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Phase equilibria, structure and properties of complex oxides in the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system as potential cathodes for SOFCs

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ABSTRACT

The phase equilibria in the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system were studied at 1373 K in air. The homogeneity ranges and crystal structure of $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ solid solutions were determined by the X-ray powder diffraction, the unit cell parameters were refined by the Rietveld analysis. It was found that $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ with $0.0 \le x \le 0.6$ and $0.1 \le y \le 0.9$ possesses orthorhombic structure (sp. gr. *Pbnm*) that reveals *O*-type → *O′*-type → *O*-type structural transition. The orthorhombic distortion decreases with the increasing of strontium content, as a result $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ solid solutions with $0.7 \le x \le 0.9$ and $0.1 \le y \le 0.9$ possess the cubic structure (sp. gr. *Pm*3*m*). Isothermal-isobaric phase diagram for the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system at 1373 K in air has been presented. A series of samples with the overall composition $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ ($0.0 \le y \le 1.0$) were characterized by the thermogravimetric analysis, iodometric titration, dilatometry and electrical conductivity measurements. The oxygen nonstoichiometry in $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ ($0.0 \le y \le 1.0$) increases with increasing temperature and cobalt content. Gradual substitution of iron by cobalt in the $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ oxides leads to the increase of the average thermal expansion coefficients. The electrical conductivity exhibits maximum within the range of 600–750 K and significantly increased with cobalt content at $T < 800$ K. Chemical compatibility of $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.12}O_{3-\delta}$ solid electrolytes has been studied. The single cells based on the LSGM electrolyte, $Sr_2Ni_{0.75}Mg_{0.25}MoO_6$ anode and $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ ($y = 0.3$ and 1.0) cathode were fabricated and examined.

1. Introduction

In recent years perovskite materials of general formula $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ were reported as promising electrodes for the solid oxide fuel cells (SOFCs) [1–4]. Its crystal structure, oxygen content, thermal expansion, electrical conductivity and electrochemical performance were studied earlier [1–8], however in all these works Sr-content have not been exceeded the value of $x = 0.6$ [4] or 0.7 [8]. The obtained results confirmed that the value of electrical conductivity increased with the raise of Sr-content especially at low and intermediate temperatures [1,8]. Introduction of Sr also increases the value of oxygen deficiency [8], which can enhance the oxygen mobility and therefore improve electrochemical properties of mixed conductor.

One more important issue that needs to be known for the successful preparation and usage of these materials is the information about phase equilibria. Although the phase diagrams for the parent systems, namely Nd_2O_3 – SrO – Fe_2O_3, Nd_2O_3 – SrO – CoO, SrO – CoO – Fe_2O_3 and Nd_2O_3 – CoO – Fe_2O_3 were reported earlier [9–12], no systematic study of phase relations for the Nd – Sr – Co – Fe – O system has been undertaken yet.

The aims of the present work are: i) establishing of phase equilibria in the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system at 1373 K in air and determination of the crystal structure of intermediate phases; ii) characterization of oxygen content, thermal expansion and total electrical conductivity of the $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ solid solutions to fill the lack of information relating to the rich Sr-doped neodymium ferrites-cobaltites which are considered as promising candidates for the cathode application in SOFCs; iii) investiga-

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tion of electrochemical performance of $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ as the SOFC cathodes by testing the single cells based on the $La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.12}O_{3-\delta}$ (LSGM) electrolyte with $Sr_2Ni_{0.75}Mg_{0.25}MoO_6$ as an anode material [13] and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (CDS) as an interlayer.

2. Experimental

Powder samples of $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ with various x and y values were synthesized by the glycerol-nitrate combustion method, which was described in details in our previous work [8].

The LSGM and CDS electrolytes were prepared by the similar glycerol-nitrate combustion method utilizing of high purity pre-calcined La_2O_3, $SrCO_3$, MgO, metallic Ga and Sm_2O_3 and $Ce(NO_3)_3 \times 6H_2O$ as starting materials. The starting components taken in the appropriate ratio were dissolved in dilute nitric acid, and then glycerol was added as fuel and complexing agent in amount needed for a complete reduction of nitrate ions. The obtained solutions were dried to viscous gels; the following heating lead to a formation of white powders. Annealing of CDS electrolyte was performed at 1373 K in air during 24 h with intermediate grindings. LSGM electrolyte was calcined at 1373 K in the air during 10 h, followed by pelletizing and sintering at 1573 K for 10 h.

The powder sample of $Sr_2Ni_{0.75}Mg_{0.25}MoO_6$ (SNMM) was synthesized by the nitrate solutions method described by Filonova et al. [13].

The phase purity and crystal structure of the prepared oxides were determined by the XRD analysis using a Shimadzu XRD 7000 instrument ($Cu_{K\alpha}$ radiation, $10^\circ \le 2\theta \le 90^\circ$, scan step 0.02°–0.04° with the exposure time 5–10 s). The unit cell parameters were refined by the Rietveld method using the Fullprof package.

The changes of oxygen content in $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ ($0.0 \le y \le 1.0$) were determined by the TGA method using a STA 409PC Netzsch GmbH instrument. The measurements were performed within the temperature range of 298–1373 K in air in dynamic (heating/cooling rate of 1–2 K/min) and static regimes (stepwise heating/cooling with exposure at each temperature during 4–8 h). The absolute values of oxygen content in $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ were determined by means of the reduction of the samples inside the TGA cell in a flow of hydrogen at 1373 K for 10 h. It was also calculated from the average oxidation state of 3*d*-transition metals (Fe and Co) that was determined by the iodometric titration method [14].

