TAILORING NON-STOICHIOMETRY AND MIXED IONIC-ELECTRONIC CONDUCTIVITY IN NANOSTRUCTURED Pr-SUBSTITUTED CERIA

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High concentrations of mobile oxygen vacancies are crucial for devices such as SOFCs, SOECs, gas permeation membranes, and sensors, while for other applications such as ferroelectrics and piezoelectrics, oxygen vacancies are detrimental. Hence there is great interest in tailoring the oxygen vacancy concentration and mobility for given materials. Changes in oxygen non-stoichiometry also result in dilation of the crystal lattice, known as chemical expansion, and therefore there is a coupling between the electrical, chemical, and mechanical properties known as *electro-chemo-mechanical coupling*. Confined systems, such as thin films, are being investigated as a way to tailor the non-stoichiometry and transport properties of materials, shifting the paradigm away from searching for new materials or compositions.

Pr substituted CeO_2 (PCO) is an excellent model mixed ionic-electronic conductor (MIEC) for fundamental studies. In high pO_2 conditions, vacancy formation is accompanied by the reduction of Pr^{4+} to Pr^{3+} and the material displays MIEC behavior via oxygen vacancy migration and small polaron electron hopping between the valence-active cations. PCO has been extensively studied, and the defect chemistry, chemical expansion, and transport properties are well described in the bulk material.[1,2] Also, measuring the optical absorption has been demonstrated as a powerful tool for monitoring non-stoichiometry in PCO.[3] This makes it an excellent choice for studying the interplay of strain, space-charge, and electro-chemo-mechanical coupling effects at homogeneous and heterogeneous interfaces, including their impact on transport properties.

In this contribution, we demonstrate how non-stoichiometry and transport properties can be modified in PCO for three nanostructured systems: (1) nano-granular polycrystalline films, (2) multilayers of PCO and $SrTiO_3$, (3) vertically aligned nano-composites (VANs). Each system was fabricated by pulsed laser deposition and comprehensively analyzed by using high-resolution X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy combined with electron energy loss spectroscopy.

In this work we measure both the optical absorption and conductivity *in-situ* as a function of pO_2 and temperature to deconvolute and extract the concentration of charge carriers and their mobility in the nanostructured materials. This contribution not only provides crucial insights into the way grain boundaries and interfaces affect electro-chemo-mechanical coupling, but also demonstrates a variety of routes in which mixed ionic-electronic conductivity can be tailored for a range of different device architectures.

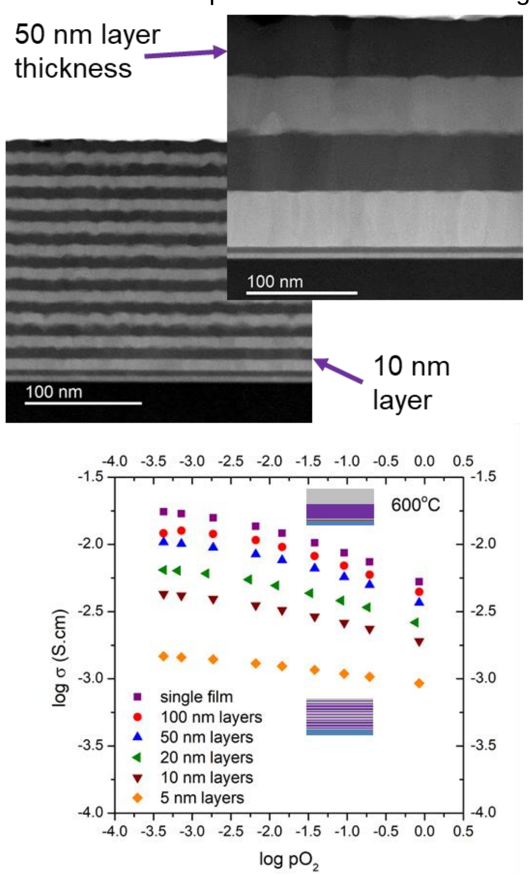

Figure 1 – STEM images of PCO/ $SrTiO_3$ multilayers. Conductivity as a function of pO2 and layer thickness

References:
[1] Bishop, et al., Phys. Chem. Chem. Phys. 13 (2011) 10165
[2] Bishop, et al., J. Eur. Ceram. Soc. 31 (2011) 2351
[3] Kim, et al., Chem. Mater. 26 (2014) 1374