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The effect of microwave sintering on stability and oxygen mobility of praseodymium nickelates-cobaltites and their nanocomposites

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ABSTRACT

Co-doped praseodymium nickelates $PrNi_{1-x}Co_xO_{3-\delta}$ and their composites with yttrium doped ceria $Ce_{0.9}Y_{0.1}O_{2-\delta}$ are known to be promising materials for intermediate temperature solid oxide fuel cells and membranes for oxygen separation. Powdered samples were obtained via Pechini route and ultrasonic dispersion followed by mechanical activation. Pellets were sintered at 870–1100 °C by using microwave radiation. In comparison with conventionally sintered materials, the phase transition leading to Ruddlesden–Popper phase formation was shifted down for about 50 °C–100 °C. The effect of sintering by microwave radiation consisted of dramatically increased sample density, improved phase purity and enhanced oxygen mobility. When undesirable phase transitions at elevated sintering temperatures hinder gas-tight layers preparation, the microwave sintering technique can be used without any deterioration of transport properties of materials in comparison with conventional calcination.

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1. Introduction

State-of-the-art SOFC cathode materials are based on Sr-doped lanthanum manganites, ferrites-nickelates and ferrites-cobaltites (LSM, LSFN, LSFC) [1]. Despite showing good performance as SOFC cathodes, these materials have many disadvantages like thermomechanical incompatibility and interaction with electrolyte causing cell degradation and failure. Moreover, they are unstable to carbonization [2]. Problems of chemical instability can be overcome by substituting La cations with Pr because praseodymium zirconates and cerates are thermodynamically unstable [3]. Moreover, Pr-based perovskites are stable to carbonization, while being comparable with traditional materials by performance [4–7]. Praseodymium nickelate-cobaltites $PrNi_{1-x}Co_xO_{3-\delta}$ ($PN_{1-x}C$) are analogues of lanthanum nickelate-cobaltites $LaNi_{1-x}Co_xO_{3-\delta}$ and Sr-doped praseodymium nickelates-cobaltites $Pr_{1-x}Sr_xNi_{1-x}Co_xO_{3-\delta}$ known as materials with a high mixed electronic-ionic conductivity [4]. $PN_{1-x}C$ and their composites with $Ce_{0.9}Y_{0.1}O_{2-\delta}$ ($PN_{1-x}C$–YDC) show total conductivity ~200 S/cm at 600 °C [5], oxygen tracer diffusion coefficient and oxygen exchange constant ~10^{-7} cm^2/s and 10^{-6} cm/s, respectively, at 700 °C, with SOFC power density being about 0.3 W/cm^2 at 600 °C [6,7]. These characteristics are comparable or even exceed those for LSM, LSFC and LSFN cathode materials. However, from the point of view of SOFC manufacturing procedures, both $PN_{1-x}C$ and $PN_{1-x}C$–YDC materials have a certain disadvantage: at temperatures above 1100 °C, perovskite phase becomes unstable resulting in $Pr_4(Ni_{1-x}Co_x)_3O_{10+\delta}$ Ruddlesden–Popper homologue phase formation, whereas at temperatures below 1100 °C, the sinterability of these materials is not sufficient to provide the required strong attachment of cathode layer to electrolyte. To obtain non-porous well-sintered ceramics based on $PN_{1-x}C$ calcined at temperatures below 1000 °C–1100 °C, the microwave (MW) radiation sintering technique was used.

Application of MW heating for sintering of ceramic materials has certain specific features [8–10]: a significant (50 °C–100 °C) decrease in process temperature, especially at the intermediate stage of sintering; and a reduction in the duration of the high-temperature stage of the sintering process due to rapid bulk heating. In some cases, like conventional sintering (CS), MW sintering allows to obtain ceramics with homogenous particle size distribution, while pore size distribution is even more homogenous [11].

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Table 1
List of MW sintered samples used in current work.

Sample name	Composition	Sintering temperature (°C)	Sintering time (min)	Heating rate (°C/min)	Porosity (%)
P-MW1	$PrNi_{0.5}Co_{0.5}O_{3-\delta}$	950	60	60	28
P-MW2		950	60	600	26
P-MW3		1000	5	750	19
P-MW4		870	1	48	28
P-MW5		1000	60	40	18
P-MW6		1000	60	55	14
P-MW7		950	60	26	32
P-MW8		1000	60	30	28
P-MW9		1000	60	30	26
P-MW10		1000	60	23	26
P-MW11		1000	30	26	27
P-MW12		1000	60	75	29
Conventional sintering		1000	60	5.5	30
		1100	60	5.5	25
		1300	60	5.5	5
C-MW1	$PrNi_{0.5}Co_{0.5}O_{3-\delta}$	1100	60	60	8
C-MW2	(50 wt.%)–	1100	2	54	6
C-MW3	$Ce_{0.9}Y_{0.1}O_{2-\delta}$	930	1	50	9
C-MW4		1100	60	65	7
C-MW5		1050	60	60	4
C-MW6		1100	60	40	4
C-MW7		1100	60	40	
C-MW8		1100	60	48	
C-MW9		1000	60	25	
C-MW10		1100	60	29	
Conventional sintering		1300	60	5.5	5

Under certain conditions, the influence of MW irradiation on the mass transport in ceramics can be considered as being caused by "the microwave field nonthermal effect" [12]. In this manner, the MW field should be also capable to affect chemical and phase transitions in solids where they are often limited by the mass transport. There are a number of studies demonstrating that the temperature of solid-state phase transitions is changed under microwave heating [13–15].

