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Transition metal-doped lanthanum germanate apatites as electrolyte materials of solid oxide fuel cells

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ABSTRACT

In this study, the effects of Fe, Mn, Ni, and Ti dopants on the densification, phase structure, microstructure, and electrical conductivity of the $La_{9.5}Ge_{6.0}O_{26.25}$ ceramics were examined. After sintering, the $La_{9.5}Ge_{5.5}Mn_{0.5}O_{26}$ and $La_{9.5}Ge_{5.5}Ti_{0.5}O_{26.25}$ ceramics displayed hexagonal symmetry while the $La_{9.5}Ge_{5.5}Ni_{0.5}O_{25.75}$ and $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$ ceramics produced triclinic lattice. The $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$ ceramic sintered at 1400 °C showed the best electrical conductivity of 0.033 Scm^{-1} and the lowest densification temperature among the apatite ceramics evaluated, and the calculated thermal expansion coefficient of this system emerged to be 10.5×10^{-6} K^{-1}, compatible with those of the common adjacent materials used in solid oxide fuel cells (SOFCs). Single cells of $NiO\text{-}SDC/La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}/LSCF\text{-}SDC$ were built and evaluated. The open circuit voltages of the single cell read 0.96 and 1.01 V respectively at 950 and 800 °C, both in accord with the redicted theoretical values and verifying the pure ionic conduction in apatites. The maximum power densities (MPDs) of the single cell were 0.384, 0.280, 0.201, and 0.125 Wcm^{-2} respectively at the measurement temperatures of 950, 900, 850, and 800 °C. The MPDs of the single cell with the $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$ electrolyte are superior to those of the SOFCs with apatite ceramics as electrolyte previously reported in the literature, thereby testifying to the potential of the $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$ ceramic as a promising electrolyte material for SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) system has been drawing substantial attention for application in heat and power generation devices in residential and commercial properties, large-size stationary power facilities, and auxiliary power units for transportation vehicles. To enhance SOFC performance, electrolytes are expected to have high ionic conductivity and electrodes low polarization resistance (Rp). In addition to currently used oxide ion conductors such as the fluorite-structured $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) and $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) and perovskite-structured $La_{0.9}Sr_{0.41}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) [1], apatite-type materials with the general formula of $A_{10-x}M_6O_{26\pm\delta}$ (A = rare earth or alkaline earth; M is Si and Ge) have also been considered to be potential candidate as SOFC electrolytes [2]. The conduction of the apatite materials has been proposed to occur via interstitial oxide ions, in contrast to the dominant ion conduction mechanism in fluorite- or perovskite-type materials which relies on oxygen vacancy. The hexagonal structure with space group of $P6_3/m$ consists of isolated MO_4 tetrahedra forming channels running parallel to the c-axis with A cations located in two cavity sites, one 7 coordinate and one 9 coordinate. The loosely bounded extra oxide anions in the channels are considered mobile and presumed to be responsible for the high level of oxide ion conductivity [3]. In regard to these systems, the high oxide ion conductivity of $La_{10-y}(Si/Ge)_6O_{26\pm\delta}$ have recently generated considerable interest after first reported by Nakayama et al. [4–6].

Several approaches have been adopted to raise the conductivities of the apatite-type materials, including the doping regimes that trigger nonstoichiometry in the form of either cation vacancy or oxygen excess [7,8]. The oxide conductivity in $La_{9.33}Si_6O_{26}$ (2.0×10^{-3} Scm^{-1} at 800 °C) is lower than that in $La_{10}Si_6O_{27}$ (3.46×10^{-2} Scm^{-1} at 800 °C), but higher than the one in $La_8Sr_2Si_6O_{26}$ (5.6×10^{-7} Scm^{-1} at 800 °C) [2,9,10]. Substitution of Si sites of $La_{10-y}Si_6O_{26\pm\delta}$ with dopants like Mg, Fe, Al, and Co ions was found to exert a positive effect on conducting properties [11–14]; $La_{10}Si_{5.2}Co_{0.8}O_{26.6}$, for instance, exhibits an electrical conductivity of 3.3×10^{-2} Scm^{-1} at 800 °C [8]. Although the $La_{10-y}Si_6O_{26\pm\delta}$ apatites possess high conductivity at low temperatures, their over-1700 °C sintering temperatures appear to be a technical barrier against SOFC applications [15]. Synthesis of apatite powders via wet chemical process, such as epoxide-driven sol–gel route, has been conducted to reduce the sintering temperature of the apatites but found to betray the disadvantage of necessitating expensive chemicals and a time-consuming process [16–18]. Other than the silicon-based

