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The $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$–$CeO_2$ system: Phase equilibria, crystal structure of components and transport properties

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ABSTRACT

Phase equilibria, crystal structure, and transport properties in the $(100-x)$ $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$–$xCeO_2$ (LNFCx) system (x=2–75 mol%) were studied in air. Evolution of phase compositions and crystal structure of components was observed. The LNFCx ($2 \le x \le 10$) are three-phase and comprise the perovskite phase with rhombohedral symmetry ($R\bar{3}c$), the modified ceria with fluorite structure ($Fm\bar{3}m$), and NiO as a secondary phase. These multiphase compositions exhibit metallic-like conductivity above 300 °C. Their conductivity gradually decreases from 395.6 to 260.6 S/cm, whereas the activation energy remains the same (E_a=0.04–0.05 eV), implying the decrease in the concentration of charge carriers. Phase compositions in the LNFCx ($25 \le x \le 75$) are more complicated. A change from semiconducting to metallic-like conductivity behavior was observed in LNFC25 at about 550 °C. The conductivity of LNFCx ($25 \le x \le 75$) could be explained in terms of a modified simple mixture model.

1. Introduction

Materials with perovskite and fluorite structures exhibit high electrical conductivity, good thermochemical stability under oxidizing atmosphere and have been considered for versatile technological applications (catalysts, membranes, electrodes, and electrolytes in power generating solid state devices) [1–4]. Good chemical compatibility of adjacent components (in particular in long term) is one of the challenges for the implementation of existing materials and the design of new ones. Different processes could occur at the interfaces between the adjacent components (interdiffusion of elements, preferable dissolution of certain element(s), evaporation or sorption of elements), and lead to a change in structural and transport properties of the adjacent components, thereby influencing the electrochemical performance of the whole system [5–10]. Therefore, it is necessary to know phase equilibria; structure of compounds formed and transport properties of multicomponent systems.

$LaNi_{1-y}Fe_yO_{3-\delta}$ perovskites are considered as promising materials for the application as an electrode and current collector in solid oxide fuel cells (SOFC) at intermediate temperatures due to their high metallic-like electrical conductivity [11]. The $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ perovskite has the highest electronic conductivity among $LaNi_{1-y}Fe_yO_3$ series. Besides, *A*-site deficient perovskites show a low capability of insulating phase formation at the interface with electrolytes, which could result in better long term electrochemical performance. Transport properties of CeO_2 based electrolytes have been actively explored to optimize their ionic conductivity [12–15]. $Ce_{1-x}Ln_xO_{2-\delta}$ (Ln=Gd, Sm, and $x \le 0.2$) compositions show the most promising transport properties [14]. Two-layered electrodes are generally used to enhance electrochemical performance of SOFC and minimize Cr-poisoning effect [16–18]. The outer layer of the two-layered electrodes is a perovskite phase, whereas the layer adjusted to the electrolyte is a mixture of the perovskite and electrolyte. This design would require good chemical stability at the phase interfaces in long term.

The simplified system $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$–$CeO_2$ has been specially chosen in the present investigation to identify any interactions between major components (phase evolution and crystal structure of new phases) and study their electrical properties. The presence of a dopant in the $Ce_{1-x}Ln_xO_{2-\delta}$ electrolyte ($x \le 0.2$) may change the kinetics of phase evolution at the phase interfaces, but the La solubility in the fluorite structure of CeO_2 according to the literature [13,19] is much higher (up to 50 mol%) than the acceptor dopant concentration. This assumes that La redistribution between the main phases could occur and can be more accurately defined investigating the $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$–$CeO_2$ system, although the absolute value of an additional La dissolution may alter depending on a dopant type and its concentration in cerium oxide.