This paper presents the results of research aimed at the elucidation of specific effects of microwave sintering on structural, textural and transport properties of cathode materials based on $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ perovskite and its nanocomposite with $Ce_{0.9}Y_{0.1}O_{2-\delta}$.

2. Experimental

$PrNi_{0.5}Co_{0.5}O_{3-\delta}$ (PNC) and $Ce_{0.9}Y_{0.1}O_{2-\delta}$ (YDC) complex oxide powders were prepared via the modified Pechini route. $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ (50 wt.%)–$Ce_{0.9}Y_{0.1}O_{2-\delta}$ (PNC–YDC) nanocomposites were prepared by ultrasonic dispersion of the mixture of PNC and YDC powders in propane-2-ol. Powdered nanocomposite obtained after drying were calcined at 900 °C, then mechanically activated in a ball mill AGO-2 (ZAO NOVIC, Russia) for 5 min with the addition of ethanol. Suspensions were dried at 70 °C then pressed in disks at 550 MPa. Pellets were sintered at 870 °C–1100 °C for 1–60 min by microwave radiation using a specially built setup. Temperature of sample sintering was determined with a pyrometer. A description of the samples is given in Table 1. True density and residual porosity of samples were estimated by weighing dry pellets and pellets soaked in ethanol.

All materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD patterns were obtained with a D8 Advance (Bruker, Germany) diffractometer using Cu-K_α monochromatic radiation ($\lambda = 1.5418$ Å) in 2θ range 20°–90° with a step 0.05° (2θ) and accumulation time 3 s per step. Plasticine was used to fix the pellet in a cuvette before measurement. The phase composition analysis was carried out using diffraction databases PDF-2 and ICSD. Primary XRD patterns processing was carried out using EVA (Bruker) software. The lattice parameters were determined by using the PowderCell (V. 2.4) software [16]. Perovskite (Pnma) cell parameters determination accuracy was ±0.001 Å, 0.001 Å (a, c), ±0.002 Å (b). The TEM images 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).

Temperature programmed desorption of oxygen (TPD O_2) experiments for powdered samples (0.5–1 mm fraction obtained by crushing and grinding of pellets) pretreated in O_2 (the temperature ramp 5 °C/min from 25 °C to 880 °C in He stream followed by 70 min isotherm) was used to characterize the bonding strength of oxygen with the surface of perovskites and composites along with the amount of highly mobile oxygen. The outlet gas mixture composition was monitored by TEST-1 (Boner, Russia) gas analyzer. To estimate the amount of oxygen desorbed in each single peak, TPD curves were decomposed into Gaussian components. Effective activation energies were estimated by analyzing the ascending part of the peak using Wigner–Polanyi equation assuming pseudo-zero reaction order. This allowed an estimation of the fractions of oxygen with different bonding strengths/mobility related to fluorite phase, perovskite–fluorite interfaces and α-, β- and γ-oxygen of perovskite phase with activation energy ~40, 80–120 and 160–400 kJ/mol, respectively [17].

The oxygen mobility and surface reactivity of powdered or ground (0.25–0.5 mm fraction) samples were studied by using the oxygen isotope exchange with $^{18}O_2$ and $C^{18}O_2$ in the temperature programmed (TPIE) modes (heating rate 5 °C/min) in closed and flow reactors

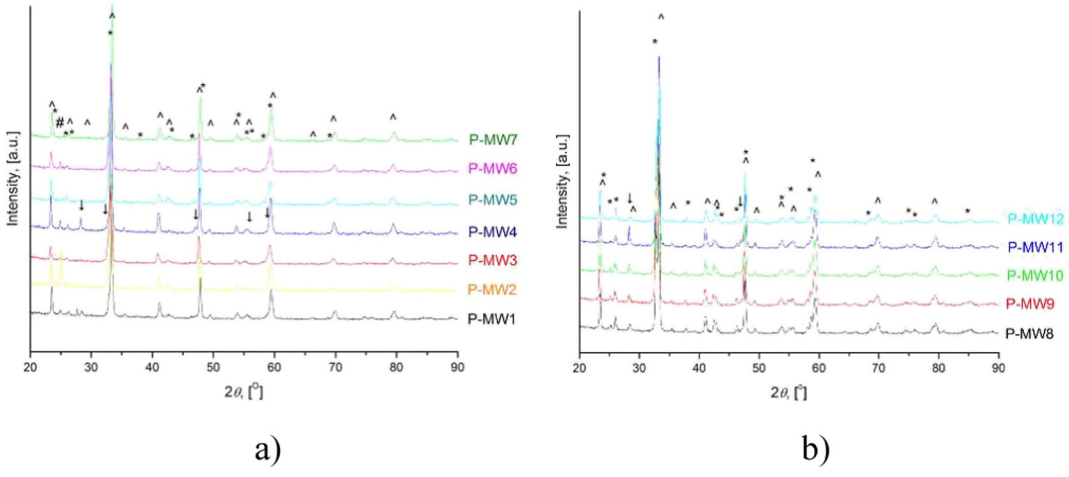

Fig. 1. XRD patterns of $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ samples sintered by microwave radiation. ^, $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ perovskite; ↓, Pr_6O_{11}; *, $Pr_4Ni_{1.5}Co_{1.5}O_{10+\delta}$; #, plasticine.

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