Thermal expansion measurements were carried out within the temperature range 298–1373 K in air using a dilatometer (Netzsch GmbH DIL 402C) at a heating/cooling rate of 5 K/min. The ceramic samples for the measurements in a form of rectangular bar with the size of about 3 × 3 × 25 mm were preliminary sintered at 1573 K in air during 10 h, with subsequent slow cooling (1.5 K/min). The same ceramic samples were used for the electrical conductivity measurements. The temperature dependences of total conductivity were measured by the 4-probe method in the temperature range 298–1373 K in air.

Chemical compatibility of $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ ($y = 0.3$ and 1.0) oxides with the electrolyte materials LSGM and CDS was carried out by annealing of 50:50 (wt%) mixtures at 1573 K for 1 h. The chemical compatibility of the SNMM anode material with the LSGM electrolyte was previously studied by Filonova et al. [13].

The electrochemical performance of the studied materials was examined by measuring the *I–V* plots for the single SOFCs using $Nd_{0.2}Sr_{0.8}Fe_{1-y}Co_yO_{3-\delta}$ as cathode with $y = 0.3$ (NSFC) and $y = 1.0$ (NSC) as an example. The scheme of the single fuel cell is shown in Fig. 1. The sintered LSGM electrolyte pellet with the density higher than 90% of the theoretical value was polished down to 0.5 mm thickness. The powders of NSFC, NSC, CDS and SNMM were thoroughly grounded separately in alcohol media. The CDS slurry was painted at the surface area of the ceramic electrolyte pellet followed by firing for 2 h at 1573 K. Then the side of electrolyte pellet covered by the CDS interlayer was painted by the cathode (NSFC or NSC) slurry and the opposite side was painted by the anode SNMM slurry with the following firing for 1 h at 1523 K in air. The geometrical area of each electrode was about 0.07 cm^2. After that the single cell was fixed to a zirconia tube with the help of high-temperature glass sealant. Pt-mesh and Pt-wire connected to the both sides to the cell served as current collectors. Pure hydrogen with the flow rate of 250 ml/min was fed to the anode side as fuel and cathode side was exposed to the ambient air. Current-voltage (*I–V*) plots were measured in-situ during cell operation at 973, 1023, 1073 and 1123 K.

3. Results and discussion

3.1. Phase equilibria in the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system

Thirty nine samples of various composition within the general formula $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ were prepared and analyzed by X-ray powder diffraction using the Rietveld profile methods in order to study the phase equilibria in the $NdFeO_{3-\delta}$ – $SrFeO_{3-\delta}$ – $SrCoO_{3-\delta}$ – $NdCoO_{3-\delta}$ system at 1373 K in air.

3.1.1. Crystal structure of $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$

The XRD results for quenched samples reveal that the orthorhombically distorted perovskite structure (sp. gr. *Pbnm*) forms at 1373 K in air as long as the Sr content varied within the range of $0.0 \le x \le 0.6$ while the ideal cubic structure (sp. gr. *Pm3m*) appears within the range of $0.7 \le x \le 1$. As it will be shown later the latter is true not for the entire range of y values (Fe/Co ratio).

Closer inspection of the ratio of unit cell parameters a, b, $c/\sqrt{2}$ for the orthorhombic structure and the distortion parameter D that can be calculated according to the formula:

$$D = \frac{1}{3}\sum_{i=1}^{3}\left|\frac{\alpha_i - \overline{\alpha}}{\overline{\alpha}}\right| \cdot 100\%, \quad (1)$$

where $\alpha_1 = a$, $\alpha_2 = b$, $\alpha_3 = c/\sqrt{2}$ and $\overline{\alpha} = (a \times b \times c/\sqrt{2})^{1/3}$, indicates the appearance of two types of orthorhombic structure: *O*-type that is characterized by the parameter's ratio $a \le c/\sqrt{2} \le b$ or $b \le c/\sqrt{2} \le a$, and *O′* − type with the parameter's ratio $c/\sqrt{2} \le b \le a$. The structural transition *O*-type → *O′*-type → *O*-type observed for $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ solid solutions was described in details for the samples with $0.0 \le x \le 0.6$ and $y = 0.3$ in our previous work [8]. The values of unit cell parameters, unit cell volume and parameter of orthorhombic distortions for $Nd_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ with $0.0 \le x \le 0.6$ and $0.1 \le y \le 0.9$ are listed in Table 1. Fig. 2*a* demonstrates XRD pattern, refined by the full-profile Rietveld method for the $Nd_{0.9}Sr_{0.1}Fe_{0.5}Co_{0.5}O_{3-\delta}$ solid solution, as an example.

Further introduction of strontium into neodymium sublattice leads

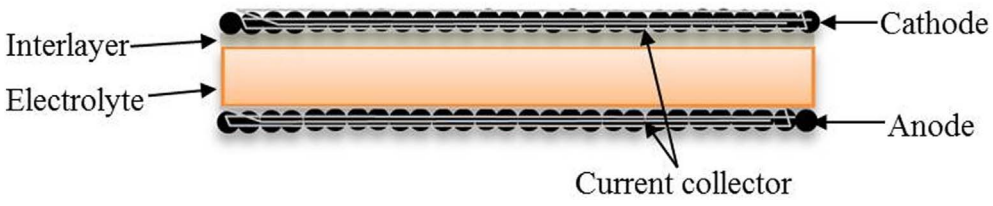

Fig. 1. The scheme of the single fuel cell.