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Oxygen transport and chemical compatibility with electrode materials in scheelite-type $LaW_xNb_{1-x}O_{4+x/2}$ ceramic electrolyte

Giovanna Canu [a,*], Vincenzo Buscaglia [a], Chiara Ferrara [b], Piercarlo Mustarelli [b], Sónia Gonçalves Patrício [c], Ana Inês Batista Rondão [c], Cristina Tealdi [b], Fernando Manuel Bico Marques [c]

[a] CNR-ICMATE – Institute of Condensed Matter Chemistry and Technologies for Energy, via De Marini 6, 16149, Genova, Italy
[b] Department of Chemistry and INSTM, University of Pavia, viale Taramelli 16, 27100, Pavia, Italy
[c] Department of Materials and Ceramic Engineering/CICECO, University of Aveiro, 3810-193, Aveiro, Portugal

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ABSTRACT

$LaW_xNb_{1-x}O_{4+x/2}$ ceramics ($x = 0.16$) were prepared via a solid state route and studied with respect to phase stability and mixed ionic and electronic conductivity under conditions of technological relevance for fuel cell applications. The chemical compatibility against standard cathode materials revealed that Sr-doped $LaMnO_3$ could be used without detectable chemical interaction up to at least 1000 °C. Impedance spectroscopy measurements performed in the range 400–850 °C, using different atmospheres (air and N_2+H_2, both dry and water vapour saturated), suggest oxygen transport numbers equal to 1 under oxidising conditions, and decreasing when exposed to extreme reducing conditions. The total conductivity at 800 °C increases from $1.4 \cdot 10^{-3}$ S cm^{-1} in air to $2.5 \cdot 10^{-3}$ S cm^{-1} in wet hydrogen and $6.1 \cdot 10^{-3}$ S cm^{-1} in dry hydrogen, but the observed onset of n-type conductivity has little practical impact under typical fuel cell operating conditions.

1. Introduction

Lanthanum niobate, with general formula ABO_4, was recently reported as proton conductor by either A-site or B-site doping or even by co-doping with acceptors, namely with A^{2+} and B^{4+} elements [1]. In particular, $LaNbO_4$-based materials are promising because of their moderate conductivity while being almost pure proton conductors, and for their stability in CO_2-containing atmosphere and water vapour environment. The highest proton conductivity reported to date in the $LaNbO_4$ system is for alkaline earth-doped lanthanum niobate, reaching the value of 10^{-3} S cm^{-1} at 800 °C for the composition $La_{0.99}Ca_{0.01}NbO_4$ [1].

$LaNbO_4$ crystallises in two polymorphs, a high temperature tetragonal scheelite phase and a low temperature monoclinic phase, which can be regarded as a distorted scheelite structure, with phase transformation occurring around 500 °C [2]. The activation energy for proton migration is lower in the scheelite phase, which is therefore more favourable for applications. Attempts to retain the scheelite structure at low temperature with incorporation of vanadium on niobium site were successfully reported, although the level of proton conductivity was lower than for state-of-the-art $La_{0.99}Ca_{0.01}NbO_4$ [3].

Other materials with scheelite structure were reported to possess ionic conductivity. Undoped $CaWO_4$ ceramics and $CaMO_4$ (M = W, Mo) ceramics doped with lithium on calcium site showed respectively proton or lithium-ion conduction [4,5]. $PbWO_4$ doped with lanthanide elements, such as Sm^{3+} or La^{3+}, and undoped $CeNbO_{4+\delta}$, due to the mixed valence state of Ce^{3+}/Ce^{4+}, showed instead oxygen ion conductivity [5,6]. Therefore, it is interesting to note that materials with scheelite structure can show either cation or oxide ion conduction depending on the specific material composition and doping.

Little is reported on the introduction of positive charge excess in lanthanum niobate. The introduction of oxygen excess in lanthanum niobate to balance doping with either Th^{4+} on A-site or W^{6+} on B-site was reported long ago, with high conductivity at least in the case of thorium doping [7]. The reported phase diagram of $LaNbO_4$-$LaWO_{4.5}$ shows a single phase region between 11% and 22% $LaWO_{4.5}$, with structure changing from monoclinic to tetragonal by increasing the W content; it is also reported that the

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* Corresponding author.
E-mail address: giovanna.canu@ge.icmate.cnr.it (G. Canu).

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introduction of a W^{6+} ion on the Nb^{5+} site originates the formation of an incommensurate superstructure [7].

Single-phase 8% tungsten-substituted lanthanum niobate was successfully synthesised [8,9]; Li et al. [8] reported the conductivity in wet and dry air, indicating no proton conductivity. Fuel cell/water vapour electrolysis tests using an electrolyte with 16% tungsten content were also reported [10]. The measured fuel cell open circuit voltage (OCV) close to 1V was an indication of dominant ionic conductivity within a broad oxygen activity range. In this work, a combination of electrical conductivity measurements under well-defined oxygen activity conditions is used to obtain further insight on the ionic and electronic transport properties of these materials. The dopant level (16% W) was also selected here for closely matching the middle of the $LaNbO_4$-$LaWO_{4.5}$ single-phase region.

