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Solid State Ionics 176 (2005) 2395 – 2398

SOLID STATE IONICS

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Magnesium doped lanthanum silicate with apatite-type structure as an electrolyte for intermediate temperature solid oxide fuel cells

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Received 2 December 2004; received in revised form 11 April 2005; accepted 20 June 2005

Abstract

Electrical properties of magnesium doped lanthanum silicates as an electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs) have been investigated. Dense ceramic disks of $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ with apatite-type structure have been prepared by sintering first at 1600 °C and then at 1750 °C. The ionic conductivity is remarkably increased by magnesium doping and $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ has exhibited a conductivity of 30 mS cm^{-1} at 800 °C. Owing to low activation energy, the compound shows higher conductivity than yttria stabilized zirconia below 780 °C. Oxygen gas concentration cell measurements revealed that the compound is an oxide ion conductor. A solid oxide fuel cell using $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ as an electrolyte was found to work at 608, 706 and 805 °C with power densities of 1.3, 5.8 and 20.0 mW cm^{-2}, respectively, which demonstrates that magnesium doped lanthanum silicates can be used for IT-SOFC electrolytes. The low power densities are probably due to insufficient performance of Pt paste electrodes.

PACS: 66.30.D
Keywords: Oxide ion conduction; Apatite; Solid oxide fuel cell; Solid electrolyte

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted great interest as a clean and high efficient electrical power source. Most SOFCs up to now manufactured use yttria stabilized zirconia (YSZ) as an electrolyte, because YSZ is a pure ionic conductor over a wide oxygen partial pressure range and easy to fabricate as dense ceramics. The ionic conductivity of YSZ, however, is not so high that an operating temperature of 1000 °C is required. Such high operating temperature causes serious problems concerning cell life arising from reaction of the components and thermal expansion and contraction. Reducing the operating temperature to 600–800 °C not only enhances the cell life but also enables a use of metallic interconnect which greatly improves reliability of the cell. In order to realize the intermediate temperature SOFCs (IT-SOFCs), ionic conductors which have high conductivity at lower temperature are strongly desired. For this purpose, extensive researches have been conducted on fluorite- and perovskite-type ionic conducting oxides. Doped cerium oxides with fluorite-type structure have high ionic conductivity. However, they suffer considerable electronic conduction in a reducing atmosphere. On the other hand, $LaGaO_3$-based perovskite oxides have superior conductivity and stability in electrical properties, thus being considered as a promising candidate for IT-SOFC.

Recently, rare earth silicates with apatite-type structure have been found to exhibit ionic conduction [1]. These compounds have low activation energy and considerably high ionic conductivity at intermediate temperature. Nakayama et al. have shown that, among these rare earth silicates, $La_{10}Si_6O_{27}$ has the highest conductivity [2]. They also suggested that the conduction species seems to be oxide

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0167-2738/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2005.06.026

ion because a slope of EMF of the oxygen concentration cell against oxygen partial pressure showed the theoretical value. Tao et al. assumed that oxide ions of these apatite oxides migrate via an interstitial conduction mechanism [3] in contrast to a vacancy mechanism which is common to most oxide ion conductors. They prepared $La_{10}Si_6O_{27}$ and $La_{9.33}Si_6O_{26}$ to investigate the conduction mechanism; however, dense samples suitable for the conductivity measurements could not be obtained because of very high temperature ($\geq$1700 °C) required for the sintering. Quite recently, we have examined the sintering conditions to prepare dense lanthanum silicate ceramics having different La contents and elucidated the relation between the conductivity and the La content which supports the interstitial conduction mechanism [4]. Sansom et al. [5] and León-Reina et al. [6] have discussed the defect structure obtained from neutron powder diffraction measurements in relation to the conduction mechanism. Atomistic simulations describing the interstitial oxide migration have been performed by Islam, Tolchard and Slater [7,8].

