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Electrochemical study of the $Nd_{1.95}NiO_{4+\delta}$/oxide electrolyte interface

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ABSTRACT

Nickelate-based oxides are potential cathodes in Solid Oxide Fuel Cells operating at intermediate temperatures. The chemical compatibility between apatite electrolyte, i.e., $La_9Sr_1Si_6O_{26.5}$, and Nd-deficient nickelate, i.e., $Nd_{1.95}NiO_{4+\delta}$, has been characterized. The equilibrium between the nickelate material and the gas phase has been studied as functions of temperature and oxygen partial pressure, using potentiometric measurements with microelectrodes, i.e., metallic or ceramic point electrodes. Two solid electrolytes were used, i.e., apatite and yttria-stabilized zirconia. The response of the nickelate is discussed in terms of oxygen stoichiometry.

1. Introduction

In the quest for the development of Solid Oxide Fuel Cells (SOFC) working at temperature lower than 800 °C, compounds with apatite structure as electrolyte and nickelate-based solid solutions as cathode, are considered as alternative materials. Silicate electrolytes with apatite structure ($La_9Sr_1Si_6O_{26.5}$) exhibit a good chemical stability and a sufficiently high ionic conductivity, i.e., 8.8×10^{-3} S cm^{-1} at 700 °C, for potential application as SOFC electrolytes [1–5]. Moreover, it has been shown recently that their electronic transport number is extremely low [6,7]. In parallel, a new family of compounds formulated $A_2MO_{4+\delta}$, with the K_2NiO_4-type structure has been recently proposed as cathode materials [8–12], as oxygen separation membranes, or as oxidation catalyst [13]. Thin films of lanthanum nickelates have been deposited on various substrates using reactive magnetron sputtering [14]. These compounds exhibit relatively high oxygen conductivity, an electronic conductivity of $\sigma_e \approx 50$–100 S cm^{-1} at 700 °C, high oxygen exchange coefficients, TECs compatible with commonly used electrolytes such as YSZ, doped ceria and lanthanum gallates and chemical compatibility with the other SOFCs components.

The most studied materials are pure and doped $La_2NiO_{4+\delta}$ compounds [10,15–18]. However, it has been recently shown that $Nd_2NiO_{4+\delta}$, and, especially, the Nd-deficient compound ($Nd_{2-x}NiO_{4+\delta}$) exhibit a high oxygen diffusion coefficient and promising electrocatalytic properties as cathode materials for SOFCs [19–23].

The aim of this paper is, firstly, to estimate the chemical compatibility between apatite electrolyte, i.e., $La_9Sr_1Si_6O_{26.5}$, and Nd-deficient nickelate, i.e., $Nd_{1.95}NiO_{4+\delta}$, and secondly to carry out potentiometric measurements using microelectrodes, electrical conductivity measurements and TGA experiments as functions of temperature and oxygen partial pressure. The behaviour of Nd-deficient nickelate on apatite electrolyte and on the mostly used solid electrolyte, i.e., yttria-stabilized zirconia, is discussed.

2. Experimental

2.1. Manufacture of the dense pellets of the strontium doped lanthanum silicate electrolyte

High purity La_2O_3 (Ampere Industrie, 99.99%), SiO_2 (CERAC, 99.5%) and $SrCO_3$ (NEYCO, 99.9%) starting materials were used to prepare the silicate electrolyte of composition $La_9Sr_1Si_6O_{26.5}$ [23–24]. The dried materials were ball-milled in the stoichiometric ratio, for 12 h at 100 rpm using zirconia balls, 15 mm in diameter. Then, the powder was calcinated at 1500 °C for 2 h. The samples were then ground by attrition, at 1500 rpm for 1 h. After attrition, the $La_9Sr_1Si_6O_{26.5}$ powder showed a single particle size population with a mean diameter of 1 μm and a specific surface area (BET) of 3.8 m^2 g^{-1}. X-ray diffraction revealed a single phase of $La_{9.33}Si_6O_{26}$-type with a slight difference of the cell parameters due to the substitution of lanthanum by strontium. Lattice parameter *a* decreases with strontium concentration, whereas lattice parameter c increases [25–26]. After sintering at 1575 °C for 2 h, the pellet density was 98% of the theoretical one.

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2.2. Preparation of the nickelate powder

$Nd_{1.95}NiO_{4+\delta}$ powder was synthesized using the polyacrylamide gel route. Solutions of cations chelated by triammonium citrate were mixed in a stoichiometric ratio. The organic gels were made using monomers of acrylamide to form chains and the cross-linker *N,N'*-methylene-bis-acrylamide. α,α'-Azoisobutyronitrile (AIBN) dissolved in a few mL of acetone was used as polymerisation initiator. The gel was transferred in a porcelain bowl and heated in a ventilated furnace at 3 °C/min, up to 800 °C for 1 h. A final annealing at 1000 °C was required to obtain the single phase $Nd_{1.95}NiO_{4+\delta}$. The oxide was characterised by X-ray diffraction using a Philips 1710 diffractometer (CuKα radiation).

2.3. Thermogravimetry analysis

Thermogravimetry analyses were performed by heating the sample up to 900 °C (at 0.5 °C/min) under various oxygen partial pressures, i.e., 0.21 bar, 10^{-3} bar, and 10^{-4} bar, using a Setaram MTB 10–8 equipment. All the measurements were carried out on one sample. The initial oxygen content (δ) of the sample at room temperature was determined by iodometry analysis [8]. The oxygen partial pressure was modified at 900 °C (the corresponding variation of the stoichiometry $(4+\delta)$ can be observed in Fig. 2). The thermogravimetric curves were identical under successive cooling and heating.

