

# High-temperature redox chemistry of Ruddlesden-Popper oxides monitored by *in situ* neutron diffraction and XANES under H<sub>2</sub> and O<sub>2</sub> flow

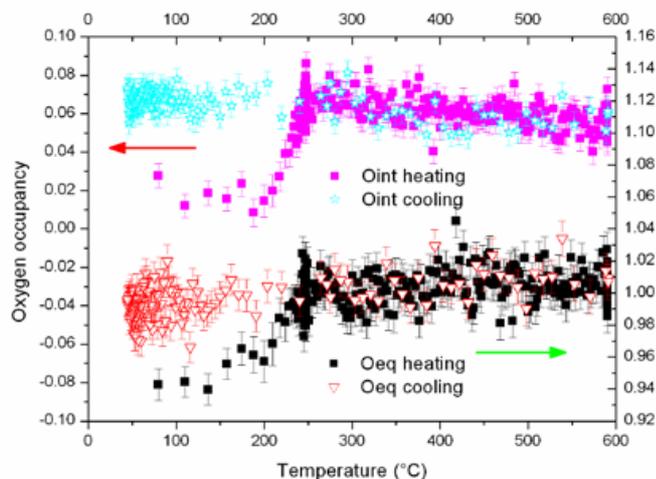


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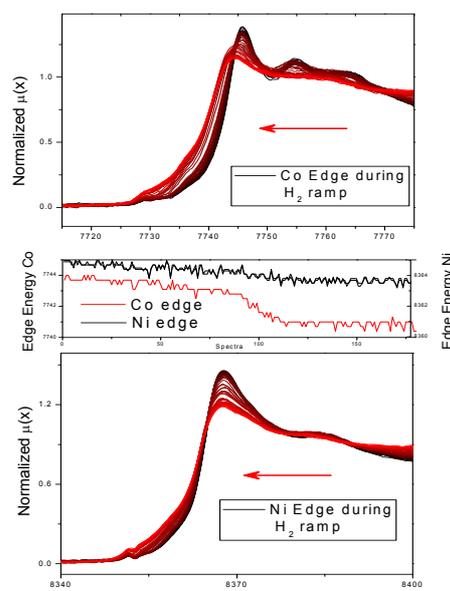
Solid oxide fuel cells (SOFCs) promise to improve energy efficiency in a range of fuels and to provide society with a clean energy producing technology. Recently, our interest has been focused on new Ruddlesden-Popper  $n = 1$  (*i.e.*  $K_2NiF_4$ -type) oxides  $Ln_{2-x}Sr_x(Cr,M)O_{4+\delta}$  ( $Ln = La, Pr, Nd$ ;  $M = Mn, Ni$ ) and  $(La,Sr)_2Co_{0.5+x}Ni_{0.5-x}O_{4+\delta}$  which sustain oxygen vacancies along with thermal stability under hydrogen [1,2]. A novel reaction cell has been designed for *in situ* neutron powder thermodiffraction studies under different gas flows. The structural behavior, particularly the disorder of the oxygen atoms, has been monitored *in situ* and in real time under H<sub>2</sub> and O<sub>2</sub> flow up to 800 °C, *i.e.* under the working conditions of a SOFC (instrument D20, ILL/Grenoble). Sequential Rietveld refinements showed, for the stoichiometric Cr-based compounds, deintercalation of oxygen from the equatorial site ( $O_{eq}$ ) with retention of the structural symmetry. Conversely, in the “Co,Ni” analogues which exhibit excess oxygen ( $\delta > 0$ ), deintercalation of oxygen from the interstitial positions ( $O_{int}$ ) proceeds first followed by removal of  $O_{eq}$  thus inducing progressive rotation of the transition-metal polyhedra around the  $c$ -axis. Moreover, in these reduced compositions, the  $O_{int}$  site appears surprisingly not completely emptied raising questions about the conduction mechanism.



Sequential Rietveld refinements of the *In situ* neutron diffraction data under O<sub>2</sub> flow reveal the sequence in which the equatorial ( $O_{eq}$ ) and interstitial ( $O_{int}$ ) oxygen sites refill in  $La_{1.7}Sr_{0.3}Co_{0.5}Ni_{0.5}O_{4+\delta}$

The Maximum Entropy Method revealed the details of the average nuclear density distribution and identified possible anisotropic diffusion pathways at the highest temperature reached.

Redox cycles under H<sub>2</sub> and O<sub>2</sub> gas flow, monitored *in situ* by XANES (instrument SAMBA, SOLEIL/Saclay) between 298 and 800°C, highlighted the active cations and showed the sequence in which the Co and Ni ions react. From the isothermal data, the rate of redox reactions of representative materials has been evaluated.



XANES for  $La_{1.6}Sr_{0.4}Co_{0.8}Ni_{0.2}O_{4+\delta}$  under H<sub>2</sub> flow reveals that Co is mainly involved in the reduction while Ni is only partially reduced. Moreover, for Co two reduction steps are clearly visible

The reduced phases are stable in air at RT and exhibit excellent thermal stability under H<sub>2</sub> (up to at least 800°C for the Cr-based compositions), thus opening the door to chemical tuning of the physical properties for use as electrode materials in solid oxide fuel cells.

1. F. Tonus, M. Bahout, P. F. Henry, S.E. Dutton, T. Roisnel, P. D. Battle, Chem. Commun. 18 (2009) 2556
2. F. Tonus, C. Greaves, H. El Shinawi, T. Hansen, O. Hernandez, P. D. Battle and M. Bahout, J. Mater. Chem, 2011 (in Press)