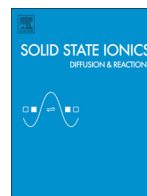




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Oxygen mobility and surface reactivity of $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ perovskites and their nanocomposites with $\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{2-\delta}$ by temperature-programmed isotope exchange experiments

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ABSTRACT

Cobalt-doped praseodymium nickelates $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ and Y/(Pr, Y)-doped ceria oxides were synthesized via Pechini route. Nanocomposites were prepared via ultrasonic dispersion of the mixture of perovskite and fluorite nanopowders in isopropanol with addition of polyvinyl butyral followed by drying, pressing and sintering at 1000–1100 °C. The oxygen mobility and reactivity of perovskites, fluorites and powdered composites obtained by crushing and milling of pellets were estimated by oxygen isotope heteroexchange with $^{18}\text{O}_2$ and C^{18}O_2 using both closed and flow (SSITKA) reactors in the temperature-programmed (TPIE) mode. Co-existence of two routes of oxygen bulk diffusion—the fast one and the slow one in perovskites and composites was revealed. In perovskites, the fast oxygen diffusion is a minor channel related to some defects in their structure. In composites, the fast oxygen diffusion is the main route being related to both phases disordered due to cation redistribution between them, first of all, to fluorite-like domains of Pr,Y-doped ceria and perovskite/fluorite interfaces.

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1. Introduction

Mixed ionic–electronic conducting composites $\text{LnNi}_{1-x}\text{Co}_x\text{O}_3$ (Ln = La, Pr)–Gd(Sm)-doped ceria are known to be promising cathode materials for thin film solid oxide fuel cells demonstrating a high and stable performance in the intermediate temperature range exceeding that of respective perovskites [1–3]. Optimization of their performance is to be based upon estimation of oxygen mobility and reactivity for thin porous layers of these materials, which requires specific methods of studies. Earlier [3,4] for $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (PNC_x , $x = 0.4\text{--}0.6$) perovskites and their nanocomposites with Y-doped ceria $\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{2-\delta}$ (YDC) sintered at 1300 °C into dense ceramics and then milled into powders, oxygen mobility and reactivity were estimated by using a unique combination of isothermal and temperature-programmed methods of oxygen isotope heteroexchange (with C^{18}O_2 and $^{18}\text{O}_2$ in both flow and closed reactors), O_2 temperature-programmed

desorption (for powders) and weight relaxation technique (for pellets). Disordering of perovskite and fluorite phases due to redistribution of cations between neighboring domains in nanocomposites was suggested to be responsible for the effect of pronounced non-additive enhancement of oxygen mobility in these samples. However, direct comparison with the oxygen mobility in separate perovskite phases was not made since at such high sintering temperature they were transformed into the mixture of $\text{Pr}_4\text{Co}(\text{Ni})_3\text{O}_{10}$ and (Ni,Co)O phases. Moreover, it remained unclear if for porous $\text{PNC}_x\text{--YDC}$ nanocomposite cathode layers supported on the layer of solid electrolyte and sintered at lower (~1000 °C) temperature cation redistribution, and, hence, oxygen mobility enhancement would be substantial as well.

This work presents results of such studies for powdered samples of $\text{PNC}_x\text{--YDC}$ nanocomposites and PNC_x perovskites annealed at 1000–1100 °C using temperature-programmed oxygen isotope heteroexchange with C^{18}O_2 and $^{18}\text{O}_2$ in both flow and closed reactors. Since characteristics of oxygen mobility and reactivity were found to depend rather moderately on the Ni/Co ratio in perovskites, here mainly results obtained for samples with Ni/Co ratio = 1 will be presented. For comparison, samples of Pr-deficient perovskite $\text{Pr}_{0.8}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ and Pr, Y-doped ceria $\text{Ce}_{0.65}\text{Pr}_{0.25}\text{Y}_{0.1}\text{O}_2$ (PYDC) were prepared and studied as well.

