

Surface defect chemistry and oxygen exchange kinetics in $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ 

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ABSTRACT

Surface oxygen exchange kinetics and diffusion in $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ ($x = 0; 0.1; 0.3$) have been studied by the isotope exchange method with gas phase equilibration in the temperature range of 600–800 °C and oxygen pressure range 0.13–2.5 kPa. Despite an enhanced electrical conductivity of $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ their oxygen surface exchange (k^*) and oxygen tracer diffusion (D^*) coefficients were significantly lower in comparison with $\text{La}_2\text{NiO}_{4+\delta}$. The rates of the elementary stages of oxygen exchange have been calculated. Upon Ca doping the change of the rate-determining stage was observed. The surface of the oxides was found to be inhomogeneous towards oxygen exchange process according to the recently developed model. The reasons of such inhomogeneity are discussed as well as Ca influence on the surface defect chemistry and oxygen surface exchange and diffusivity.

1. Introduction

$\text{La}_2\text{NiO}_{4+\delta}$ overstoichiometric compounds have attracted the increasing attention of the fuel-cell community, as they are good cathode materials for intermediate temperature solid oxide fuel cells [1–5]. Understanding of the electrode materials surface defect chemistry (chemical composition, phase content, thermodynamics and kinetics of the segregation processes on the surface etc.) is particularly important as electrode performance is largely governed by the processes occurring on the surface such as surface oxygen exchange. However in spite of the surface properties importance, little attention is often paid to their detailed investigation.

In our previous work [6] oxygen surface exchange kinetics and diffusion in $\text{La}_2\text{NiO}_{4+\delta}$ have been studied by the isotope exchange method with gas phase equilibration. Careful surface analysis performed by the Low Energy Ion Scattering (LEIS) method showed that the surface composition was significantly different from the bulk $\text{La}_2\text{NiO}_{4+\delta}$. In particular, no Ni cations in the outermost layer were detected, which is in agreement with observed depletion of transition metals at the near surface regions in $\text{La}_2\text{NiO}_{4+\delta}$ [7] and perovskite compounds [8,9]. In addition, the oxide surface was found inhomogeneous towards oxygen exchange [6]. The inhomogeneity was associated

with the existence of kinetically not equivalent apical and equatorial La–O sites, as grains with different crystallographic orientation were observed in $\text{La}_2\text{NiO}_{4+\delta}$ polycrystal sample. Various grain orientations resulted in the different rate-determining stages of oxygen exchange process for every grain. Overall, for the studied polycrystal the dissociative adsorption rate was found to be rate-determining.

In the other study [10] we have investigated the effect of rare earth metal (Ca) doping in lanthanum nickelate on the oxygen exchange kinetics and the electrochemical properties. It was shown that for $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ despite enhanced electrical conductivity oxygen surface exchange (k^*) and oxygen tracer diffusion (D^*) coefficients decreased significantly in comparison with undoped lanthanum nickelate. Upon Ca doping the change of the rate-determining stage was observed. While for $\text{La}_2\text{NiO}_{4+\delta}$ this stage was dissociative adsorption, for $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ oxygen incorporation was the rate-determining stage. It was concluded that Ca doping leads to significant electrochemical activity decrease.

The information on the exact reasons of the rate-determining stage change and k^* and D^* behavior upon Ca doping is still lacking. The aim of the present study is to examine the effect of Ca doping on the surface defect structure and oxygen exchange kinetics in $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$.

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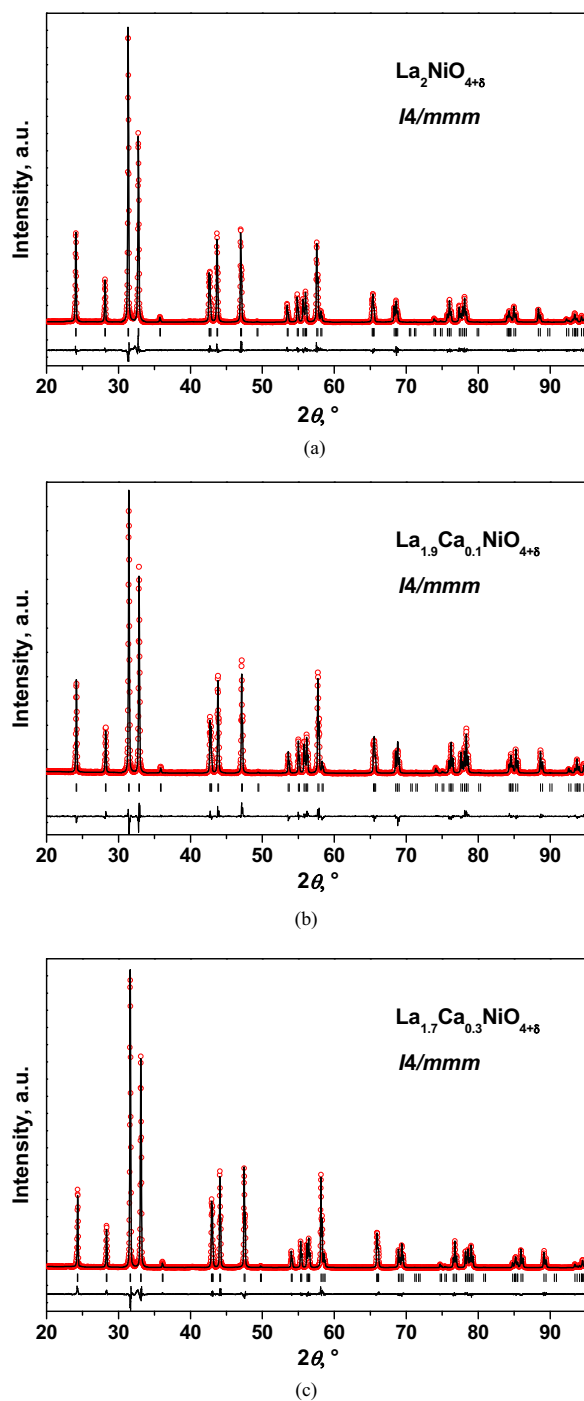


