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Oxygen Transport Properties of Ca/W-Substituted Lanthanum Nickelate

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Lanthanum nickelates (LNO) are mixed oxygen-ionic and electronic conductors (MIECs) and candidate materials for the cathode of solid oxide fuel cells operating at intermediate temperature (IT-SOFC) and for oxygen permeation membranes. The advantage of LNO compared to the well-known La$_{1-x}$Sr$_x$MnO$_{3-d}$ is the thermal stability and the comparable thermal expansion coefficient to the mostly used electrolytes. La$_2$NiO$_4$ has a K2NiF4-type crystal structure, with the perovskite-like layers separated by rock-salt La$_2$O$_2$ layers. In contrast to perovskite MIECs the LNO has oxygen excess with oxygen anions in interstitial positions in the La$_2$O$_2$ layers of the structure which are charge compensated by p-type electronic charge carriers. Doping with the alkaline-earth cations decreases oxygen excess and ionic conductivity but increases the electronic conductivity.

Powders of lanthanum nickelates partially substituted with Ca on A side and/or W on B side were prepared by combustion synthesis. The gel was dried and fired at 300 °C, and subsequently calcined at different temperature to achieve a single phase material. The calcined powders were pressed in rectangular bar shape and sintered at 1300 °C for 10 h. The dense bars were ground and polished to certain size and used for the electrical conductivity measurements. Crystal structures of powders as well as bars were analyzed by x-ray diffraction and the microstructure of polished surface was investigated by scanning electron microscope. The oxygen transport properties of the samples were studied by electrical conductivity relaxation (ECR), which is a well-established method to determine the oxygen transport properties of MIECs; oxygen surface exchange coefficient ($k_{ex}$) and the chemical diffusion coefficient ($D_{chem}$). The conductivity of Ca and/or W substituted LNO is thermally activated and activation energies from 4 - 16 kJ/mol were measured for different substitutions. The highest conductivity of 68 S/cm at 500 °C was measured for La$_{1.4}$Ca$_{0.6}$Ni$_{0.9}$W$_{0.1}$O$_{4+d}$. The total conductivity is decreasing with the $p_{O_2}$, indicating that LNO is a p-type electronic conductor. However, the $p_{O_2}$ dependence of the conductivity for the Ca and Ca-W substituted LNO is very low. While, for the W substituted LNO (La$_2$Ni$_{0.9}$W$_{0.1}$O$_{4+d}$) much stronger dependence was observed and the oxygen transport properties were determined. At 500 °C and for $p_{O_2}$ change from 0.2 to 0.1 bar the $k_{ex}$ is 5x10$^{-3}$ cm/s and $D_{chem}$ is 5x10$^{-3}$ cm$^2$/s, which is several times higher than observed for LNO doped with aluminum [1]. The electrical properties and strategies to achieve fast oxygen transport in substituted LNO as well as possible applications of the materials will be discussed.