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Validation of calcium-doped neodymium nickelates as SOFC air electrode materials

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ABSTRACT

The search for new electrode materials that can be applied to the solid oxide fuel cell (SOFC) technology is an active field of research. In continuing our studies of Ca-substituted layered nickelates, in this work we investigated $Nd_{2-x}Ca_xNiO_{4+\delta}$ materials synthesized via the solution assistant solid state reaction method to evaluate their prospective usage as cathode materials for the intermediate temperature SOFC. It was found that Ca doping resulted in the temperature decreasing for the *Fmmm* → *I4/mmm* transition in $Nd_2NiO_{4+\delta}$ (NNO) and the tetragonal structure stabilizing at room temperature at $x \geq 0.2$ in ambient air. The coefficient of thermal expansion calculated from the linear expansion under heating and cooling was different; however there was a common tendency for it to decrease when the Ca content was increased above 5 mol% ($x = 0.1$). The *dc* four-probe measurements revealed an increase in total electrical conductivity with doping. The polarization resistance of the $Nd_{2-x}Ca_xNiO_{4+\delta}$ electrodes in contact with $Ce_{0.8}Sm_{0.2}O_{1.9}$ depended non-linearly on the Ca content with a moderate maximum at $x = 0.1$. Ca-doping was found to decrease the interaction of the electrode materials with the electrolyte. It resulted in the polarization resistance of the composite electrodes containing doped materials decreasing compared to the composite electrodes based on $Nd_2NiO_{4+\delta}$. The polarization resistance of the $Nd_{1.7}Ca_{0.3}NiO_{4+\delta}$-$Ce_{0.8}Sm_{0.2}O_{1.9}$ (NCNO3-SDC) electrode formed at 1200 °C is equal to $0.56\ \Omega\ cm^2$ at 700 °C in ambient air and comparable with the resistance of the NNO electrode ($0.51\ \Omega\ cm^2$). Due to its superior stability and lower interaction with the electrolyte this electrode composition can be recommended for preferential usage in IT-SOFCs.

1. Introduction

At present, most research is concentrated on the study of mixed ion and electron conducting (MIEC) materials related to the layered lanthanide nickelates, $Ln_2NiO_{4+\delta}$ (Ln = La, Pr or Nd) [1–5]. Compared to perovskite oxides these compounds exhibit lower values of the coefficient of thermal expansion (CTE) [5,6], are compatible with solid electrolytes, possess good thermo-chemical stability [7–9] and have high coefficients of both oxygen surface exchange and oxygen diffusion due to the presence of highly mobile interstitial oxygen in their layered structure [6,10–15] and consequently rate quite highly as solid oxide fuel cell (SOFC) cathodes. Among them, $Nd_2NiO_{4+\delta}$ (NNO) has been reported to possess the highest level of oxygen over-stoichiometry δ in the series (0.22 at 27 °C in air) and the lowest value of CTE ($12.7 \times 10^{-6}\ K^{-1}$, measured in a range of 27–1000 °C in air) [6]. Its values for the coefficient of oxygen diffusion and surface exchange are close to those for $Pr_2NiO_{4+\delta}$ (PNO) [6,10,12] and equal to $1.8 \times 10^{-9}\ cm^2\ s^{-1}$ and $2.6 \times 10^{-8}\ cm\ s^{-1}$ (500 °C, $pO_2 = 0.21$ atm) [6]. Despite the fact that the activity of the NNO electrodes to the oxygen reduction reaction (ORR) was found to be lower than that of PNO, it showed superior phase stability in terms of resistance against Cr contamination and CO_2 poisoning [15–17]. Concerning reactivity with electrolytes, $Nd_2NiO_{4+\delta}$ showed better stability in this respect than did other members of the $Ln_2NiO_{4+\delta}$ series [7,18–20]. Nevertheless, its chemical interaction with electrolytes is strongly influenced by the synthesis method, Nd deficiency, temperature and time of treatment and appeared to be more significant at increased temperatures [7,21–23]. For instance, according to [7], $Nd_2NiO_{4+\delta}$ did not react with $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and $La_9SrSi_6O_{26.5}$ electrolytes either at 1150 °C (1 h) or at 800 °C (5 days). However it reacted with $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ in both treatment regimes with formation of some amount of $Nd_6Ga_2O_{12}$; according to [18] a fine powder of $Nd_2NiO_{4+\delta}$ reacted with

