# Electrical Conductivity, Thermal Expansion and Electrochemical Properties of Perovskites $PrBaFe_{2-x}Ni_xO_{5+\delta}^1$

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Abstract—In order to evaluate applicability of mixed-conducting  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  perovskites for cathodes of solid oxide fuel cells (SOFCs), their crystal structure, thermal and chemical expansion, electrical conductivity and electrochemical behavior were studied. The solubility limit of nickel in PrBaFe<sub>2</sub>O<sub>5+\delta</sub> corresponds to x = 0.8. At x > 0.2, the disordered cubic phase transformed into the tetragonal phase. The maximum level of conductivity (50–120 S/cm) at the operating temperatures of SOFC was found for the composition with the maximum nickel content, PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5+\delta</sub>. This material is also characterized by moderate thermal and chemical expansion relative to other ferrite-nickelates. The polarization resistance of a porous PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5+\delta</sub> cathode in a cell with a protective Ce<sub>0.6</sub>La<sub>0.4</sub>O<sub>2-\delta</sub> layer and a solid electrolyte (La<sub>0.9</sub>Sr<sub>0.1</sub>)<sub>0.98</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-\delta</sub> was ~0.9 Ohm cm<sup>2</sup> at a temperature of 1073 K, atmospheric oxygen pressure, and current density of -120 mA cm<sup>-2</sup>.

*Keywords:* perovskite, ferrite-nickelate, electrical conductivity, thermal expansion, chemical expansion, SOFC cathode, polarization resistance

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# INTRODUCTION

Perovskite-like phases based on LnBaCo<sub>2</sub>O<sub>5 + δ</sub> (Ln is a rare-earth cation) are of interest as materials for membranes with mixed ion-electron conductivity for oxygen generators and cathodes of solid oxide fuel cells (SOFCs) [1-6]. The significant difference between the radii of  $Ln^{3+}$  and  $Ba^{2+}$  leads to cation ordering in the A sublattice of the ABO<sub>3</sub> perovskite structure [7-9]. This factor, along with the stability of cobalt cations in pyramidal oxygen surroundings, leads to the formation of structural planes with high contents of anion vacancies, which is responsible for increase of oxygen mobility and the rate of surface exchange with the gas phase [1, 5, 8-12]. The high oxygen-ion conductivity, which shows itself even at 573–673 K, leads to dominant electron conductivity and high electrochemical activity, due to which these compounds can be used for SOFC cathodes at temperatures below 973-1073 K, when the use of standard manganite-based cathodes is impossible [1, 3, 13]. A limitation on the use of cobaltites are significant changes in the volume during heating or redox cycling

regardless of the ordering of the *A* sublattice, which are partly due to the formation of relatively large  $Co^{2+}$  cations during the reduction and disproportionation of  $Co^{3+}$ . Due to the ratio of the radii of the  $Co^{4+}$ ,  $Co^{3+}$ , and  $Co^{2+}$  cations [14], as well as the endothermic character of both reactions [15, 16], these processes make an additional contribution to the total thermal expansion, which increases when the temperature increases and the average degree of cobalt oxidation decreases [17–19].

The (Ln,A)FeO<sub>3 -  $\delta$ </sub> solid solutions, where A is an alkaline earth element, represent an alternative group of electrode materials, where the level of thermal expansion is generally lower than in cobaltite-based analogues [20]. Doping of ferrites with nickel makes it possible to improve the electrochemical activity of electrodes. For example, an electrochemical cell with a cathode based on LaNi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>3 -  $\delta$ </sub> demonstrated a specific capacity of over 700 mW/cm<sup>2</sup> at 1023 K [21]. The perovskite La<sub>0.6</sub>Ca<sub>0.4</sub>Fe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3 -  $\delta$ </sub> was reported to have relatively high activity both as a cathode [22, 23] and anode [23] component, although this material is unlikely to show phase stability under anode conditions. The composition PrBaFe<sub>1.6</sub>Ni<sub>0.4</sub>O<sub>5 +  $\delta$ </sub> was tested as an electrode for symmetric SOFCs, where

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Fig. 1. Dilatometric curves of  $PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$  in air and oxygen atmosphere obtained in the thermal cycling mode with isothermal dwellings.

the cathode and anode are made of the same materials; the cell capacity was  $50 \text{ mW/cm}^2$  at 923 K [24].