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2. Experimental

Nanocrystalline oxides $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (PNC), $\text{Pr}_{0.8}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$, $\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{2-\delta}$ and $\text{Ce}_{0.65}\text{Pr}_{0.25}\text{Y}_{0.1}\text{O}_{2-\delta}$ were synthesized via polymerized complex precursor (Pechini) route [3,4] and calcined in air at 700–1100 °C. Nanocomposites PNC–YDC were synthesized via powerful ultrasonic dispersion of the mixture of these nanocrystalline oxide powders calcined at 700 °C (1:1 weight ratio) in isopropanol using a T25 (ULTRA-TURRAX IKA, Germany) homogenizer with the addition of 1 wt.% polyvinyl butyral. The suspension was dried at room temperature. Powders of perovskites and composites were pressed into pellets under ~20 MPa and calcined at 1000–1100 °C in air for 2 h. For subsequent characterization, samples were finely ground using an agate pestle and mortar.

XRD patterns were obtained with a D8 Advance (Bruker, Germany) diffractometer using $\text{Cu K}\alpha$ monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$) in 2θ range 5–90°.

Transmission Electron Microscopy (TEM) micrographs were obtained with a JEM-2010 instrument (lattice resolution 1.4 Å, acceleration voltage 200 kV). Analysis of the local elemental composition was carried out by using an energy-dispersive EDX spectrometer equipped with Si(Li) detector (energy resolution 130 eV).

The oxygen mobility and surface reactivity of powdered samples were characterized by the oxygen isotope exchange with $^{18}\text{O}_2$ (enrichment 95%) or C^{18}O_2 (enrichment 89%) using temperature-programmed modes (TPIE) with MS control of the gas phase isotope composition [3–6]. The experiments were carried out in the flow and closed reactors. In the first case, after pretreatment in oxygen (1% O_2 in He at 700 °C, 40 min) followed by cooling down to 100 °C in the same gas stream, it was switched to either 1% $^{18}\text{O}_2$ in He or to 1% C^{18}O_2 in He (O_2 admixture 5 ppm) followed by the linear temperature ramp of 5/min up to 800 °C. In the static mode of exchange, samples were pretreated in air at 650 °C for 2 h, then, after degassing at the same temperature up to $\sim 10^{-6}$ – 10^{-7} Torr, samples were cooled down to room temperature. After introducing a labeled reagent into the reactor space (gas phase volume ~680 cm^3 , pressure 1.4 ÷ 2.1 Torr), the linear temperature ramp of 5 K/min up to 700 °C was started. Analysis of the oxygen isotope exchange data was carried out using approaches earlier described in details [3–8].

3. Results and discussion

3.1. Textural and structural characteristics

Specific surface areas of perovskites and nanocomposites sintered at high temperatures (Table 1) vary in the range of 0.5–2 m^2/g decreasing

with sintering temperature, so that residual porosity of nanocomposite pellets decreases from 30% at 1000 °C to 25% at 1100 °C.

According to XRD data, doped ceria samples calcined at 700 °C are single-phase oxides with Fm3m cubic type structure, the lattice parameters being equal to 5.420 Å (PYDC) and 5.410 Å (YDC). Their specific area varies in the range of 30 (YDC)–40 (PYDC) m^2/g with X-ray domain sizes being in the range of 25–30 nm. The structure of $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ and $\text{Pr}_{0.8}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ samples calcined under air at temperatures up to 1100 °C corresponds to the orthorhombic perovskite phase [1] with a small (<1%) admixture of Pr_6O_{11} phase (Fig. 1a). The unit cell volume of the perovskite phase slightly increases with Ni content from 221.37 Å³ (xNi = 0.4) to 222.52 Å³ (xNi = 0.6).

