OXYGEN TRANSPORT AND ELECTROCHEMICAL ACTIVITY OF $La_2NiO_{4+\delta}$-BASED CATHODE MATERIALS

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Development of highly active cathodes is of significant interest for intermediate-temperature SOFCs operating at 773-1023K. The present work is focused on the study of one alternative group of potential cathode materials, $La_2NiO_{4+\delta}$-based phases.

Solid solutions $La_2Ni_{1-x}M_xO_{4+\delta}$ (M = Fe, Co; x = 0.02-0.10) and $La_2Ni_{1-x}Cu_xO_{4+\delta}$ (x = 0.20-0.80) were prepared by the standard ceramic technique and glycine-nitrate method, and characterized by XRD, SEM/EDS, TEM, dilatometry, and the measurements of shrinkage, total conductivity and oxygen permeability. The average thermal expansion coefficients, calculated from the dilatometric data in air, vary in the range $(11\text{-}14)\times10^{-6}$ K^{-1} at 400-1273 K. Steady-state oxygen permeation through dense $La_2NiO_{4+\delta}$-based membranes is limited by both bulk ionic conductivity and oxygen surface exchange, and decreases with decreasing oxygen hyperstoichiometry. Decreasing grain size of the nickelate ceramics also leads to lower oxygen transport.

Substitution of nickel with copper was found to decrease sintering temperature necessary to achieve sufficient mechanical strength of highly porous electrode layers, consisting of ceramic grains smaller than 0.1 μm. The studies of the overpotential – current density dependencies of porous nickelate-based cathodes in contact with La(Sr)Ga(Mg)$O_{3-\delta}$ (LSGM) solid electrolyte showed that their performance at 873-1073 K is similar to that of perovskite-type electrode materials, such as La(Sr)Fe(Co)$O_{3-\delta}$ and LaFe(Ni)$O_{3-\delta}$, despite the fact that $La_2NiO_{4+\delta}$-based phases showed higher ionic conductivity. This indicates that one cannot assume a simple direct correlation between the bulk ionic and electronic conductivities of oxide materials, and their electrochemical activity as porous cathode layers. The performance of a single SOFC-type cell with $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$ cathodes, LSGM electrolyte, and Ni-YSZ-CGO anodes was studied at 873-1173 K under air/10%H_2-N_2 gradient.

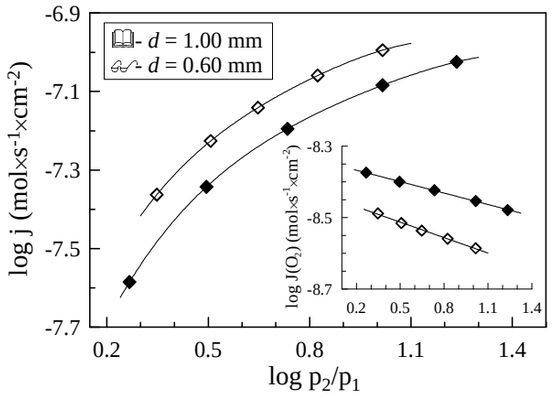

Fig.1: Oxygen permeability of $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$ membranes with thicknesses d=1.00 and 0.60 mm

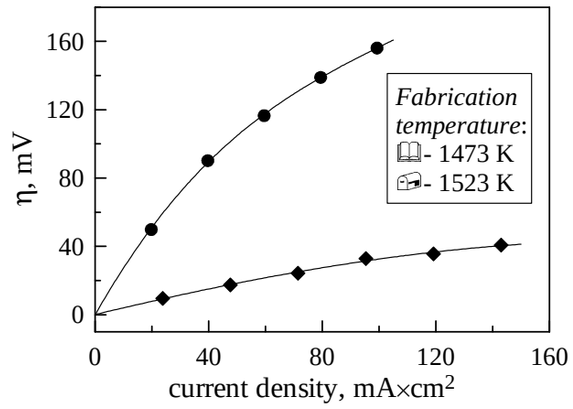

Fig.2: Cathodic polarization curves of $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$ electrodes fired at 1473 K and 1523 K.