2. Experimental

The initial perovskite $La_{0.95}Ni_{0.6}Fe_{0.4}O_3$ (LNF) was produced by combustion spray pyrolysis and supplied by PRAXAIR Inc., USA. CeO_2 delivered by ACROS ORGANICS (New Jersey, USA) was

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calcined at 1000 °C for 5 h to remove adsorbed water. The initial powders LNF and CeO_2 have comparable specific surface area: 6.00 and 2.34 m^2/g, respectively. Further, compositions in the following series $(100-x)$LNF · $xCeO_2$ (LNFC), where $x=2$, 5, 8, 10, 25, 50, and 75 mol%, were obtained by mechanical mixing of LNF and CeO_2 in mortar in relevant ratios, and followed by a calcination in air at 1350 °C for 5 h. The initial composition LNF was also calcined under the same conditions. The temperature of 1350 °C was specially chosen to enhance mobility of chemical elements and observe any changes in a phase composition and crystal structure within a shorter time scale. Although there is a general trend in the lowering of sintering temperature of ceramic units and operating temperature of solid oxide fuel cells, but this approach does not allow long term stability of multicomponent systems to be predicted.

X-ray powder diffraction (XRD) data were recorded in air at room temperature (RT) in transmission mode on a Stoe Stadi-P diffractometer with Cu$K\alpha$ radiation (Stoe & Cie GmbH, Germany) and for some nominal compositions in reflection mode on a Philips analytical X-ray PW1710 diffractometer with Cu$K\alpha$ radiation (Nederlandse Philips Bedrijven B.V., The Netherlands). The diffraction spectra for all samples were registered in the angular range of $15 \le 2\Theta \le 96$ with a step size of 0.1 and a recording time of 70 s for each step. Si powder (Alfa Aesar, Karlsruhe, Germany) was used as the external standard for the calibration of the diffractometer. The diffraction data were refined by the Rietveld method [20], using the Generalized Structure Analysis System (GSAS) program [21]. Electrical conductivity was measured on sintered pellets (rD~85% for LNFCx with $2 \le x \le 25$, 76% for LNFC50, and 73% for LNFC75) by the standard DC four terminal method between 50 and 900 °C in static air [22]. A current of 100 mA (Keithley model 220, USA) was applied in both directions and resistance was calculated as a gradient of potential *vs.* current. This was converted to conductivity using the geometrical factor of the sample.

3. Results and discussion

3.1. Phase equilibria and crystal structure at room temperature

According to neutron diffraction study [23], the *A*-site nominal composition $La_{0.95}Ni_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) comprises the cation stoichiometric phase $LaNi_{0.579}Fe_{0.421}O_3$ with rhombohedral structure (space group $R\bar{3}c$, no. 167) and 5.2 mol% NiO (space group $R\bar{3}m$, no. 166). The XRD analysis does not allow structural and quantitative characterization of NiO because only two very weak peaks could be observed in the XRD patterns recorded in the reflection mode. The peaks related to NiO phase are less discernible in the XRD patterns recorded in the transmission mode because of a high fluorescent background, Fig. 1a. CeO_2 has a fluorite-type structure (space group $Fm\bar{3}m$, no. 225) [24,25]. Very weak peak, which is close to the {1 1 1} cubic reflection of CeO_2, was observed in the XRD pattern of LNFC2, assuming a low solubility limit of CeO_2 in the perovskite structure. The LNFCx with 2 mol% $\le x \le$ 10 mol% are three phase: the perovskite phase with rhombohedral structure, the modified cerium oxide with fluorite