The compatibility between pure $LaNbO_4$ and several mixed conductors, which could be used as electrodes in fuel cells, such as $LaMnO_3$, $LaFeO_3$, $LaCoO_3$ and La_2NiO_4, and considered as model systems for the more complex oxide materials actually used in a real device, was extensively studied [11,12]. Considerable reactivity was observed between $LaCoO_3$ and $LaNbO_4$ and between La_2NiO_4 and $LaNbO_4$ at 1150 °C and 1000 °C, respectively, with the formation of a stable perovskite phase of composition $LaM_{2/3}Nb_{1/3}O_3$ (M = Co, Ni). Such reactivity was not observed for the Mn and Fe counterparts, treated under the same experimental conditions of temperature and time. However, the compatibility of W-doped lanthanum niobate with such electrode materials was tested only for the well-known strontium-doped lanthanum manganite for a short time (2 h), and with the testing temperature limited to 1200 °C [10]. In the present work, the compatibility against some commonly used electrode materials for fuel cells was tested using lanthanum niobate doped with 16 mol% W as electrolyte.

2. Materials and methods

2.1. Raw materials, powder synthesis and ceramics preparation

$LaW_xNb_{1-x}O_{4+x/2}$, with $x = 0.16$, hereby denoted as LW16N, was prepared by conventional solid state synthesis, using as precursors $La(OH)_3$ (Treibacher Industrie AG, 99.9%), Nb_2O_5 (H.C. Starck, ceramic grade) and WO_3 (H.C. Starck, electronic grade). These materials were selected for their submicrometric particle size, which ensures a homogeneous composition of sintered ceramics. Stoichiometric amounts of the precursors were mixed for 24 h in distilled water with the ammonium salt of polyacrylic acid (APA) as dispersant, forming a viscous slurry, and zirconia beads as grinding media. The powders were then freeze-dried, sieved and calcined at 1100 °C for 4 h with 5 °C/min as both cooling and heating rates. In order to prepare the ceramics, the powder was sieved with a 53 μm mesh, compacted by cold isostatic pressing at 1500 bar, and subsequently sintered for 4 h at either 1400 °C or 1500 °C with 3 °C/min as both cooling and heating rates. The samples were embedded in a powder bed of the same composition to avoid tungsten loss.

The materials considered as possible electrodes for compatibility tests, commercially available, were $La_{0.8}Sr_{0.2}MnO_3$ (LSM) (Aldrich), $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) (Marion Technologies) and $Pr_2NiO_{4+\delta}$ (PN) (Marion Technologies).

2.2. Characterisation techniques

X-ray diffraction (XRD) patterns were collected in the 2-theta range 10–80°, 0.02° steps (Panalytical CubiX, Cu Kα radiation or Bruker D8Advanced diffractometer for the compatibility tests). A Scanning Electron Microscope (SEM) (LEO 1450VP, LEO Electron Microscopy Ltd.) coupled with Energy Dispersive X-ray Spectroscopy (EDS) for elemental analysis was used to estimate the size and morphology of the powders and, on polished cross-sections of the ceramics, to verify the absence of secondary phases and evaluate the average composition of the samples. Sample density was measured by the Archimedes' method. Cell parameters and thus theoretical density were obtained from Rietveld refinement (FullProf software package [13]), using the measured XRD pattern.

The Specific Surface Area (SSA) of powders was measured with the Brunauer–Emmett–Teller (BET) method for N_2 absorption (Micromeritics ASAP 2010). The equivalent BET diameter, d_{BET}, was calculated assuming spherical geometry as:

$$d_{BET} = 6/(\rho \cdot SSA), \qquad (1)$$

where ρ is the sample theoretical density. The internal structure of the particles and their crystal structure were investigated by high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20). A small amount of powder calcined at 1400 °C for 4 h was dispersed into ethylic alcohol and a drop of suspension was put onto a 400 mesh, carbon-coated Cu grid.

Ceramic discs about 1 mm thick and 8 mm in diameter were used for impedance spectroscopy measurements. Platinum electrodes were brush-painted on both sides of the sample and annealed at 950 °C for 20 min with a heating and cooling rate of 5 °C/min. Measurements were performed in the temperature range 400–880 °C in the direction of decreasing temperature, in the 20–10^6 Hz frequency range with a LCR meter (Hewlett Packard 4848A). Samples were exposed to different atmospheres, with the following sequence: dry air, humidified air, humidified N_2 + (10 vol %) H_2, and dry N_2 + (10 vol%) H_2. The latter atmosphere was selected as the last working condition to avoid the risk of phase decomposition due to the extreme reducing conditions reached in such circumstances.

Gases were humidified by forcing them through a bubbler within a water container kept in a thermostatic bath at 59 °C (temperature stable within ±1 °C), and preventing water condensation before entering the furnace (with adequate thermal insulation and heating of tubes throughout gas transport). Heavily humidified hydrogen is an excellent buffer gas mixture with well-defined oxygen activity based on tabulated thermodynamic data for the reaction $H_2 + ½\, O_2 = H_2O$.

Impedance spectroscopy data were fitted using the software ZView (Scribner Associates). Deconvolution of spectra into bulk and grain contributions was hardly meaningful due to enormous arc overlap even at low temperature. Thus, the adopted equivalent circuit consisted of a parallel R-CPE circuit (R-resistor and CPE-constant phase element), to fit all points besides those corresponding to the low frequency electrode response. In this manner, only a total cell resistance could be estimated. At higher temperature the definition of the high frequency arc was lost and the high frequency intercept of the electrode arc was taken as the cell total resistance.

For the electrolyte/electrode compatibility tests, 50:50 wt% mixtures of both materials were prepared by carefully mixing the two components. The powders were compacted by cold isostatic pressing at 1500 bar and subsequently treated at increasing temperature. Two thermal treatments of 6 h each were performed at 600 °C and 800 °C for all the three samples. For the LSM and LSCF samples, additional thermal treatments at 1000 °C for 6 h and 1200 °C for 6 h and 24 h were performed to increase the mixture reactivity. Heating and cooling were achieved with 2 °C/min rate.