The goal of the present study was to investigate the  $PrBaFe_{2 - x}Ni_{x}O_{5 + \delta}$  oxide system and analyze the transport, electrochemical, and thermomechanical properties of some materials of this system. As these properties depend on the degree of cation ordering in the A sublattice, we also considered the structural factors. At present, the stability of the ordered configurations of  $Pr^{3+}$  and  $Ba^{2+}$  in the crystal lattice of  $PrBaFe_2O_{5+\delta}$  under oxidation conditions remains an open question. On the one hand, in view of the large difference in the ionic radii of  $Pr^{3+}$  and  $Ba^{2+}$  and the existence of binary perovskites  $LnBaCo_2O_{5+\delta}$  and LnBaMn<sub>2</sub>O<sub>5 + δ</sub> [1, 3, 5, 8, 25, 26], praseodymiumbarium ferrite is expected to have a significant tendency toward ordering. However, the  $La_{0.5}Ba_{0.5}FeO_{3-\delta}$ and  $Pr_{0.5}Ba_{0.5}FeO_{3-\delta}$  solid solutions have a disordered cubic structure [27, 28]; their analogs with Ln = Ndand Sm are characterized by orthorhombic distortion of the lattice [27]. For GdBaCo<sub>2</sub>O<sub>5 +  $\delta$ </sub> binary perovskite with more than 30% of cobalt replaced by iron, a GdFeO<sub>3</sub> impurity phase with a disordered structure formed [10].

#### **EXPERIMENTAL**

PrBaFe<sub>2-x</sub>Ni<sub>x</sub>O<sub>5+δ</sub> (x = 0-1.0) was synthesized by the glycine-nitrate method [29]. At the first stage of the synthesis, the required amounts of Pr(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, Ba(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and glycine (≥99%) were dissolved in distilled water, while vigorously stirring the mixture on a magnetic stirrer. Then the mixture was evaporated; further combustion of the mixture gave finely disperse powder, which was calcinated in air at 1173 K for 2 h to remove the organic residue. The powder was ground, and final annealing was performed at 1503–1603 K. The X-ray diffraction (XRD) analysis of the materials was performed at room temperature on a Siemens D-500-Braun X02-1787 diffractometer (Siemens, Germany) (Cu $K_{\alpha 1}$  radiation, step  $0.02^{\circ}$ ,  $10^{\circ} \le 2\theta \le 120^{\circ}$ ). The XRD patterns were processed with the PowderCell (version 2.4) program package. The ceramic samples were prepared by hydroforming (80–100 MPa) followed by sintering at 1473–1553 K in air. The specific electric conductivity was measured by the standard DC four-probe method at 373-1273 K. The microstructure analysis was performed using a LEO SUPRA 50VP (Carl Zeiss, Germany) scanning microscope with a field emitting cathode at accelerating voltages of 5-10 kV.

The thermomechanical measurements were performed on a Linseis L75VS1400 (Germany) vertical dilatometer. In the dynamic mode of measurements. the sample was heated at a constant rate (1-3 K/min)to 1373 K and then cooled at the same rate. In the thermocyclic mode, the sample was kept at 1273 K and then cooled stepwise to 923 K (step 50 K) with isothermal dwellings at each temperature until complete equilibrium with the phase was reached. The air and oxygen flows were interchanged during the measurements, and the thermal cycle was repeated; the examples of this mode for  $PrBaFe_{1,2}Ni_{0,8}O_{5+\delta}$  are shown in Fig. 1. The thermal expansion coefficients (TECs) were determined from the slope of the temperature dependence of the relative elongation of the sample  $(\Delta L/L_0)$ . The isothermal chemical expansion  $\varepsilon$  during the air  $\rightarrow$  oxygen transition was calculated by the equation

$$\varepsilon = \frac{L_{\text{atm},T} - L_{\text{air},T}}{L_{\text{air},T}},$$

where  $L_{\text{atm},T}$  and  $L_{\text{air},T}$  is the length of the sample at a temperature T in oxygen and air, respectively.