Fig. 1. The results of Rietveld refinement of XRD patterns for (a) $\text{La}_2\text{NiO}_{4+\delta}$; (b) $\text{La}_{1.9}\text{Ca}_{0.1}\text{NiO}_{4+\delta}$ and (c) $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ oxides.

2. Experimental

2.1. Samples preparation and characterization

The $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ ($x = 0; 0.1; 0.3$) samples were prepared using solid state synthesis. Starting reagents (La_2O_3 , NiO and CaCO_3) of high purity grade were fired at 1100°C and 1270°C for 2 and 5 h, respectively, with the intermediate milling. After that the powder was grounded, pressed into pellets about 14 mm in diameter and sintered at 1500°C for 2 h to obtain dense ($\sim 96\%$) ceramic samples suitable for the isotope exchange experiments. Having produced a dense material, the specimens were polished with successive grades of diamond paste

Table 1

Unit cell parameters and the atomic positions of $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ ($x = 0; 0.1; 0.3$) obtained by Rietveld refinement of XRD data. Numbers in parentheses are standard deviations of the last significant digit; if there is no standard deviation digit, the value is not refined.

Chemical formula	$\text{La}_2\text{NiO}_{4+\delta}$	$\text{La}_{1.9}\text{Ca}_{0.1}\text{NiO}_{4+\delta}$	$\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$
Sp. gr.	$I4/mmm$		
$a = b, \text{Å}$	3.8652(3)	3.8554(1)	3.8282(2)
$c, \text{Å}$	12.6870(1)	12.6534(3)	12.6021(9)
$V, \text{Å}^3$	189.54(4)	188.08(3)	184.68(9)
La (4e)			
x	0	0	0
y	0	0	0
z	0.3608(1)	0.3611(3)	0.3620(3)
Occ.	0.125	0.11875	0.09375
Ca (4e)			
x	—	0	0
y	—	0	0
z	—	0.3611(3)	0.3620(3)
Occ.	—	0.00625	0.03125
Ni (2a)			
x	0	0	0
y	0	0	0
z	0	0	0
Occ.	0.0625	0.0625	0.0625
O1 (4c)			
x	0	0	0
y	0.5	0.5	0.5
z	0	0	0
Occ.	0.125	0.125	0.125
O2 (4e)			
x	0	0	0
y	0	0	0
z	0.1733(1)	0.1719(2)	0.1740(8)
Occ.	0.125	0.125	0.125
$R_{wp}, \%$	11.20	11.50	10.7
$R_{exp}, \%$	5.81	5.97	5.81
$R_p, \%$	7.77	8.01	7.57
C	3.73	3.71	3.41

(ASM 7/5 NVM, grit size 5–7 μm and ASM 1/0 NOM, grit size 1 μm) to the final finish of microns.

The X-ray powder diffraction study was carried out on Rigaku D/MAX-2200 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda(\text{K}\alpha) = 1.5406 \text{Å}$) at room temperature in ambient air. The diffraction patterns were recorded in the 2θ range of 20 – 95° with steps of 0.02° . The collection time was 3.5 h for each XRD-pattern. Structural Rietveld refinement of XRD patterns was carried out by means of FullProf software [11]. The line shape of the diffraction peaks was generated by a Thompson-Cox-Hastings pseudo-Voigt function and the background was refined by a 5th degree polynomial. The following parameters were refined: background coefficients, zero point, half width, Thompson-Cox-Hastings pseudo-Voigt and asymmetry parameters for the peak shape, scale factor, unit-cell parameters, atomic positions and isotropic thermal factors. Positional occupancy factors for all atoms were not refined for XRD data.

Surface morphology of the samples was investigated by scanning electron microscope Tescan MIRA 3 LMU with X-Ray energy-dispersive microanalysis system (EDX) Oxford Instruments INCA Energy 350 with X-max 80 non-gas detector and electron backscatter diffraction system (EBSD) INCA Synergy Premium diffraction system with Nordlys II F + detector. The cross-sections of the ceramic samples were prepared by polishing machine Allied MetPrep 4 / PH-4 System with diamond suspensions. Preliminary, samples were impregnated by the epoxy resin under vacuum to keep the microstructure.

The chemical composition of the outermost and near-surface layers in $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ after the isotope exchange experiment were determined by low energy ion scattering (LEIS) method. The LEIS experiments were performed in Qtac100 (ION-TOF GmbH, Germany) instrument fitted with a double toroidal energy analyzer which collects the scattering ions at scattering angle of 145° from all azimuthal angles. The LEIS spectra were collected using 3 keV He^+ primary ion beams directed perpendicular to the sample surface. The primary beam was rastered over a large area ($1.0 \times 1.0 \text{mm}^2$) to maintain ion fluence

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