Electrical conductivity and dimensional stability of co-doped lanthanum chromites

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The electronic- and ionic conductivity, the TEC, and the expansion on reduction of a number of co-doped lanthanum chromites were determined using dilatometry, high-temperature X-ray-diffraction, and four point steady state and transient conductivity measurements. The samples were further characterized by thermogravimetry. The study focuses on the three compositions: $La_{0.8}Sr_{0.2}Cr_{0.88}Fe_{0.09}V_{0.03}O_3$, $La_{0.9}Sr_{0.1}Cr_{0.88}Mg_{0.09}V_{0.03}O_3$ and $La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3$ and the differences in behavior are discussed in terms of simple structural models based on Shannon ionic radii.

Alkaline earth doped lanthanum chromites have been widely studied because they are thermodynamically stable at high temperature under oxidizing as well as highly reducing conditions whilst possessing high electronic conductivity (tens of S/cm in air). For these reasons they can be used as interconnect material in solid oxide fuel cell stacks (1). They have further been studied for use as protective coatings on metallic interconnects (1), and for electrodes in sensors and fuel cells (2, 3).

The acceptor doped chromites are predominantly electronic conductors, but do show some ionic conductivity as well. When used as interconnect this will result in an ionic leak current through the interconnect representing a parasitic consumption of fuel. Hence, the ionic conductivity is a drawback for the use as interconnect as well as for the use as protective coating, whereas for the use as a catalyst or electrode some ionic conductivity is probably advantageous.

The acceptor doped chromites are well known to expand on reduction (4). The loss of oxygen from the material, and the associated reduction of the chromium ions, is accompanied by a volume expansion, giving rise to stresses that may in some cases be detrimental for the component (5). For the technological use of the doped chromites it is thus important to know both transport properties (ionic and electronic conductivity) as well as the thermo-mechanical properties (TEC, expansion on reduction).

The electronic conductivity and the TEC increase with increasing amounts of aliovalent doping, but so does the magnitude of the expansion on reduction. Hence, requirements of mechanical compatibility with other components, high dimensional stability and high electronic conductivity may well be partly conflicting. In a search for materials that meet the requirements for a specific use a great number of co-doped lanthanum chromites have been investigated (6, 7, 8, 9). Here, the properties of the two co-doped chromites $La_{0.9}Sr_{0.1}Cr_{0.88}Mg_{0.09}V_{0.03}O_3$ (LSCM) and $La_{0.8}Sr_{0.2}Cr_{0.88}Fe_{0.09}V_{0.03}O_3$ (LSCF) are compared to those of the only Sr-containing end-member of the series: $La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3$ (LSC) and to those of other materials belonging to the series: $La_{1-x}Sr_xCr_{1-y}Mg_yV_{0.03}O_3$.

At 1000 °C in air the total conductivities were 15, 22 and 33 S/cm for the LSCM, LSCF and LSC, respectively. The electronic conductivities of all three materials were observed to decreases with decreasing pO_2 as is typical for this type of materials. The results were analyzed using a simple point defect model, that in the case of the iron-containing sample was generalized to take into account two redox-couples.

The expansion on reduction between air and a pO_2 of 10^{-16} atm. (-967 mV vs. air @ 1000 °C), determined by dilatometry, was 0.08 %, 0.17 %, and 0.11 % for the LSCM, LSCF and LSC, respectively. From the high temperature X-ray diffraction expansions of 0.08 % and 0.15 % were found for LSCM and LSCF, respectively, in good agreement with the dilatometry results. The thermal expansion coefficients of the materials (average between room temperature and 1000 °C) were 10.0, 10.6 and 10.5 ppm/K for LSCM, LSCF and LSC, respectively.

The oxygen diffusion coefficient, as determined by the conductivity relaxation method, was found to increase with decreasing pO_2. For the LSC-sample, D was found to be ca. $1.2 \cdot 10^{-5}$ cm²/s at a pO_2 of 10^{-16} atm (@ 1000 °C). The surface exchange rate constant, K, determined at the same pO_2 was ca. $2 \cdot 10^{-4}$ cm/s. K was found to increase slightly with decreasing pO_2. For the Fe- and Mg-containing samples somewhat lower values of both K and D were observed. At 10^{-16} atm. D was ca. $5 \cdot 10^{-6}$ cm²/s for LSCF and ca. $2 \cdot 10^{-6}$ cm²/s for LSMC, whilst the K- values were in the range from $5 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ cm/s.

The consequences of the ionic conductivity for the use of the materials as coatings or interconnects are assessed. The oxygen leakage fluxes through the materials are calculated, as are the overall strains and stresses caused by the dimensional instability. Analytical expressions for the latter problem are presented.

The reason for the differences in behavior between the three materials is discussed in terms of a simple structural picture considering the "misfit-stresses" arising from i) the differences between measured unit-cell volumes and calculated ideal unit cell volumes assuming Shannon ionic radii and either the A-O or the B-O sub-lattice to be structurally dominating, and ii) local size differences between majority and minority species.

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