Much Ado About Nothing: Tailoring the concentration and mobility of oxygen vacancies in non-stoichiometric oxides for electrochemical devices

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Traditionally, the search for new electrolytes and electrodes for SOFCs/SOECs with improved properties has been focused on compositional tuning and the search for new functional oxides. Recently, there has been increasing interest on the interplay of the chemical, electrical, and mechanical properties in electroceramic materials, referred to as *electro-chemo-mechanics*. This approach may offer a route to better than state-of-the-art SOFC/SOEC materials making use of composites, nanoscale design, and engineered interfaces. In this presentation, I will examine rare-earth substituted ceria as an excellent model material to study these effects, and present key findings which may lead to electrolytes and electrodes with enhanced functional properties.

Perturbing the crystal lattice away from the equilibrium structure via an applied lattice strain has been investigated from some time as a method to realise considerable improvements in oxygen-ion conductivity. Interest in this approach has, however, waned over recent years for two primary reasons: (i) a lack of consistency and reproducibility in the reported experimental findings and (ii) typically only modest changes in ionic transport are observed. Using rare-earth substituted CeO_2 as a model system, I will address both reasons and make the case for lattice strain still being a promising route to enhanced oxygen transport.

Second, I will explore the extent that charge carrier concentrations in mixed ionic-electronic conductors (MIECs) can by modified at interfaces. Pr-substituted CeO_2 (PCO) is an excellent MIEC for fundamental studies as it has been extensively investigated, and the defect chemistry, chemical expansion, transport, and optical properties are well described in the bulk material. By fabricating nano-granular polycrystalline films and multilayer heterostructures, we have investigated the effects of homogeneous and heterogeneous interfaces on the concentration of oxygen vacancies and small polarons. Using a combination of impedance spectroscopy in conjunction with *in-situ* optical transmission measurements, to unambiguously extract the non-stoichiometry, we observe substantial deviations from bulk behaviour in materials dominated by a high density of interfaces. By engineering the density and proximity of interfaces, we demonstrate that the non-stoichiometry and density of charge carriers to be tailored.