

POINT-DEFECT INTERACTIONS AND IONIC TRANSPORT IN OXYGEN-DEFICIENT (La,Sr)CoO_{3-δ}

E. Naumovich¹, E. Tsipis², M. Patrakeev³, A. Yaremchenko¹, I. Marozau¹,
J.C. Waerenborgh¹, V. Kharton²

¹ Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

² Chemistry Department, Instituto Tecnológico e Nuclear, CFMC-UL, EN 10, 2686-953 Sacavém, Portugal

³ Institute of Solid State Chemistry, Ural Division of RAS, 91 Pervomayskaya Str., Ekaterinburg 620219, Russia
E-mail: enaumovich@ua.pt

Perovskite-type (La,Sr)CoO_{3-δ} possess a very high level of oxygen ion mobility and electronic conductivity, and are thus of great interest for high-temperature electrochemical applications, including the high current density electrodes and oxygen separation membranes. This work was centered on phenomenological modeling of the steady-state oxygen transport through dense La_{1-x}Sr_xCoO_{3-δ} (x = 0.3-0.7) membranes, expressing the oxygen chemical potential using the results of statistical thermodynamic analysis of the experimental p(O₂)-T-δ diagrams. The oxygen vacancy-ordering processes at moderate p(O₂) were additionally assessed by the Mössbauer spectroscopy analysis of 1% ⁵⁷Fe-doped cobaltites, in combination with X-ray diffraction (XRD) and thermogravimetry.

The equilibrium p(O₂)-T-δ diagrams of La_{1-x}Sr_xCoO_{3-δ}, collected at 973-1223 in the p(O₂) range 10⁻⁵ – 1 atm, were adequately described using the rigid-band approach for delocalized holes, Co³⁺ disproportionation and formation of Co²⁺-V_O pair clusters decreasing the concentration of mobile oxygen vacancies. Attempts to account for higher-order defect clusters failed as the corresponding contributions to the oxygen chemical potential variations are low compared to the electronic sublattice, disordered vacancies and pair associates. Nonetheless, the evidence of long-range ordering at x ≥ 0.5 was unambiguously revealed by Mössbauer spectroscopy of ⁵⁷Fe-doped samples. The data on Fe³⁺ coordination, combined with XRD, suggests the formation of a vacancy-ordered tetragonal superstructure even in relatively oxidizing atmospheres, p(O₂) ≈ 10⁻⁴ atm. In agreement with numerous literature data, strontium additions result in higher oxygen nonstoichiometry and ionic transport. However, the role of surface exchange kinetics evaluated from the membrane thickness dependencies of the oxygen fluxes, also increases with x and becomes critical at x ≥ 0.5. Reducing p(O₂) and decreasing temperature increases the flux-limiting role of surface kinetics. Analysis of the permeation data showed that exchange rate at the membrane feed-side surface is substantially affected by the oxygen vacancy concentration, at least for x = 0.5-0.7. At 1123-1223 K the bulk ionic conductivity can be described neglecting the long-range vacancy ordering and Coulombic repulsion, and tends to decrease on reducing p(O₂) due to progressive vacancy clustering.