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Structure, morphology, and electrical properties of proton conducting $La_{0.99}Sr_{0.01}NbO_{4-\delta}$ synthesized by a modified solid state reaction method

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HIGHLIGHTS

- Sr-doped $LaNbO_4$ powder is prepared by a modified solid state reaction method.
- The sintering temperature of Sr-doped $LaNbO_4$ could be reduced to 1350 °C.
- The conductivity is governed by grain boundary current-constriction blocking effects.
- The modified solid-state sample shows fewer grain boundary blocking effects.

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ABSTRACT

Acceptor-doped $LaNbO_4$ has attracted considerable interest in applications for proton conducting fuel cells. The starting materials used for the conventional solid state reaction method (La_2O_3 and Nb_2O_5) have low reactivity, leading to difficulty in producing single phase $LaNbO_4$. The present work reports the synthesis of $La_{0.99}Sr_{0.01}NbO_{4-\delta}$ by a modified solid state reaction method using $La(CO_3)_3.xH_2O$, $SrCO_3$ and $C_4H_4NNbO_9.xH_2O$. Thermogravimetric analysis/Differential Scanning Calorimetry was used to study the decomposition of the starting materials. Powder samples were calcined at temperatures from 400 °C to 1100 °C and examined by X-ray diffraction (XRD) and Fourier transform infra-red spectroscopy (FTIR). A calcination schedule of 1100 °C for 5 h was chosen. Samples could be sintered to 97% relative density at 1350 °C. XRD of sintered samples revealed the monoclinic phase of $LaNbO_4$ and a La_3NbO_7 second phase. The electrical conductivity of the sample showed the activation energy of 0.9 eV, similar to that of the sample prepared by the conventional solid state reaction method. While the high frequency bulk conductivity is lower by a factor of ca. 3, the blocking effects due to the grain boundaries became weaker for the sample prepared by the modified solid state reaction method.

1. Introduction

Proton conducting ceramics are currently receiving much attention as electrolyte materials for use in proton conducting solid oxide fuel cells at intermediate temperatures [1–3]. Proton conductivity has been found in several types of acceptor-doped perovskite ceramic such as $SrCeO_3$ [4], $LaScO_3$ [5], $BaCeO_3$ [6] and $BaZrO_3$ [7]. Acceptor-doped $BaZrO_3$ has reasonable proton conductivity at temperatures up to 500 °C [1] and good chemical stability in CO_2 and H_2S-containing environments [8,9]. However, it is difficult to sinter to high density, requiring sintering temperatures of >1700 °C for up to 30 h [10,11]. Acceptor-doped $BaCeO_3$ is easier to sinter and has higher proton conductivity (up to 0.01 S/cm) [6], but is chemically unstable in CO_2-containing atmospheres [9,12].

As well as perovskites, there are also rare-earth ortho-niobates and tantalates $LaNbO_4$ and $LaTaO_4$ which become proton conducting when doped e.g. with Ca, Sr, Mg, Sn and Yb [13–17]. These materials have two polymorphs: a low-temperature monoclinic Fergusonite-type form and a high temperature tetragonal Scheelite-like form [18]. The phase transformation takes place at ~450 °C for $LaNbO_4$ but does not cause a drastic change in unit cell volume

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[18]. These materials have lower sintering temperatures than Y-doped $BaZrO_3$ (1500 °C) and better CO_2 stability than Y-doped $BaCeO_3$. Proton conductivity is an order of magnitude lower than that of perovskite proton conductors (~0.001 S/cm at 950 °C), but conductivity is almost entirely protonic at temperatures below 1000 °C i.e. there is little contribution to the conductivity from electrons, holes or oxygen ions [13,19]. These materials would make suitable electrolytes for proton conducting fuel cells operating in CO_2-containing atmospheres e.g. syngas if an electrolyte layer a few microns thick could be fabricated. $LaNbO_4$ electrolyte layers have been prepared by methods including spin-coating [20] and electrophoretic deposition [21].

$LaNbO_4$ powders are commonly prepared by the solid state reaction of La_2O_3 and Nb_2O_5. These oxides have low reactivity, requiring multiple ball milling and calcination steps in order to produce single phase $LaNbO_4$ [13,14]. Several other methods have been used to prepare powders of $LaNbO_4$ such as spray pyrolysis [22], molten-salt [16], sol-gel [15,23,24], co-precipitation and auto-combustion methods [25]. Although wet chemical methods can prepare ceramic powders with good chemical homogeneity and fine particle size, the procedures are complex and require expensive precursors. A modified solid state reaction method using ammonium niobium oxalate as the niobium source instead of Nb_2O_5 has been used to prepare nano-powders of $(K_{0.5}Na_{0.5})NbO_3$ [26]. The calcination temperature could be reduced from 800 °C when Nb_2O_5 was used as the Nb source to 500 °C when ammonium niobium oxalate was used. In the present work, a similar modified solid state reaction method was used to prepare powders of $La_{0.99}Sr_{0.01}NbO_{4-\delta}$. The oxide starting materials usually used in the preparation of $LaNbO_4$ are replaced with lanthanum carbonate and ammonium niobium oxalate respectively. Powders are prepared by both the conventional solid state (i.e. using oxides) and modified solid state reaction methods. The calcination behaviour of the modified solid state reaction method powder is studied at different temperatures. The sintering behaviour, structure, microstructure and electrical properties of powders prepared by both methods are then compared. Lowering the sintering temperature would reduce production costs as well as allowing the possibility of co-firing the electrolyte with the electrodes.

