygen partial pressure in $La_{0.7}Sr_{0.3}MnO_3$ thin films at T = 300 ~ 900 °C. Reprinted with permission from ref. 3. Copyright © 2008 American Institute of Physics.

Resonant soft X-ray reflectivity (RXR) is a non-destructive approach for the characterization of the structure and composition of thin films, multilayers, and buried interfaces.[4] Resonant anomalous X-ray reflectivity (RAXR) is a derived technique of RXR with the capacity of measuring composition profiles across surfaces and buried interfaces.[5] Using RAXR spectra, Perret *et al.* determined Sr distributions in $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ thin films at 973 K and 150 Torr oxygen partial pressure (Fig. S2a).[6] Information of elemental distribution at each layer can be fitted to match the measured data (Fig. S2b), which can then be further revised by crystal truncation rods (Fig. S2c). These results demonstrate that temperature dependent RAXR has the capacity to provide atomic scale insights into cation segregation behaviors at near operating conditions for SOCs.



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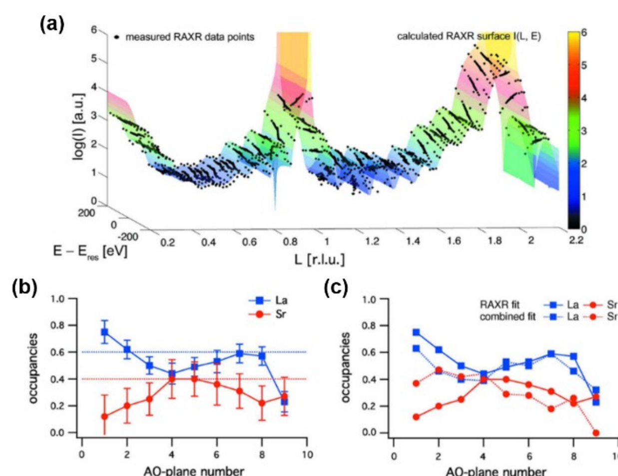


Fig. S2 (a) Fit of all measured RAXR data points at 973 K and 150 Torr oxygen partial pressure. (b) Sr and La distribution by fitting RAXR data. (c) A comparison of RAXR fitted elemental distribution (solid lines) and results from a non-resonant and a resonant crystal truncation rod (dotted lines). Reprinted with permission from ref. 6. Copyright © International Union of Crystallography.

*In situ* Raman spectroscopy has been used to characterize the reaction products of impurities in SOC electrodes, such as reacting with silicon or carbon deposition.[7, 8] The results can reflect the long-term durability of the electrodes of SOCs to a certain degree.[9] For example, Pomfret *et al.* used *in situ* Raman spectroscopy and found that butane, pyrolysis methane, ethylene, and propylene reacted with Ni/YSZ anodes to form a variety of carbon deposits which significantly affect anode performances above 700 °C and/or under electric polarization (Fig. S3).[10] More detailed reviews of the application of *in situ* Raman spectroscopy in the study of SOCs can be found in ref 8.

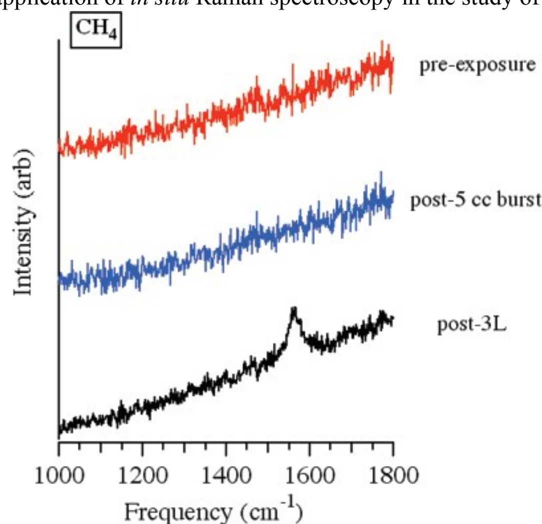


Fig. S3 Raman spectra of a Ni/YSZ porous anode which is pre-exposure to $CH_4$ (top), after exposure to 5 $cm^3$ of $CH_4$ (middle), and after exposure to 3 L of $CH_4$ (bottom). All measurements were made at open circuit voltage (OCV) and 715 °C. Reprinted with permission from ref. 10. Copyright © 2008 American Chemical Society.



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