The electrochemical studies were performed by the three-electrode technique. The model cells were gastight disks of the  $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) solid electrolyte with porous layers of the working electrode, Pt counter electrode, and Pt reference electrode. The powders of the chosen working electrode and the protective sublayer of  $Ce_{0.6}La_{0.4}O_{2-\delta}$ (LDC) were mixed with a Heraeus V-006 binder (50: 50 wt %) and deposited on LSGM in sequence by screen printing followed by burning-in at 1473 K. The measurements were performed using an AutoLab PGSTAT302N potentiostat/galvanostat (The Netherlands) at 973-1123 K in an air or oxygen flow. The storage time was 30-60 min for each experimental point. The ohmic and polarization resistance values were determined from the impedance spectra obtained in the frequency range from 0.1 Hz to 100 kHz.



**Fig. 2.** X-ray diffraction patterns of  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  powders synthesized in air at 1503–1603 K. Insert: enlarged region of the peaks of impurity phases in PrBaFeNiO<sub>5+\delta</sub>.

## **RESULTS AND DISCUSSION**

The results of the XRD studies of the PrBaFe<sub>2-x</sub>Ni<sub>x</sub>O<sub>5 +  $\delta$ </sub> system are presented in Fig. 2 and Table 1. At low nickel contents (x < 0.4), the materials have a cubic structure (space group  $Pm\overline{3}m$ ). The unit cell volume decreases when iron is replaced by nickel, which is consistent with the ratios of the cationic radii [14]. Also note that at minor variations of oxygen nonstoichiometry, the introduction of Ni<sup>2+</sup> increases the average oxidation level of iron, increasing the concentration of the relatively small Fe<sup>4+</sup> cations. A similar effect of nickel doping was observed for

the LaFe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3-\delta</sub>, La<sub>0.9</sub>Sr<sub>0.1</sub>Fe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3-\delta</sub>, and Pr<sub>0.7</sub>Sr<sub>0.3</sub>Fe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3-\delta</sub> systems [30-32]. A decrease in the average radius of cations in the *B* sublattice leads to a tetragonal distortion of the structure observed at  $0.4 \le x \le 0.8$ . The transition to the tetragonal crystal system (*P4/mmm*) is accompanied by the appearance of an inflection on the dependence of the pseudocubic cell parameter on *x* (Fig. 3). At *x* = 1.0 impurity phases form (Fig. 2), which suggests the limit of the range of ordering in the *A* sublattice over the whole range of nickel solubility.

Material	Space group	<i>a</i> , nm	<i>c</i> , nm	V, nm <sup>3</sup>
$PrBaFe_2O_{5+\delta}$	$Pm\overline{3}m$	0.3930	_	0.0607
$PrBaFe_{1.8}Ni_{0.2}O_{5+\delta}$	$Pm\overline{3}m$	0.3919	—	0.0602
$PrBaFe_{1.6}Ni_{0.4}O_{5+\delta}$	P4/mmm	0.3920	0.3887	0.0597
$PrBaFe_{1.4}Ni_{0.6}O_{5+\delta}$	P4/mmm	0.3917	0.3872	0.0594
$PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$	P4/mmm	0.3913	0.3858	0.0591

**Table 1.** Crystal lattice parameters of  $PrBaFe_{2-x}Ni_xO_{5+\delta}$ 

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**Fig. 3.** Dependences of the pseudocubic cell parameter, TEC in the high-temperature range, specific electric conductivity at 673 and 1073 K, and activation energy of conductivity on the nickel concentration.



**Fig. 4.** Temperature dependences of the relative elongation of  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  under conditions of continuous heating in air. The heating rate was 3 K/min at x = 0-0.2 and 1 K/min at x = 0.4-0.6.

