Thermal stability, oxygen non-stoichiometry, electrical conductivity and diffusion characteristics of $PrNi_{0.4}Fe_{0.6}O_{3-\delta}$, a potential cathode material for IT-SOFCs

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ABSTRACT

The potential use of a double B mixed-perovskite as a promising cathode material in intermediate temperature solid oxide fuel cells (IT-SOFCs) has been anticipated as a result of this work. A thorough investigation of some important parameters like thermal stability, thermal expansion, oxygen non-stoichiometry, electrical conductivity and diffusion characteristics of the $PrNi_{0.6}Fe_{0.4}O_{3-\delta}$ ceramic sample have been investigated as functions of temperature (20–1000 °C) and oxygen partial pressure (0.6–21,000 Pa). According to the measurements, the composition was phase stable at $pO_2 > 1$ Pa up to 1000 °C and shows p-type semiconductivity with a low conductivity versus pO_2 dependence.

The perovskite has been found to have comparable thermal expansion coefficients with those of commonly used solid electrolytes like CeO_2 and ZrO_2 based oxides. In case of the chemical diffusion experiments higher oxygen diffusion mobility observed during reduction processes in comparison with those during oxidation have been explained by the already known formation of neutral defect clusters.

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1. Introduction

New cathode materials for use in solid oxide fuel cells (SOFCs) are constantly being studied all over the world. Out of the SOFCs that exist, intermediate temperature solid oxide fuel cells (IT-SOFCs) are very popular since they allow the use of low-cost interconnects and have less frequent problems with sealing and thermal degradation, just to name a few. Despite the advantages, one major problem faced by this type of SOFC is the fact that polarisation resistance on the cathode side is generally higher than that on the anode side leading to breakdown in the functioning of the fuel cell. Lanthanum strontium manganate (LSM) cathodes have since long been the most commonly and widely studied materials and only recently Fe–Co based perovskite cathodes have entered the scenario. Fe–Co based perovskites have many important properties out of which one is a reasonably low polarisation resistance as in the case of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$/Gd doped CeO_2 cathode at

600 °C [1]. Although the latter could have been a good candidate as a cathode material in IT-SOFCs, its major drawback lies in its relatively high difference in thermal expansion coefficient (TEC) as compared to that of the common electrolytes, e.g. with YSZ (difference of 7.5×10^{-6} K^{-1}) and with CeO_2 based oxides (difference of $(6–15) \times 10^{-6}$ K^{-1}). Such a difference in TECs between the cathode and electrolyte would cause thermal stress at the interface during the operation of the fuel cell at high temperatures leading to cracking and delamination.

Similarly, other candidates like Fe–Ni perovskites with high electronic conductivity and comparable thermal expansion coefficients with that of CeO_2 and ZrO_2 based oxides have also been studied. Hashimoto et al. [2] have studied conductivity profiles of $PrNi_{1-x}Fe_xO_3$ ($x = 0.4–0.6$) materials at high temperature and also their impedance and polarisation curves on $Ce_{0.9}Gd_{0.1}O_{2-\delta}$(CGO10) electrolyte and compared them with $LaFe_{0.4}Ni_{0.6}O_{3-\delta}$. On the other hand, according to magnetic and electronic structure studies on similar substances carried out by Kumar et al. [3], the substitution of Ni for Fe site in $PrFeO_3$ is said to increase their conductivity and stabilise the ferromagnetic ordering.

$PrNi_{1-x}Fe_xO_3$ ceramics have been shown to have high electronic conductivity, thermal expansion coefficients comparable to CGO and hence are very promising as SOFC electrodes and oxygen per-

meable membranes [1]. It has to be noted, that an effective pO_2 gradient within the SOFC cathode is formed once current begins flowing. Therefore, it is particularly important to know the properties of these materials as a function of oxygen partial pressure and temperature [4,5]. Also, no data about thermal stability, oxygen non-stoichiometry, and electrical conductivity at low oxygen partial pressures (pO_2) for these compounds are available up to date. In the present investigation, we aim to study these parameters in $PrNi_{0.4}Fe_{0.6}O_{3-\delta}$ a double B mixed perovskite, as functions of temperature and oxygen partial pressure.

2. Experimental

2.1. Powder synthesis and physical characterisation

$PrNi_{0.4}Fe_{0.6}O_{3-\delta}$ powder was prepared by the solid-state reaction method. The constituent metal oxide powders Pr_6O_{11} (99% pure, Alfa Aesar), NiO (99% pure, Alfa Aesar) and Fe_2O_3 (Analytical Reagent, Reanal Hungary) were first ball-milled in an agate mill in stoichiometric amounts along with some minimum amount of ethanol for 24 h. The resultant paste was left to dry and form a mass which was ground in a mortar using a pestle to form uniform powder and then pre-calcined in air up to a temperature of 1000 °C for 17 h with a heating and cooling rate of 5 °C min^{-1}. The cooled mass was then ground again to a fine powder and then further treated as required for various experiments as discussed below. This powder pre-calcined at 1000 °C has been analysed at room temperature (RT) by XRD measurements (Siemens D5000 diffractometer, Cu K$_\alpha$ radiation) using a PVC sample holder.

