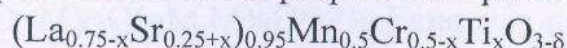


Transport and electrode properties of perovskite-type



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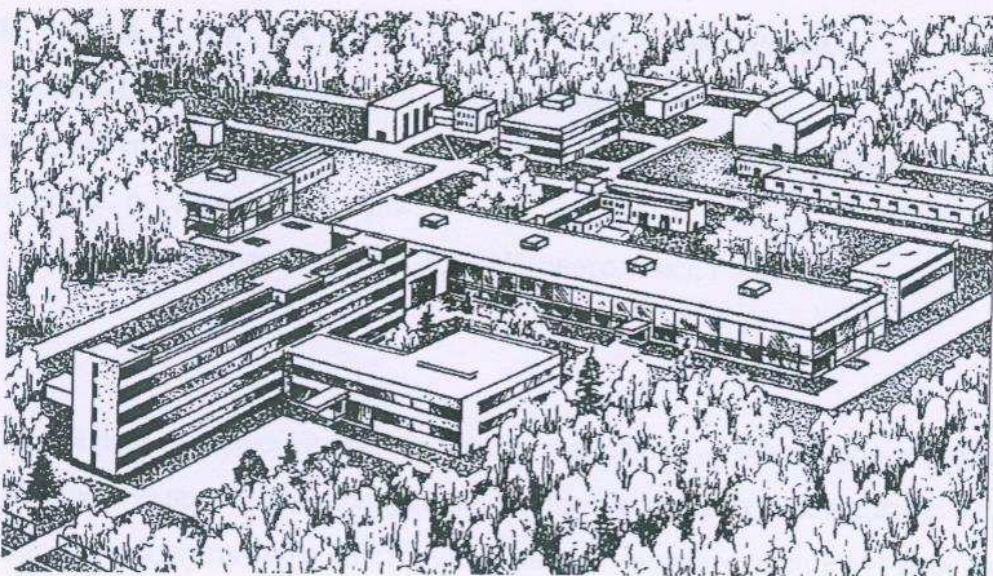
One important challenge in the developments of solid oxide fuel cells (SOFCs) and high-temperature electrolyzers relates to the search for electrochemically active electrode materials stable in both reducing and oxidizing gases. In addition to the electrochemical properties, critical requirements to such materials include a high electronic conductivity, thermodynamic stability under fabrication and operation conditions, catalytic activity towards oxidation of hydrocarbons and other C-containing species enabling to suppress carbon deposition, compatibility with solid-electrolyte ceramics, and low costs. The conventional Ni-based cermet anodes exhibit serious disadvantages, primarily fast coking in hydrocarbon-fueled SOFCs and large volume changes on redox cycling, leading to degradation. A relatively good stability and substantially high performance are known for (La,Sr)(Cr,Mn)O₃-based perovskites (LSCM), such as (La_{0.75}Sr_{0.25})_{1-y}Cr_{0.5}Mn_{0.5}O_{3-δ} (y=0–0.05). At the same time, diffusion and volatilization of Cr-containing species make it necessary to avoid the presence of chromium or, at least, to decrease its content in the SOFC materials in order to avoid poisoning of the electrochemical reaction zones and electrolyte degradation. This work is focused on the appraisal of (La_{0.75-x}Sr_{0.25+x})_{0.95}Mn_{0.5}Cr_{0.5-x}Ti_xO_{3-δ} (x=0–0.5) system. Primary emphasis is given to the properties relevant for the electrode applications, namely, phase stability and mixed ionic-electronic conductivity in various atmospheres, thermal and chemical expansion, and behavior of porous layers applied onto perovskite-type (La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) and apatite-type La₁₀Si₅AlO_{26.5} solid electrolytes.

Increasing Sr²⁺ and Ti⁴⁺ concentrations in (La_{0.75-x}Sr_{0.25+x})_{0.95}Mn_{0.5}Cr_{0.5-x}Ti_xO_{3-δ} (x=0–0.5) was found to result in slightly higher thermal and chemical expansion, whereas the total conductivity activation energy tends to decrease. The average thermal expansion coefficients determined by controlled-atmosphere dilatometry vary in the range (10.8–14.5)·10⁻⁶ K⁻¹ at 373–1373 K, being almost p(O₂)-independent. Analysis of the conductivity and Seebeck coefficient, studied in the oxygen partial pressure range 10⁻¹⁸ to 0.5 atm, suggests that the electronic transport under oxidizing and moderately reducing conditions is dominated by p-type charge carriers and occurs via a small-polaron mechanism. Contrary to the hole concentration, the hole mobility decreases with increasing x. The oxygen permeation fluxes through dense ceramic membranes are quite similar for all compositions due to the very low level of oxygen deficiency, and are strongly affected by the grain-boundary diffusion and surface exchange. The porous (La_{0.75-x}Sr_{0.25+x})_{0.95}Mn_{0.5}Cr_{0.5-x}Ti_xO_{3-δ} electrodes exhibit a considerably better electrochemical performance in contact with LSGM if compared to La₁₀Si₅AlO_{26.5} electrolyte. At atmospheric oxygen pressure, strontium and titanium additions have no essential influence on the polarization resistance. In H₂-containing gas mixture when the electronic conductivity of all (La_{0.75-x}Sr_{0.25+x})_{0.95}Mn_{0.5}Cr_{0.5-x}Ti_xO_{3-δ} perovskites becomes relatively low, co-doping leads to a moderately higher anodic polarization, which can be however decreased by infiltrating Ni and CeO_{2-δ} into the porous electrode matrix.

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