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$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and $Zr_{0.92}Y_{0.08}O_{1.96}$ electrolytes already at 1000 °C with formation of $Nd_2Ce_2O_7$ and $Nd_2Zr_2O_7$, respectively, but a coarse $Nd_2NiO_{4+\delta}$ powder, prepared by a solid state reaction method, stayed un-reacted with these electrolytes under the same conditions. It was shown in [21], that a reaction between a fine $Nd_2NiO_{4+\delta}$ powder (prepared by the modified Pechini method) with $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Zr_{0.92}Y_{0.08}O_{1.96}$ occurred very slowly at 1000 °C; in [23] there were no reactions observed between $Nd_{1.95}NiO_{4+\delta}$ and $La_9SrSi_6O_{26.5}$ until 1200 °C and $Nd_{1.95}NiO_{4+\delta}$ was found to react with $Zr_{0.92}Y_{0.08}O_{1.96}$ at 1100 °C with formation of trace amount of $Nd_2Zr_2O_7$.

Promising results were obtained for Sr-substituted $Ln_2NiO_{4+\delta}$ materials. First of all, Sr doping stabilized $Pr_2NiO_{4+\delta}$ under the SOFC working conditions (at 550–900 °C, 10^{-4} – 0.21 atm) and increased electronic conductivity of all substituted $Ln_2NiO_{4+\delta}$ materials [24–30]. Data on polarization resistance (ASR) of the $La_{2-x}Sr_xNiO_{4+\delta}$ and $Pr_{2-x}Sr_xNiO_{4+\delta}$ electrodes in contact with different oxygen ion conducting electrolytes are contradictory, however it was found that its reduction usually occurred at a high Sr content (usually at about $x \geq 0.3$ for La- and $x \geq 0.7$ for Pr-based systems [25–27]). For the electrodes based on $Nd_{2-x}Sr_xNiO_{4+\delta}$, the optimal amount of Sr to attain a minimal ASR value is also under discussion. Sun et al. [29] reported the lowest ASR at x = 0.4 (0.93 at 700 °C in air); Bhoga et al. [30] revealed the minimal ASR value at x = 0.2 (0.52 at 700 °C in air). It was shown that a decrease in the activation energy of the polarization conductivity ($\sigma_p = 1 / R_p$) with Sr doping lead to the doped electrodes showing even better characteristics below 600 °C than that based on $Nd_2NiO_{4+\delta}$ [31,32]. Moreover, at high concentrations of strontium in $Nd_{2-x}Sr_xNiO_{4-\delta}$ an observed increase in the electrochemical activity could be explained by the increased ionic conductivity in perovskite layers [32,33]. However, despite all the advantages of Sr-doping there remains a problem with SrO segregation on the surface of Sr-containing (especially Sr-rich) electrodes which causes performance degradation [34,35].

Recently, we presented a study of the electrochemical properties of $La_{2-x}Ca_xNiO_{4+\delta}$ and $Pr_{2-x}Ca_xNiO_{4+\delta}$ electrodes [36–40]. Within this work we continue our investigation of such systems and present our results on physico-chemical properties of $Nd_{2-x}Ca_xNiO_{4+\delta}$ materials with a low Ca content (x = 0.0–0.3) and features of their electrochemical behavior in contact with oxygen-ion conducting $Ce_{0.8}Sm_{0.2}O_{1.9}$ electrolyte in comparison to earlier investigated La and Pr-based layered nickelates, substituted with Ca.

2. Experimental procedure

$Nd_{2-x}Ca_xNiO_{4+\delta}$ (x = 0–0.3, NCNO, notations are shown in Table 1) powders were synthesized via a solution-assisted solid state reaction method. Raw materials Nd_2O_3 (99.99% purity), $Ca(NO_3)_2 \cdot 4H_2O$ (99.97%), $Ni(NO_3)_2 \cdot 6H_2O$ (99.97%) were mixed in agate drums of a SAND planetary mill in isopropyl alcohol with steel balls. Then the resulting homogeneous suspension was moved to a heat-resistant glass beaker where an excess amount of aqueous ammonia solution was added under continuous stirring. Nickel and calcium hydroxides precipitated on the highly dispersed particles of neodymium oxide (19.6 m^2/g, BET surface-area analysis was carried out by a SORBI N.4.1 analyzer). After evaporation of the liquid and subsequent final drying in the laboratory drying cabinet the preliminary synthesis was carried out at a temperature of 600 °C, 2 h and the final synthesis was performed in one or two stages with intermediate activation of the powders in the mill at 1100 °C, 10 h and 1150 °C, 10 h. Chemical analysis of the synthesized materials was performed by an inductively coupled plasma optical emission spectroscopy method using an Optima 4300 DV device. It showed a close concurrence between the calculated and experimental data (Table S1). The XRD analysis was performed by means of a Shimadzu XRD-7000 diffractometer with graphite monochromated CuKα radiation in the angle range of $20^\circ \leq 2\theta \leq 80^\circ$ with 0.02° step and a counting time of 5 s at each point. The XRD data were analyzed using the Rietveld structure profile refinement with FullProf Suite software [41].