In situ high-temperature structural studies in the temperature range from RT to 900 °C were performed at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) with the powder diffractometer at beam-line B2 [6]. For this set of experiments, 0.3 mm diameter quartz capillaries were filled with powdered samples and subsequently mounted inside a STOE furnace equipped with a Eurotherm temperature controller and a capillary spinner (Debye–Scherrer geometry). The furnace temperature was mea-sured by a Ni/CrNi thermocouple. The wavelength of 0.651254 Å was selected using a Si(1 1 1) double flat-crystal monochromator and determined from eight reflection positions of LaB$_6$ reference material (NIST SRM 660a). All diffraction patterns have been collected at fixed temperatures during the heating–cooling cycle using an image-plate detector [7] (2θ range 8–62°, step size of 0.004°). Additional check-patterns were taken after the heat treatment at room temperature. Data evaluation was performed using the package 'FullProf' [8], the averaged structure was analysed by the full-profile Rietveld method.

Thermal expansion coefficients were measured on porous samples in air in a LINSEIS dilatometer, temperature range of 20–850 °C with a ramp-rate of 10 °C min^{-1}. SEM images were recorded using a Zeiss DMS 982 Gemini field emission scanning electron microscope equipped with a Noran Voyager energy-dispersive spectroscopy system.

2.2. Sample preparation

Porous ceramic samples for conductivity and oxygen exchange measurements were prepared by sintering pressed bars (dimensions: 10 mm × 3 mm × 1.5 mm) in air at 1200 °C for 17 h, whereas gas dense ones for oxygen diffusion measurements were prepared by sintering similar bars at 1500 °C in air for 17 h (Fig. 1a). To check gas-tightness of the sintered samples, discs of 15 mm diameter were sintered at 1500 °C in air for 17 h. Apparatus shown in Fig. 1b was used for the examination of the discs. If the sample was porous, lower pressure was created inside the jar 4 pre-filled with helium, due to the faster diffusion of the smaller He atoms outside in comparison with the diffusion of larger N$_2$ and O$_2$ molecules from air into the jar.

2.3. Oxygen content and electrical conductivity measurements

Oxygen non-stoichiometry and electrical conductivity of the ceramic samples were investigated using a solid electrolyte measuring technique ZiroxySystem (Zirox, Greifswald, Germany)
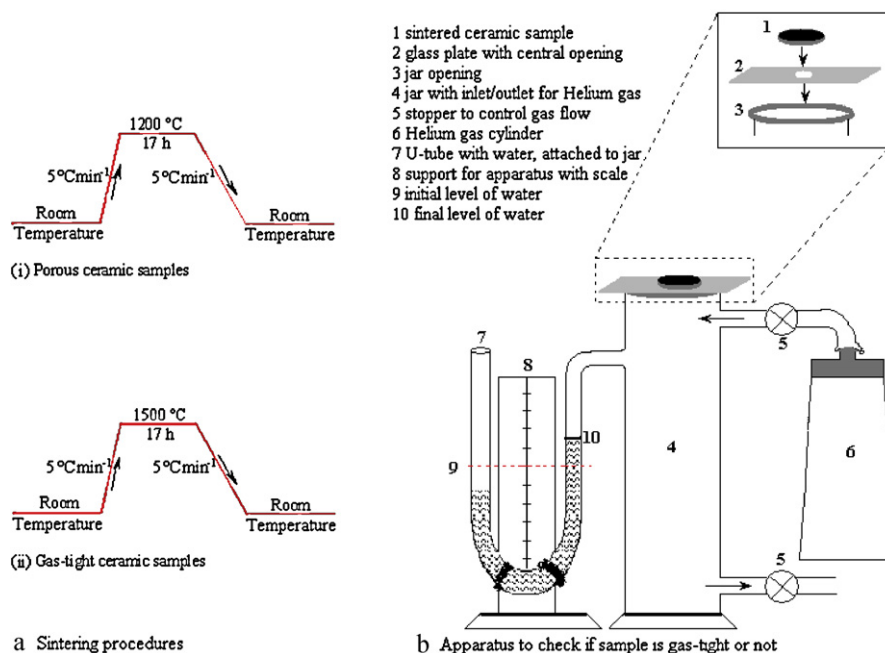

Fig. 1. (a) Schematic representations showing sintering procedures for (i) porous ceramic samples and (ii) gas-tight ceramic samples. (b) Apparatus to check if sintered sample is gas-tight or not.