

Nanoionics: Modifying electronic and ionic conductivity through interfacial engineering

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Non-stoichiometric oxides are materials capable of supporting high concentrations of point defects, such as oxygen vacancies. Materials with a high concentration of oxygen vacancies, which are significantly mobile, exhibit appreciable ionic conductivity that forms the basis for a range of high temperature electrochemical devices such as solid oxide fuel cells (SOFC), solid oxide electrolyser cells (SOECs), gas permeation membranes, and sensors. Traditionally, efforts for improving oxygen transport in these *electroceramics* has been based on compositional tuning and searching for new material families. However, recently interfacial engineering has opened up a new route to tailor the functional properties of electroceramics. Often referred to as *nanoionics*, the transport properties can be altered by the interplay of strain, space-charge, and *electro-chemo-mechanical coupling* effects at heterogeneous interfaces. In this presentation we will demonstrate two key experimental findings.

First, we demonstrate that the migration barrier in oxygen ion conductors can be modified by lattice strain. In rare-earth substituted CeO₂ thin films, we find that the observed change is in excellent agreement with previous studies, and crucially that the modification is dependent on the size of the dopant cation, showing that defect association plays a substantial role. We rationalise our findings using static force-field simulations, suggesting that the cause is due to a combination of changes in the migration barrier and vacancy-cation configuration.

Second, we show that the charge carrier concentrations in mixed ionic-electronic conductors (MIECs) can be modified at heterogeneous interfaces. Pr substituted CeO₂ (PCO) is an excellent MIEC for fundamental studies as it has been extensively investigated, and the defect chemistry, chemical expansion, and transport properties are well described in the bulk material. We show that in multilayer films of alternating Pr_{0.1}Ce_{0.9}O_{2-d} and SrTiO₃ (STO) layers, the conductivity of the layers shows a dramatic weakening of the pO₂ dependence as the density of the interfaces is increased. This is consistent with a change in the charge carrier concentration due to a lowering of the enthalpy for Pr reduction. This effectively allows PCO to be engineered from a mixed-ionic conductor to a pure ionic conductors at a given oxygen partial pressure.