On the dilatometric curves of the  $PrBaFe_{2-x}Ni_xO_{5+\delta}$ ceramics (Fig. 4) we can isolate two linear sections with a transition at 600–650 K, when the lattice starts to actively lose oxygen on heating. In the low-temperature range, the TEC tends to increase when the nickel content increases to x = 0.6, though the corresponding changes occur in a relatively narrow range  $(13.2-13.9) \times 10^{-6} \text{ K}^{-1}$  (Table 2). This tendency is associated with an increase in the concentration of oxygen vacancies after the introduction of nickel and with the shift of equilibrium between the redox pairs  $Fe^{3+}/Ni^{3+} \Leftrightarrow Fe^{4+}/Ni^{2+}$  at increased temperature. The increase in the vacancy concentration that starts at 600-650 K leads to an abrupt growth of TEC due to the chemical contribution. The TEC of the materials in the high-temperature range is  $(21-25) \times 10^{-6} \text{ K}^{-1}$ . which is significantly higher than in solid oxide electrolytes. In the given temperature range, the material with x = 0.2 has the maximum TEC, which is (24– 25)  $\times$  10<sup>-6</sup> K<sup>-1</sup>. The TEC decreases after further doping; this is caused by the decrease in the average degree of oxidation of the cations of the B sublattice after the replacement of iron by nickel and correlates with the increase in the tetragonal distortion (Fig. 3). The latter hypothesis is consistent with the dependence of the isothermal chemical expansion during the oxidation of materials on the nickel content (Fig. 5).

The temperature dependences of electric conductivity (Fig. 6) also exhibit a behavior typical for ferrites [31], whose characteristic feature is the presence of a maximum at 600–700 K related to an active release of oxygen from the crystal lattice at high temperatures. The decrease in conductivity here is due to the dominant role of electron charge carriers of the p type, whose concentration decreases when oxygen vacancies form. The effective activation energy in the low-



**Fig. 5.** Chemical expansion of the  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  ceramics during the isothermal oxidation.

Material	Continuous heating in air*		Isothermal storage**		
	Т, К	TEC × $10^{6}$ , K <sup>-1</sup>	$p(O_2)$ , atm	TEC × $10^{6}$ , K <sup>-1</sup>	
$PrBaFe_2O_{5+\delta}$	300-640	$13.18\pm0.02$	0.21	$22.3\pm0.2$	
	640-1370	$22.04\pm0.01$	1	$22.1\pm0.6$	
$PrBaFe_{1.8}Ni_{0.2}O_{5+\delta}$	300-640	$13.22\pm0.02$	0.21	$25.0\pm0.3$	
	640-1370	$24.19\pm0.01$	1	$24.4\pm0.7$	
$PrBaFe_{1.6}Ni_{0.4}O_{5+\delta}$	300-590	$13.42\pm0.01$	0.21	$24.0\pm0.3$	
	590-1370	$23.53\pm0.01$	1	$23.6\pm0.6$	
$PrBaFe_{1.4}Ni_{0.6}O_{5+\delta}$	300-590	$13.93\pm0.01$	0.21	$22.0\pm0.1$	
	590-1370	$22.22\pm0.01$	1	$22.2\pm0.3$	
$PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$	_	_	0.21	$21.6\pm0.4$	
			1	$21.8\pm0.5$	

**Table 2.** TECs of the PrBaFe<sub>2-x</sub>Ni<sub>x</sub>O<sub>5+ $\delta$ </sub> ceramics obtained in different measurement modes

\* The heating rate is 3 K/min for the samples with x = 0-0.2 and 1 K/min for those with x = 0.4-0.6.

\*\* The temperature range is 923–1223 K.

temperature range calculated by the Arrhenius equation is 8–23 kJ/mol and decreases at nickel doping (Fig. 3). Note that the electric conductivity of the ferrite PrBaFe<sub>2</sub>O<sub>5 +  $\delta$ </sub> synthesized in the present study is two or three times higher than the published data [27], while the character of its temperature dependence is preserved. Substitution of iron with nickel leads to a nonmonotonic increase in conductivity, while the transition from cubic to tetragonal structure reduces the mobility of holes (Fig. 3). The PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5+ $\delta$ </sub> composite was chosen as a cathode material for SOFC due to its highest electric conductivity and lowest TEC.