In contrast to these extensive researches about the conduction mechanism, there has been very little work on applying these apatite oxides to SOFC electrolytes. One of the reasons for this is that the conductivity of these apatite oxides is not enough for SOFC applications. Another reason is a difficulty in fabricating dense ceramic samples as described above. We have found that the conductivity of apatite-type lanthanum silicates is greatly enhanced by Mg doping [9]; a doping level of 0.3 Mg for $La_{10}Si_6O_{27}$ gave the highest conductivity. In this study, electrical properties of dense Mg doped lanthanum silicate disks are investigated by AC impedance, oxygen gas concentration cell and solid oxide fuel cell measurements to demonstrate that the compound works as an electrolyte for IT-SOFCs.

2. Experimental

Samples were prepared by solid-state reactions. Starting materials of La_2O_3, SiO_2 and MgO powders previously dried at 1000 °C for 4 h were mixed in $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ composition, ground with ethanol and calcined at 1300 °C for 16 h. The calcined powders were further ground, pressed into disks and sintered at 1600 °C for 4 h. The first sintering only gave very porous disks because of high reactivity of the calcined powders with the atmospheric H_2O and CO_2. They were thus reground, pressed into disks and sintered again at 1750 °C for 4 h resulting in dense ceramic disks with a diameter of ~13 mm and a thickness of ~1 mm. A $MoSi_2$ furnace and Mg stabilized ZrO_2 setters were used for the high-temperature sintering. After both faces of the disks were polished, dimensions and weights of the disks were measured to calculate bulk density. One of the disks was reground and subjected to powder X-ray diffraction measurements and Rietveld analysis using RIETAN-2000 [10].

For the electrical measurements, Pt paste electrodes painted and fired at 1000 °C on both faces were used. AC impedance was measured by a Solartron 1260 impedance analyzer with frequencies ranging from 10 MHz to 0.1 Hz and temperatures from room temperature to 900 °C in air. Oxygen gas concentration cell measurements were performed with a test cell in which both faces of the sample disk were glass-sealed into alumina tubes and attached to Pt meshes with Pt leads. Open circuit voltages (OCVs) and I–V characteristic curves were measured on the cell while oxygen and N_2–20% O_2 mixed gas were supplied to both faces at a rate of 50 cm^3 min^{-1} at fixed temperatures from 601 to 900 °C. OCV and I–V measurements of SOFC setup were conducted on the similar test cell at fixed temperatures from 608 to 805 °C with H_2–H_2O moisturized at 33 °C introduced to the anode and N_2–20% O_2 to the cathode at a rate of 50 cm^3 min^{-1}.

3. Results and discussion

3.1. Sample characterization

Powder X-ray diffraction measurements showed that $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ sintered at 1750 °C has single-phase apatite-type structure ($P6_3/m$). In the previous paper, we have demonstrated from the lattice parameter measurements that Mg can be doped into $La_{10}Si_6O_{27}$ to form $La_{10}Si_{6-x}Mg_xO_{27-x}$ solid solution up to $x \sim 0.6$ [9]. Solid solution seems to form also in the present $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ sample. The Rietveld analysis revealed that the structure model with doped Mg ions locating at T site (Si site) gives a good fit to the observed pattern. Lattice parameters of $a=0.9725$ and $c=0.7208$ nm for $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ show an increase with the doping from $a=0.9714$ and $c=0.7188$ nm of non-doped $La_{9.6}Si_6O_{26.4}$ which corresponds to 0.5% expansion of the lattice volume. This is due to a difference of Si^{4+} and Mg^{2+} in the ionic radii and electrostatic forces to oxide ions which causes an increase in the average (SiMg)–O distance by 2.4% from 0.1572 to 0.1609 nm. Details of the Rietveld analysis will be published elsewhere.

It was frequently reported that dense sintered lanthanum silicates were difficult to obtain [3,5,6]. In this study, however, we found it possible to fabricate dense $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ disks by (1) first sintering at $\geq$1600 °C, (2) second sintering at $\geq$1750 °C and (3) substitution of a small amount of Mg for Si. The powder after calcined at 1300 °C has high reactivity and reacts with H_2O and CO_2 in the ambient atmosphere during a heating stage resulting in a porous sintered body after the first sintering. As the reactivity of the powder was greatly depressed after the first sintering, we can make dense ceramic disks by the two-step sintering. Though densification mechanism by Mg addition is not clear, densities of the sintered $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ pellets (4.8–5.1 g cm^{-3}) which are 88–95% of