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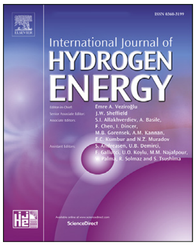

Structure, transport properties and electrochemical behavior of the layered lanthanide nickelates doped with calcium☆

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ABSTRACT

Progress in hydrogen energy and promising directions for its modern development are closely related to design of fuel cells, including solid oxide fuel cells, and solid state membranes for hydrogen, oxygen and synthesis gas production. A necessary condition for fabrication of economically competitive devices in this area is the use of cheap electrode materials combining high electrochemical activity and long-term stability. $Ln_2NiO_{4+\delta}$ oxides with the Ruddlesden–Popper layered structure possessing a high mixed ion-electron conductivity and moderate values of the coefficients of thermal expansion are promising materials for development of oxygen-conducting membranes and cathodes of intermediate-temperature solid oxide fuel cells.

In this paper structural characteristics, electrical conductivity, oxygen mobility and electrochemical properties of $Ln_{2-x}Ca_xNiO_{4+\delta}$ (Ln = La, Pr, Nd; x = 0; 0.3) samples were studied to determine factors, which have the most significant effect on the electrochemical activity of electrodes and their stability. It was found that doping with calcium lead to stabilization of the structure and increased the electrical conductivity of materials. However, addition of calcium decreased the electrochemical activity of electrodes in varying degrees depending on the nature of lanthanide. There is no direct interrelation of such a decrease of activity with either the electrical properties or the interstitial oxygen content. We have revealed correlation of the polarization resistance of electrodes with characteristics of oxygen transfer in the electrode material (self-diffusion coefficient, surface exchange constant). Using the $C^{18}O_2$ SSITKA method, the total oxygen mobility in the doped materials was shown to fall with doping due to a decrease in the content of highly mobile interstitial oxygen and hampering of the cooperative oxygen transport mechanism. In the case of $La_{1.7}Ca_{0.3}NiO_{4+\delta}$, this leads to the appearance of a slow diffusion channel and a substantial decrease in the total diffusion coefficient value which results in a sharp increase in the polarization resistance of the electrodes. This phenomenon is not observed in materials with praseodymium and neodymium. The electrodes based on $Pr_{1.7}Ca_{0.3}NiO_{4+\delta}$

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and $Nd_{1.7}Ca_{0.3}NiO_{4+\delta}$, developed in this work, have an acceptable level of the electrochemical activity along with a high electrical conductivity and increased stability in comparison with undoped compositions and can be recommended for use as cathodes for intermediate temperature fuel cells.

Nomenclature

Greek letters

α	Fraction of ^{18}O atoms
δ	Oxygen non-stoichiometry
η	Dimensionless parameter of the distance from the surface
ξ	Dimensionless sample length
σ	Electroconductivity of compacts, S cm^{-1}
τ	Contact time in the reactor, s

Latin letters

B	Dimensionless temperature factor
C	Capacity of the electrode process, F cm^{-2}
D	Oxygen self-diffusion coefficient, cm^2 s^{-1}
Ea	Activation energy, eV
f	Frequency of the electrode process at the maximum, Hz
$f_{16\text{-}18}$	Fraction of $C^{16}O^{18}O$ molecules
k_O	Oxygen surface exchange constant, cm s^{-1}
m	Mass, g
M	Molar mass, g mol^{-1}
N	Number of oxygen atoms
r	Ionic radius, Å
R^0, R^1, R^2	Rates of different type exchange according to the Muzykantov's classification, cm^{-2} s^{-1}
R^{Σ}	Total rate of heteroexchange, cm^{-2} s^{-1}
R	Resistance, Ω
$R_{1,2.3}$	Partial resistances of the electrode processes, Ω cM^2
S	Electrode surface area, cm^2
T	Temperature, °C
t	Time, s
V	Sample volume, cm^3

Superscripts

i	Type exchange according to the Muzykantov's classification ($i = 0, 1, 2$)

Subscripts

η	Polarization
bulk	Oxide volume
dc	Direct current
fast	Fast diffusion channel
g	Gas phase, on the surface and in the oxide volume
hf	High-frequency
lim	Diffusion
O	Oxygen
overall	Total
red	Reduction products
ref	Reference value
s	Oxide surface
slow	Slow diffusion channel

Abbreviations

ALS	Adler–Lane–Steele model
LnCNO	$Ln_{1.7}Ca_{0.3}NiO_{4\pm\delta}$ (Ln = La, Pr, Nd, respectively:LCNO – with lanthanum, PCNO – with praseodymium, NCNO – with neodymium)
LnNO	$Ln_2NiO_{4+\delta}$ (Ln = La, Pr, Nd)
MIEC	Mixed ionic-electronic conductor
SSITKA	Steady-State Isotopic Transient Kinetic Analysis
CE	Coefficient of efficiency
CTE	Coefficient of thermal expansion
SOFC	Solid Oxide Fuel Cell
TPIE	Temperature-programmed isotope exchange
XRD	X-ray diffraction

Introduction

At the present stage of the world energy development, due to depletion of available oil resources, the growth of atmospheric pollution from the use of non-environmentally friendly and low-efficient methods of generating electricity, a steady increase in consumers requirements for diverse and qualitative ways to supply energy, the active development of remote territories and the requirements of the defense industry, the development of alternative, small and distributed energy technologies is becoming increasingly important, and their prospects have become the subject of sharp discussion [1,2]. Nevertheless, the creation of power stations on the basis of Solid Oxide Fuel Cells (SOFCs) and electrolytic cells – both individually and in the cogeneration and energy storage system – is recognized as one of the promising areas [3]. Complex use of chemical and thermal energy in these compact and safe, for humans and the environment, power stations with ceramic electrolytes will improve the efficiency of a wide range of gaseous fuels by up to 85–90% [4]. A prerequisite for the broad-scale application of solid oxide power stations is their long-term operation and reduction in the cost of electricity generation. This requires solving problems related to design of materials for solid oxide electrochemical devices – electrolytes and electrodes with high performance at an acceptable cost, as well as to shifting their efficient operation range to intermediate temperatures (600–750 °C), which

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