Fig. 6. Temperature dependences of the specific electric conductivity of  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  in air.

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Figure 7 shows the microstructure of the cross-section of the interface between the solid electrolyte, LDC protective sublayer, and PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5 +  $\delta$ </sub> (PBFN) cathode. The protective sublayer with a thickness of ~5  $\mu$ m had a developed porous surface



**Fig. 7.** (a) Electron microscopic image of the cross-section of SOFC with the LSGM electrolyte,  $PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$  (PBFN) cathode, and  $Ce_{0.6}La_{0.4}O_{2-\delta}$  protective sublayer and (b) the surface of this cathode.



**Fig. 8.** Dependences of the cathodic overpotential on the current density for the porous  $PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$  electrode in contact with the  $Ce_{0.6}La_{0.4}O_{2-\delta}$  protective sublayer and the LSGM solid electrolyte at 973–1123 K in air and oxygen.



**Fig. 9.** Examples of impedance hodographs corrected for ohmic resistance and reduced to the geometric area of the working electrode.

and good adhesion to electrolyte and working electrode (Fig. 7a). The cathode layer with a thickness of ~12  $\mu$ m consisted of relatively large grains with sizes of 1–5  $\mu$ m with a highly developed surface formed by submicron particles (Fig. 7b). Despite the differences in the TECs, there were no traces of cracking or peeling of the cathode layer. The polarization curves (Fig. 8) are almost linear at low current densities and exhibit the Tafel behavior at overvoltages  $|\eta| > 40-50$  mV. The impedance spectroscopy shows that the cathode process includes at least two limiting stages (Fig. 9). An increase in the current leads to an increase in the low-frequency component, indicating that the mass transfer may be hindered. At the same time, an increase in



Fig. 10. Temperature dependence of the polarization resistance of the PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5 +  $\delta$ </sub> electrode in contact with the Ce<sub>0.6</sub>La<sub>0.4</sub>O<sub>2 -  $\delta$ </sub> protective sublayer and LSGM solid electrolyte in air.

the partial oxygen pressure significantly reduces the polarization resistance and overvoltage (Fig. 8), which shows that the contribution of the processes associated with sorption of molecular oxygen to the exchange kinetics of the cathode layer is significant. At a cathode current of  $-50 \text{ mA/cm}^2$ , the overvoltage is approximately -20 and -120 mV at 1123 and 1023 K, respectively. For the cathode polarization resistance at zero DC density in air, the effective activation energy reaches 227 kJ/mol (Fig. 10). For further improvement of the electrochemical activity of the cathodes based on ferrites-nickelates, their microstructural optimization is required in order to increase the exchange current and mixed ion-electron conductivity. This problem can be solved by forming composite layers with additives of doped cerium oxides.

## CONCLUSIONS

The X-rav diffraction analysis of the  $PrBaFe_{2-x}Ni_xO_{5+\delta}$  system (x = 0-1.0) showed that the solubility limit of nickel corresponds to x = 0.8. At x = 0 - 0.2, the materials have a disordered cubic structure of the perovskite type (space group  $Pm\overline{3}m$ ), and further increase in the nickel concentration leads to a tetragonal distortion (P4/mmm). This structural transition is accompanied by a certain decrease in the mobility of the electron charge carriers. In general, however, the results show a tendency toward an increase in conductivity and a decrease in its activation energy when iron is replaced by nickel. The  $PrBaFe_{1.2}Ni_{0.8}O_{5+\delta}$  composite has the highest electric conductivity (50-120 S/cm) at working temperatures of SOFC; it also has low thermal and chemical expansion relative to that of other ferrites-nickelates. The polarization resistance of the porous PrBaFe<sub>1.2</sub>Ni<sub>0.8</sub>O<sub>5+\delta</sub> cathode in a cell with the Ce<sub>0.6</sub>La<sub>0.4</sub>O<sub>2-\delta</sub> buffer layer and  $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$  solid electrolyte did not exceed 0.9 Ohm cm<sup>2</sup> at a temperature of 1073 K, atmospheric oxygen pressure, and current density of 120 mA cm<sup>-2</sup>.

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