2.4. Electrical conductivity

The total electrical conductivity of the nickelate pellets was measured using the four-probe method [8,27]. The oxygen pressure in the surrounding atmosphere was abruptly modified and the sample conductivity vs. time was recorded until equilibrium was reached.

2.5. Experimental set-ups

The experimental cell schematized in Fig. 1 was formed on a $La_9Sr_1Si_6O_{26.5}$ pellet (1.17 mm in thickness and 16 mm in diameter). Gas-tightness was obtained from gold O'rings pressed between two alumina tubes.

The counter-electrode was a porous layer of silver paint in contact with air and three different microelectrodes were gently pressed against the upper surface of the dense apatite pellet, i.e., a solidified droplet of silver (99.99% purity, Engelhard), an apatite tip with a silver layer deposited on the top of the probe as measuring electrode and a cone-shaped nickelate electrode (in that case, the current collector was gold paint) (see Fig. 1). Mauvy et al. have used the latter electrode recently for studying the oxygen reduction kinetics on YSZ electrolyte [28]. Silver was used as electrode material as it has been demonstrated that it is, by far, the metallic electrode exhibiting the smallest overpotential resistance, at low and intermediate temperatures [29]. However, the silver microstructures are highly unstable at high temperature. Gold was used as current collector because it is a poor electrocatalyst for oxygen electrode reaction [29]. As demonstrated previously [30] the metallic electrode (Ag or Pt) measures the oxygen activity on the pellet surface and the apatite point electrode enables the measurement of the oxygen partial pressure in the gas in the vicinity of the pellet surface. The e.m.f. of the nickelate point electrode vs. air was used for in-situ measurement of the oxygen activity in $Nd_{1.95}NiO_{4+\delta}$.

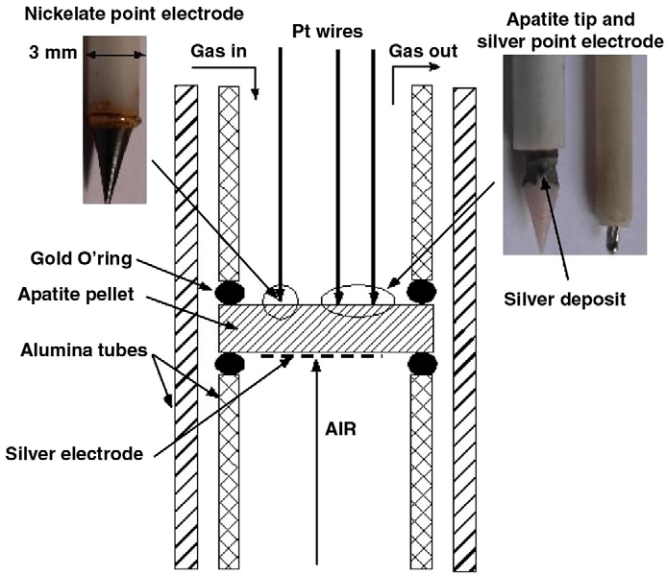

Fig. 1. Experimental set-up (apatite electrolyte).

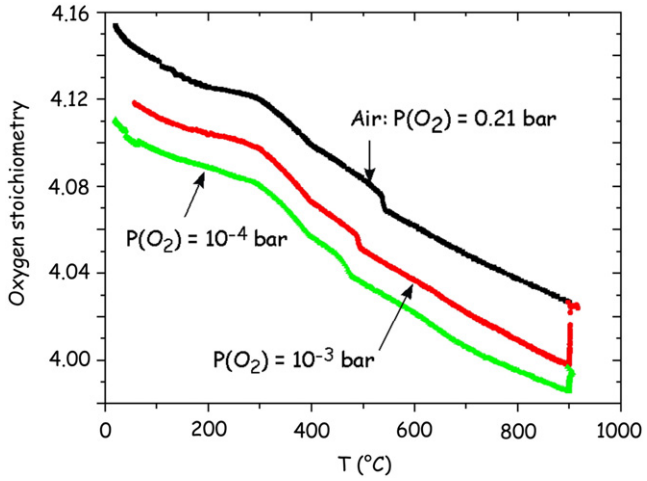

Fig. 2. Thermogravimetry analysis (TGA) of $Nd_{1.95}NiO_{4+\delta}$, under three oxygen partial pressures, i.e., 0.21 bar, 10^{-3} bar, and 10^{-4} bar.

The potentiometric measurements were also carried out using yttria stabilized zirconia (8 mol% yttria) as electrolyte. A closed-end of a zirconia tube was painted on its outer surface with platinum paste free from other compounds after baking (Demetron 9905). Air was used as the reference atmosphere. The nickelate point electrode was in contact with the inner surface of the closed-end of the zirconia tube free from metallic deposit.

The gas circuit used was previously described [30]. Mass-flowmeters (TYLAN) were used for accurate monitoring of the gas flow rates (i.e., 5 to 10 L h^{-1} NPT) in the measuring upper chamber and air was flowing around the counter-electrode of the cell. A pump-sensor zirconia device was used for oxygen monitoring [31].

The e.m.f. of the microelectrodes E were measured with respect to the large surface counter-electrode in the lower chamber supplied by air. The corresponding oxygen partial pressures obey the Nernst law:

$$P_{O_2} = 0.2\,exp\left(\frac{4FE}{RT}\right) \quad (1)$$

which leads to calculate the oxygen activity using the following equation:

$$a_O = 0.447\,exp\left(\frac{2FE}{RT}\right) \quad (2)$$

In the case of the nickelate microelectrode, the oxygen activity, a^*_{O2}, at the gas–solid interface can also be defined as the equivalent