A/B-Ratio in Strontium Doped Lanthanum Cobaltite

Martin Søgaard[a]*, Dorthe Lybye[a], Peter V. Hendriksen[a],
Torben Jacobsen[b] and Mogens Mogensen[a]

[a]Risø National Laboratory, Material Research Department
Frederiksborgvej 399, P.O. 49, DK-4000, Denmark
[b]Department of Chemistry,
Technical University of Denmark ,
DK-2850 Kgs. Lyngby, Denmark,

Sr doped $LaCoO_3$ (LSC) has been investigated intensively during the last five decades due to interesting properties such as a metal-insulator transition, a spin-state transition, good catalytic effect for oxygen reduction and its high oxide ion conductivity. LSC is a perovskite type oxide. Perovskites have the general chemical formula ABO_3 where A is a large metal ion, typically a rare earth metal and B is a small cation typically a transition metal.

Many studies have investigated the effects of Sr-doping on the electrical and catalytic properties of LSC while few studies have investigated the effect of A/B-ratio and the results of the studies have often been difficult to interpret.

This study presents detailed investigations on the perovskite compounds $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$ s=0.98, s=1.00 and, s=1.02. The compounds have been synthesized using the glycine-nitrate route. The materials have been calcined for 24 h at 1175°C in order to obtain an even cation distribution. Scanning electron microscopy (SEM) revealed Co-oxide particles present at grain boundaries in the Co-rich perovskite. No secondary phases have yet been identified with SEM on the (La,Sr)-rich perovskite. We have conducted detailed investigation on the structure for s=0.98 and s=1.00 in the temperature interval 25°C-1050°C using neutron diffraction. All reflections could be assigned to a hexagonal structure.

Figure 1 shows the electrical conductivity as function of the temperature of the three investigated materials. The conductivity of the materials is largest for the s=0.98 compound and smallest for the s=1.02 compound.

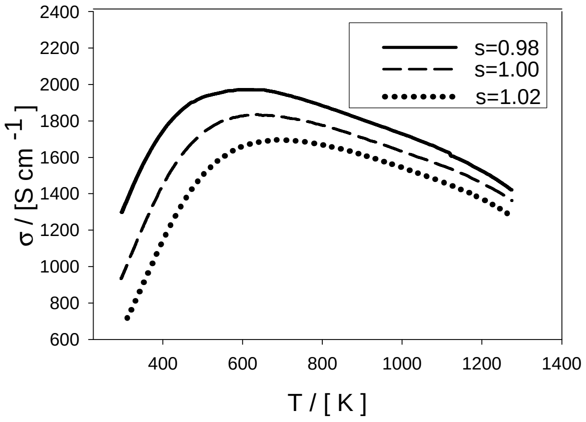

Figure 1: Electrical conductivity of the materials $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$ as function of the absolute temperature.

The changes in conductivity are so large that they may not only reflect changes in cation vacancy concentration. We suspect that the changes in conductivity also reflect small changes in the strontium doping level. The conductivity is very sensitive to the Sr-doping content in the vicinity of a 15% Sr-doping.

For $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ it was attempted to correlate the conductivity with the rhombohedral angle, α, which was calculated from the neutron diffraction data. When α was less than 60.43°, dσ/dT was negative corresponding to a metallic type conduction. This is in close agreement with the results reported by Mizusaki *et al.*[1].

Oxygen non-stoichiometry measurements on $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ were carried out using a thermal balance. The oxygen non-stoichiometry data could be fitted using *the itinerant electron model* proposed by Lankhorst, Bouwmeester and Verweij[2].

Electrical conductivity relaxation was carried out in the temperature range 850°C-1000°C. This has given information on the surface exchange coefficients and the chemical diffusion coefficient of oxygen. Figure 2 shows the chemical diffusion coefficient, D_{Chem},and surface exchange coefficient, k_{Ex},for $(La_{0.85}Sr_{0.15})_{1.02}CoO_{3-\delta}$ at 1000°C as function of the oxygen partial pressure, pO_2.

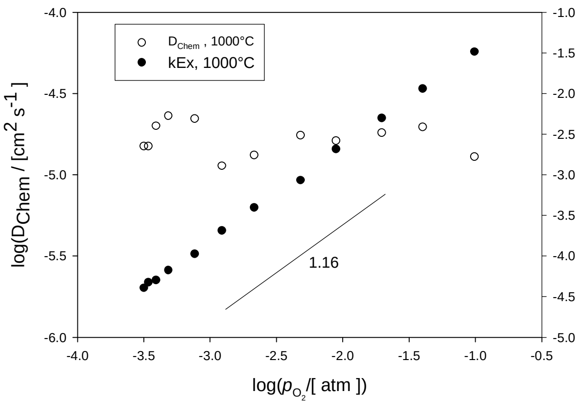

Figure 2: Chemical diffusion coefficient(left axis) and surface exchange coefficent(right axis) as function of the oxygen partial pressure.

No variation in the chemical diffusion coefficient could be found within the three investigated materials. The activation energy for D_{Chem} was found to be E_A=116 kJ mol^{-1}. For all the three investigated materials the surface exchange coefficient decreased with decreasing pO_2. The surface exchange coefficient was different for the three materials. This will be investigated further.

[1] J. Mizusaki, J. Tabuchi, T. Matsuura, S. Yamauchi, K. Fueki, J. Electrochem. Soc., **136**, 2082-8 (1989)

[2] M. Lankhorst, H. Bouwmeester and H. Verweij, Phys. Rev. Lett., **77**, 2989-92 (1996)