Abstract

Gadolinium-doped ceria (Gd-CeO_2) is an oxide-ion solid electrolyte used in intermediate-temperature solid-oxide fuel cells (IT-SOFC). In polycrystalline Gd-CeO_2 grain boundaries contribute to the ionic resistivity. An increased resistivity is attributed to space charge regions, which form from the segregation of oxygen vacancies to grain boundary cores. The electrostatic potential from this defect segregation produces charged regions (space charges) close to the grain boundary with depleted oxygen vacancy concentrations, and corresponding decreased ionic conductivities.

Analysis of grain boundary effects on ionic conductivity typically considers the space-charge potential as a characteristic parameter. The conventional Mott-Schottky analysis assumes that the grain boundary region is negligibly thin, and that oxygen vacancies are fully depleted in the space charge region. This gives an analytical description of space-charge behaviour that can be completely characterised by the space-charge potential. In practice, the space-charge potential is not directly accessible from experiment, and is instead derived from experimental conductivity data. This approach gives a single value for the space charge potential, equivalent to assuming some “average” behaviour for all grain boundaries in Gd-CeO_2.

In real Gd-CeO_2, grain boundaries exist with a range of crystallographic orientations and atomic-scale structures. To examine the effect of grain boundary orientation on space charge behaviour we have performed numerical simulations of the defect distribution at four structurally different grain boundaries in Gd-CeO_2. These grain boundaries were first modelled using classical interatomic potential, to calculate atomically resolved defect positions and defect segregation. These geometries and segregation energies were then used as the input for a 1D-Poisson-Boltzmann solver used to calculate the space charge potential and self-consistent defect profile, taking into account the explicit lattice structure of each grain boundary.

We find that the space charge potential strongly varies with grain boundary orientation. From our simulations, we have also directly calculated grain boundary resistivities and activation. Following a scheme analogous to typical analysis of experimental data, these data have been used to recalculate the space-charge potential according to the Mott-Schottky model. We find that the Mott-Schottky model underestimates the space charge potentials for each of the grain boundaries.