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Defect structure, electronic conductivity and expansion properties of $(La_{1-x}Sr_x)_sCo_{1-y}Ni_yO_{3-\delta}$

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Abstract

The perovskite $LaCoO_3$ was early recognized as a candidate material in SOFC-cathodes and the aliovalently substituted $La_xSr_{1-x}CoO_3$ has shown promising electrochemical activity towards the oxygen reduction reaction. Ni-substitution in $La_xSr_{1-x}CoO_3$ has been reported to increase both electronic and ionic conductivity as well as decrease the thermal expansion coefficient. These properties are considered highly important for materials to be exploited in SOFC.

This presentation reports on oxygen nonstoichiometry, electronic conductivity and lattice expansion of three compositions as function of T and P_{O_2} in the $(La_{1-x}Sr_x)_sCo_{1-y}Ni_yO_{3-\delta}$ materials system. The nonstoichiometry data were successfully fitted using the itinerant electron model which indicates the existence of delocalised electronic states. This was also reflected in the high electronic conductivities, above 1000 Scm^{-1} measured for all three compositions. The electronic conductivity was further shown to decrease linearly with the oxygen nonstoichiometry parameter, δ, indicating that the conductivity is dependent on p-type charge carrier concentration. Comparing calculated p-type mobilities with data reported in literature on $La_xSr_{1-x}CoO_3$ indicated that Ni-substitution into $(La_{1-x}Sr_x)_sCoO_{3-\delta}$ increases the mobility. The electronic conductivity was also found to be dependent on intrinsic properties not related to strontium substitution. Based on calculated mobilities and literature data on related composition a conductivity model is hypothesized including a metallic like conductivity of the *extrinsic* p-type charge and a small polaron conductivity of the *intrinsic* charge. Lattice expansion as function of T and δ was successfully fitted using first and second order thermal and chemical expansion coefficients. Substituting 10 % Co with Ni in $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ was found to decrease the thermal expansion with about 25 %. The results are compared and discussed in the light of recent literature.

Key words: LSCN, conductivity, thermal expansion, chemical expansion, oxygen nonstoichiometry,

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