$LaNi_{0.6}Fe_{0.4}O_3$ (LNF) for collector layers was synthesized via the two-step ceramic technology. Initial materials La_2O_3 (99.99%), NiO (99.94%) and Fe_2O_3 (99.94%) were mixed and calcined at 1150 °C, 2 h with following milling for 0.5 h. Final synthesis steps were performed at 1250 °C, 5 h and 1270 °C, 5 h with intermediate milling. According to the XRD date, the final LNF powder had a hexagonal crystal structure with the parameters $\boldsymbol{a} = \boldsymbol{b} = 5.5104$ (± 0.0012) Å and $\boldsymbol{c} = 13.2586$ (± 0.0031) Å with an amount of the NiO secondary phase of 1 wt%. After final milling for 1 h the specific surface area of the powder was 1.7 m^2/g. To ensure better sintering of the LNF collector layers at decreased temperatures, a finely-dispersed CuO (S = 10.3 m^2/g, 2 wt%) was added into the LNF powder.

$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte was synthesized via the ceramic technology using CeO_2 (99.97%) and Sm_2O_3 (99.95%). After mixing, the precursor was calcined at 1050 °C for 2 h and ball-milled. The intermediate product was dry-pressed into disks at 150 MPa. The disks were then sintered at 1550 °C for 5 h. The XRD analysis revealed the formation of a fluorite-like structure with parameter $a = 5.4372(3)$ Å, which is close to the parameter of the standard sample PDF#75-0158 in the JCPDS base. Relative density of the SDC electrolyte disks used as supports for electrochemical investigations, defined from their size and weight, was equal to 95% of the theoretical value, calculated from the XRD data.

The absolute oxygen content in the NNO and NCNO3 samples (4 + δ) was determined by high-temperature treatment of these samples in 10%H_2/90%Ar (with flow rate of 100 ml/min, log $pO_2 = -27$ atm) at 850 °C up to complete reduction with weight control using a NETZSCH STA 449 F3 Jupiter thermal analyzer. It was calculated based on the reaction that schematically describes the sample reduction:

$$Nd_{2-x}Ca_xNiO_{4+\delta} + gH_2 \rightarrow 0.5(2-x)Nd_2O_3 + xCaO + Ni + gH_2O \quad (1)$$

where g = 1 + 0.5x + δ. The completeness of the reduction and the phase composition of the reduced samples were monitored by the XRD method. Before measurements the samples were pretreated in air at 1100 °C for 5 h with a heating/cooling rate of 100 °C/h, thus providing standard conditions for comparing the oxygen content.

Volume thermal expansion of NCNO was investigated by the high temperature XRD method in air across the temperature range of 25–800 °C using a high-temperature diffractometry device HDD-2000 with graphite monochromated CuKα radiation in the angle range of $20^\circ \leq 2\theta \leq 80^\circ$ with 0.02° step and a scanning rate of 1°/min; linear expansion was studied by a dilatometric method using a quartz dilatometer and a Tesatronic TT-80 digital meter with a TESA GT-21HP measuring probe (sensitivity of 0.01 μm).

Conductivity of the NCNO compact samples (0.5 × 0.5 × 2.3 cm), prepared by a uniaxial semidry pressing with a butyral resin binder at 6 MPa followed by sintering at 1450 °C for 5 h, was measured by a *dc* four-probe technique in a temperature range of 300–900 °C in a cooling regime (300 °C/h) with steps every 50 °C. During every step the conductivity relaxation to a dynamic equilibrium was monitored using an automatic system Zirconia 318 [42]. In all experiments two identical samples were used. The difference in the values of electrical conductivity did not exceed 3%. Relative density of the compact samples was 94–96%.

Electrode slurries for the functional and collector layers were made from the electrode powders or a mixture of the electrode and SDC electrolyte powders (50:50) with addition of ethyl alcohol and a polyvinyl-butyral binder. The electrodes were symmetrically deposited on the SDC electrolyte plates (1 mm of thickness) with an effective