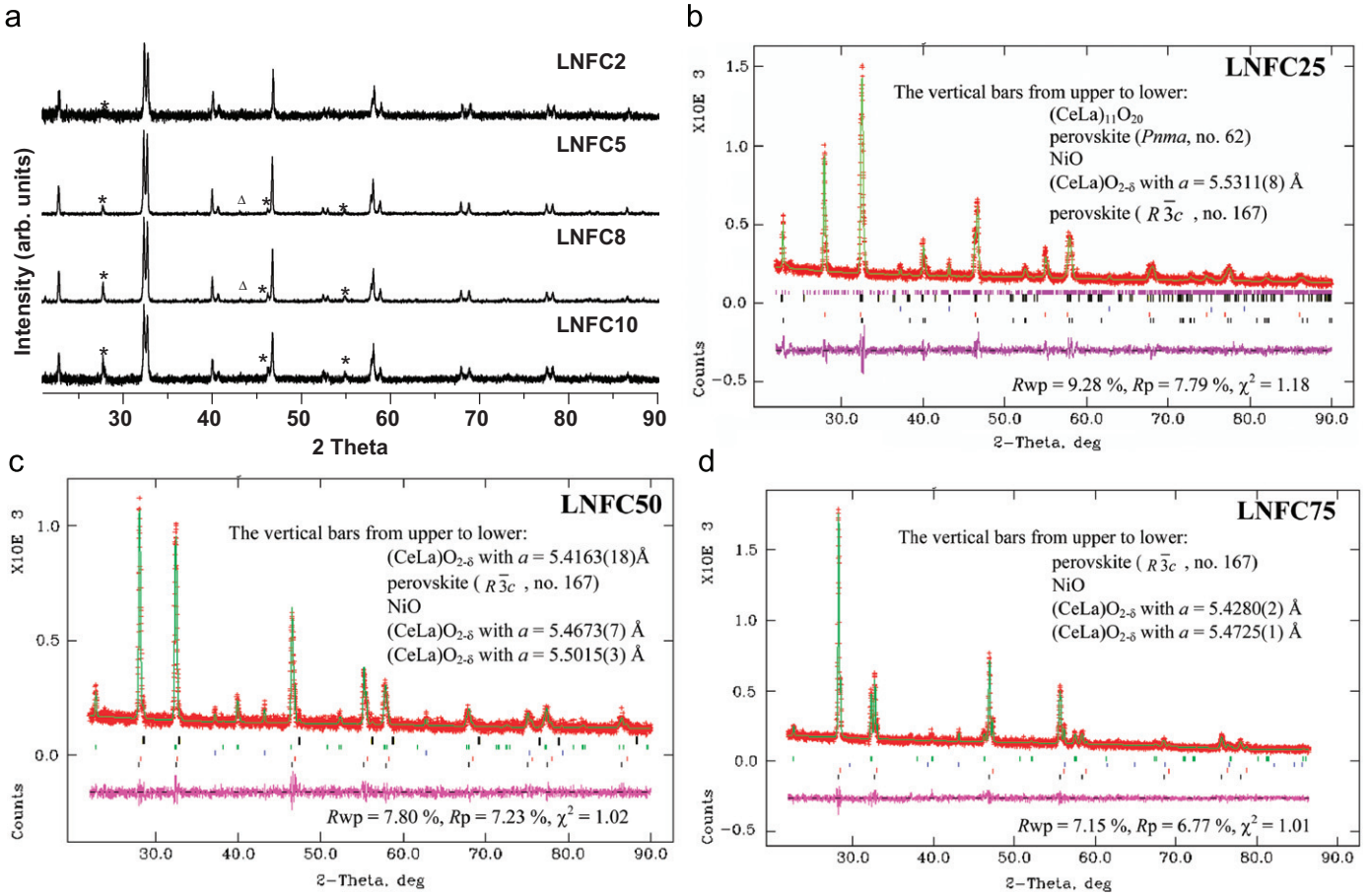

Fig. 1. Evolution of XRD patterns in the LNFC system at room temperature: (a) LNFC2, LNFC5; LNFC8, and LNFC10; the "∗" and "Δ" symbols indicate the peaks related to the modified ceria and NiO, respectively; (b) LNFC25; (c) LNFC50; and (d) LNFC75. Reliability factors are presented after the subtraction of the background. For (b)–(d): observed (cross symbols), calculated (continuous line), and difference profiles (bottom line). Vertical bars show calculated reflections for different phases. XRD patterns were recorded in the transmission mode.