For $\text{PrNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ –YDC (1:1) composites sintered under air at temperatures up to 1100 °C the orthorhombic structure of perovskite phase is preserved (Fig. 1b), while in samples sintered at 1300 °C it was transformed into the cubic one [3,4]. The unit cell volume of the perovskite phase slightly decreases with the sintering temperature to 220.17 (xNi = 0.4)–221.38 (xNi = 0.6) Å³. Similarly, for the fluorite-like phase of doped ceria in nanocomposites, the lattice cell parameter estimated by the (511) reflection decreases with the sintering temperature to 5.402–5.406 Å. Note that in nanocomposites sintered at 1300 °C the lattice cell parameter of the doped ceria phase is bigger varying in the range of 5.413–5.409 Å with the increase of Ni content in the perovskite phase [3,4]. In addition, the admixture of Ni(Co)O phase is observed (Fig. 1b).

According to high resolution electron microscopy data with EDX analysis of the elemental composition of neighboring domains of perovskite and fluorite phases (Fig. 2), this variation of the lattice parameters is caused by cation redistribution between phases. Hence, this phenomenon earlier revealed for dense PNC–YDC nanocomposites sintered at 1300 °C [3,4] also takes place in porous nanocomposites sintered at lower temperatures. The most prominent feature is the incorporation of Pr cations into doped ceria phase apparently disordering both perovskite-like and fluorite-like phases. For different domains of doped ceria, Pr/Ce ratio varies from 0 to 1, which clearly demonstrates that composition of fluorite domains is controlled by kinetic factors (diffusion of cations) and not by equilibrium. Incorporation of transition metal cations (Ni and Co) into the fluorite domains, first of all, into their surface layers [5], is also observed (Fig. 2). For perovskite-like domains, Pr/Ni + Co ratio varies from 0.98 to 0.75. With a due regard for segregation of Ni(Co)O phase detected by XRD (Fig. 1), this agrees with pronounced transfer of Pr cations into doped ceria phase at 1000–1100 °C. Note that Y and Ce cations are detected in perovskite domains as well (Fig. 2). Sintering of PNC–YDC nanocomposites at lower temperatures allows to avoid formation of $\text{Pr}_4\text{Co}(\text{Ni})_3\text{O}_{10}$ phase detected as admixture in samples sintered at 1300 °C [3,4].

Table 1
The rate of the oxygen heteroexchange R (600 K), oxygen diffusion coefficients D (600 K), activation energies of the surface exchange/bulk diffusion E and fraction of oxygen in samples corresponding to respective diffusion coefficient (%) estimated by fitting TPIE experiments in the flow reactor.

Sample composition/temperature of sintering (°C)/specific surface area (m^2/g)	The surface exchange				Bulk diffusion			
	With $^{18}\text{O}_2$		With C^{18}O_2		Fast		Slow	
	R^2 cm^2/s^2	E_{R2} kJ/mol	R cm^2/s^2	E_{R1} kJ/mol	D_1 cm^2/s	E_{D1} kJ/mol	D_2 cm^2/s	E_{D2} kJ/mol
$\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_3/1000/1.7$	8.6×10^{-11}	120	$>4.3 \times 10^{-8}$	n/d ^b	2.1×10^{-12} (5–10%)	120	5.2×10^{-16} (90%)	180
$\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_3 + \text{YDC}/1000/1.7$	n/d ^b		$>4.5 \times 10^{-6}$		7.3×10^{-12} (60%)	140	1.5×10^{-17} (40%)	200
$\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_3 + \text{YDC}/1100/0.8$			$>4.5 \times 10^{-6}$		7.5×10^{-12} (65%)	115	1.9×10^{-17} (35%)	200
$\text{Ce}_{0.65}\text{Pr}_{0.25}\text{Y}_{0.1}\text{O}_2/700/39$			$>4.7 \times 10^{-6}$		2.8×10^{-13} (100%)	60		
$\text{Pr}_{0.8}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3/700/9.2$			$>4.2 \times 10^{-7}$		2.1×10^{-13} (8%)	60	1.4×10^{-16} (92%)	160

^a Expressed in units of surface exchange coefficient k as in [3].

^b Not determined.

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