2. Experimental

For the conventional solid state reaction method, starting materials of La_2O_3 (Alfa Aesar, 99.9%), $SrCO_3$ (Aldrich, 99.9%) and Nb_2O_5 (CEPA, 99.9%) were used. Before weighing, the La_2O_3, $SrCO_3$ and Nb_2O_5 powders were dried at 250 °C for 5 h to remove adsorbed water. For the modified solid state reaction method, starting materials of $La_2(CO_3)_3.xH_2O$ (Alfa Aesar, 99.9%, 47.5 wt% La_2O_3), $SrCO_3$ (Aldrich, 99.9%) and $C_4H_4NNbO_9.xH_2O$ (Aldrich, 99.99%, 21.0 wt% Nb) were used. The $La_2(CO_3)_3.xH_2O$ and $C_4H_4NNbO_9.xH_2O$ starting materials were not dried prior to weighing. Stoichiometric amounts of the starting materials corresponding to a composition of $La_{0.99}Sr_{0.01}NbO_{4-\delta}$ were weighed out and ball milled in high purity ethanol (99.9%) in polypropylene jars using zirconia milling media. The ethanol was evaporated by using a hot plate with magnetic stirrer. The dried powders were ground using an agate mortar and pestle, and passed through a 180 μm mesh sieve to remove any agglomerates.

To study the reactions that take place on heating, the modified solid state reaction method powder was analysed by differential scanning calorimetry/thermogravimetric analysis (DSC/TGA, LABSYS evo, Setaram, France). The sample was heated in air from room temperature to 1000 °C at a heating rate of 10 °C/min. Based on the DSC/TGA results, samples of the modified solid state reaction method powder were heat treated at temperatures from 500 to 1100 °C for 5 h and examined by X-ray diffraction (XRD, Rigaku D/MAX Ultima III, Tokyo, Japan) using Cu Kα radiation, a scan range of 20–80° 2θ, a step size of 0.02° and a scan speed of 3°/min. A sample of the conventional solid state reaction method powder was also calcined at 1100 °C and examined by XRD for comparison. The heat-treated samples of the modified solid state reaction method powder were additionally examined by Fourier transform infra-red analysis (FTIR, IRPrestige-21, Shimadzu, Kyoto, Japan). Powder samples were mixed with KBr and pressed into pellets.

Based on the XRD results, both powders were calcined at 1100 °C for 5 h in a high purity alumina crucible with lid. Powders were ball milled as before to break up agglomerates. To prepare pellets for sintering, 0.5 g of powder was pressed by hand in a steel die of 10 mm diameter. The pellets were removed from the die and cold isostatically pressed at 1500 kg/cm^2 (147 MPa) pressure. Pellets were sintered in air in double high purity alumina crucibles with lids at temperatures from 1300 to 1500 °C for 5 h, with heating and cooling rates of 2 °C/min. The density of the sintered samples was measured in deionized water using the Archimedes method. For microstructure analysis, a sintered pellet was vertically cut into two halves with a low speed diamond wheel saw, mounted in resin and polished to a 1 μm finish. The polished samples were thermally etched and Pt coated for scanning electron microscopy (SEM, Hitachi S-4700, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, EMAX energy EX-200, Horiba, Kyoto, Japan).

Electrical properties were measured using impedance analysers over a wide temperature range in two temperature controlled setups. Firstly, the samples with platinum paste electrodes were equilibrated at 800 °C in wet oxygen with 2% H_2O obtained by flowing oxygen gas through a bubbler held at 17 °C. The impedance measurements from 1 MHz to 20 Hz, taking less than 30 s using an LCR meter with max. impedance of 100 MΩ (HP4284A, Agilent, USA), were performed on continuous cooling at 1 °C/min to room temperature. The cooled samples were loaded in a cryostat in vacuum and the spectra from 1 MHz to 10 mHz were taken using a frequency response analyser (Solartron 1260 combined with 1296 high dielectric interface which is capable of measuring impedances > 1GΩ) at stabilized temperatures at intervals of 10 °C from 200 °C to −70 °C. Each measurement at a particular temperature took 20 min.

3. Results and discussion

DSC/TGA analysis of the uncalcined modified solid state reaction method powder is shown in Fig. 1. There are weight loss steps at

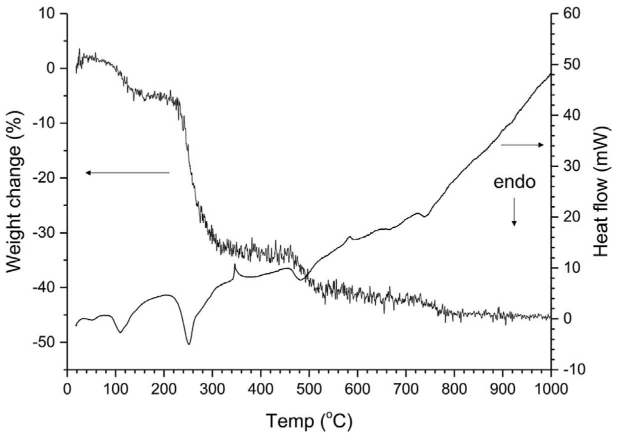

Fig. 1. Differential scanning calorimetry/thermogravimetric analysis of the uncalcined modified solid state reaction method powder.