

OXYGEN IONIC CONDUCTIVITY, MÖSSBAUER SPECTRA AND THERMAL EXPANSION OF $\text{CaFe}_2\text{O}_{4.5}$

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Oxide materials with mixed oxygen ionic and electronic conductivity are key components of the high-temperature electrochemical devices, such as ceramic membranes and electrodes of solid oxide fuel cells. The present work is centered on the study of oxygen nonstoichiometry and mixed conductivity of $\text{CaFe}_2\text{O}_{4.5}$, one of compounds in the Ca-Fe-O system, stable in a wide temperature range. The experimental data obtained by thermogravimetric analysis, Mössbauer spectroscopy, and measurements of steady-state oxygen permeation fluxes and faradaic efficiency, were analyzed in combination with the atomistic computer simulation results. Particular attention was also focused on thermal and chemical expansion. The oxygen deficiency (δ) in $\text{CaFe}_2\text{O}_{4.5}$ is very low, varying in the range 0.003-0.006 at oxygen partial pressures from 10^{-5} to 0.21 atm and 295-1223 K. This results in substantial dimensional stability on reducing $p(\text{O}_2)$ as revealed by the controlled-atmosphere dilatometry, but also in low concentrations of the ionic and electronic charge carriers. The average thermal expansion coefficients lie in the range $(12.0-13.9) \times 10^{-6} \text{ K}^{-1}$. The total conductivity, studied in the oxygen partial pressures from 10^{-17} to 0.5 atm at 1023-1223 K, is predominantly p-type electronic under oxidizing conditions. The oxygen-ion transference numbers are $(0.2-7.2) \times 10^{-4}$ at 1123-1273 K, increasing with temperature. The oxygen permeability through the dense ceramic membranes is determined by both bulk ionic conduction and surface exchange kinetics. The atomistic simulations indicated a strong energetic affinity for the defect cluster formation involving oxygen vacancies and Fe^{2+} cations, whereas the anion migration was found essentially one-dimensional. As a consequence, the partial oxygen-ionic conductivity is as low as 3 – 210 $\mu\text{S}/\text{cm}$ at 1123-1273 K in air. No evidence of any significant cationic contribution to the conductivity was found. Decreasing $p(\text{O}_2)$ leads to the p-n transition indicated by the conductivity and Seebeck coefficient variations, and to the subsequent phase decomposition.