

Thermodynamic Assessment of the La-Mn-Cr-O System for Applications on Solid Oxide Fuel Cell (Sofc) Materials Using the Calphad Approach

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Planar SOFC stacks consist of repeated layers of a cathode-electrolyte-anode unit alternating with electrical interconnects. The interconnect separates the single cells of the stack, while also connecting them electrically. Ceramic and metal interconnect materials have been tested and evaluated over the years. Cr-based alloy interconnect materials have gained popularity due to their relative ease of fabrication, low machining costs and high electrical conductivity. However the use of these alloys leads to cell degradation especially on the cathode side of the fuel cell. Evaporation of predominately hexavalent Cr, and surface diffusion processes lead to the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel and Cr_2O_3 , which block active sites as well as pores thus substantially diminishing the triple phase boundary area for the oxygen reduction reaction at the cathode/electrolyte interface.

We are investigating the thermodynamics of the impact of Cr from the interconnect alloy on a $\text{La}_x(\text{Mn,Cr})_{1+x}\text{O}_{3-\delta}$ ($x \leq 1$) model cathode using the CALPHAD (CALculation of PHase Diagrams) approach. Based on the assessments of the Mn-O, Cr-O, Mn-Cr-O, Mn-Cr-O, and La-Cr-O, we achieve an ideal extrapolation of the La-Mn-Cr-O system, which is in agreement with experimental findings. Our tentative calculations show that bulk chromium poisoning of $x(\text{Cr})=0.001$ of a model cathode of the composition $\text{La}_{0.95}(\text{Mn,Cr})_{1.05}\text{O}_{3-\delta}$ leads to the formation of tetragonally distorted spinel at > 1130 K. The higher the chromium poisoning of the cathode, the lower is the temperature of spinel formation, and the driving force for the formation of cubic spinel is increased. For a slightly manganese doped model cathode of the composition $\text{La}_{0.975}(\text{Mn,Cr})_{1.025}\text{O}_{3-\delta}$ tetragonally distorted spinel is expected to form at $T > 1400$ K. Increasing chromium poisoning leads to the transformation of tetragonally distorted spinel to cubic spinel. Cubic spinel is formed at $x(\text{Cr}) = 0.17$ and $T=1273$ K for $\text{La}_{0.975}(\text{Mn,Cr})_{1.025}\text{O}_{3-\delta}$.

Decreasing the La content promotes the decomposition of the model cathode at higher temperatures. Enrichment of chromium in a model $\text{La}_x(\text{Mn,Cr})_{1+x}\text{O}_{3-\delta}$ ($x \leq 1$) SOFC cathode leads to successively decreasing spinel formation temperature. Enhanced chromium poisoning increases the driving force of cubic spinel formation. The transformation of distorted spinel to cubic spinel may contribute to the increase of mechanical stresses of the cathode due to the differing thermal expansion properties of these two phases. Cr_2O_3 is not expected to form inside the model cathode. To understand the thermodynamics of the Cr – LSM cathode interaction we will extend our modeling to the La-Sr-Mn-Cr-O system.