apatites, germanium-containing apatites like $La_{10-y}Ge_6O_{26\pm\delta}$ have also been suggested for effective reduction in sintering temperature [2,3,10,19–21], due to the apparent difference in the melting points of GeO_2 (1116 °C) and SiO_2 (1713 °C) [22]. Substitution of Si ions by Ge ions has been found to decrease sintering temperatures and improve electrical conductivities [17,23]. As reported in the literature [17,23], the electrical conductivities of the $La_{10}Ge_6O_{27}$, $La_{9.33}Ge_6O_{26}$ and $La_{9.33}Si_2$ Ge_4O_{26} ceramics at 800 °C read respectively 0.08, 0.06 and 0.01 Scm^{-1}, all superior to that of $La_{9.33}Si_6O_{26}$ (2.02×10^{-3} Scm^{-1}). The lanthanum germanate apatites are marked with two more drawbacks: poor microstructure control and GeO_2 volatilization at temperatures above 1300 °C [23,24]. Massive GeO_2 loss would result in the formation of another conducting phase La_2GeO_5 [25]. Berastegui et al. [26] identified the existence of another triclinic apatite phase in the La–Ge–O phase diagram, a finding validated later by Leon-Reina et al. [27]. The $La_{9.33+x}(GeO_4)_6$ $O_{2+3x/2}$ apatites with composition $\sim0.17 \leq x \leq \sim0.50$ exhibited a hexagonal symmetry while samples with higher La content showed a triclinic cell [2,19]. Electrical conductivities of apatites with various La contents have been studied and reported in the literature [29,20]. Nakayama et al. showed that $La_{9.0}(GeO_4)_6O_2$ had the highest conductivity among various $La_x(GeO_4)_6O_{1.5x-12}$ apatites [20], while León-Reina et al. found $La_{9.5}(Ge_{5.5}Al_{0.5})O_{26}$ able to achieve the highest conductivity among various $La_{10-x}(Ge_{5.5}Al_{0.5})O_{26.75-1.5x}$ apatites [28].

To date, several doping studies including Bi, Ba, Sr on La sites and Al, Ga, As, Ti, Nb, and W on Si sites of the Ge-based apatites have been performed to curb GeO_2 loss (mainly by reducing the densification temperature) and/or to raise conductivity [28–32]. However, limited information has been available on the electrochemical performance of the SOFCs with either Si-based or Ge-based apatites as electrolytes [12,24]. Further investigation is needed to validate the feasibility of using apatite ceramics as SOFC electrolyte. In this study, deriving from the studies of León-Reina et al., the effects of the transition metal dopants (Fe, Mn, Ni, and Ti) substituted into the Ge sites of $La_{9.5}Ge_6O_{26.25}$ on the densification, phase structure, microstructure, and electrical conductivity of the $La_{9.5}Ge_{5.5}M_{0.5}O_{26\pm\delta}$ ceramics were examined. SOFC button cells incorporating a $La_{9.5}Ge_{5.5}M_{0.5}O_{26\pm\delta}$ electrolyte, a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)–$Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) composite cathode, and a NiO–SDC composite anode were built. The performance of the NiO–SDC/$La_{9.5}Ge_{5.5}M_{0.5}O_{26\pm\delta}$/LSCF–SDC single cell was also assessed.

2. Experimental procedure

Powders of the transition metal-doped lanthanum germinate ceramics used in this study were synthesized by solid-state reaction route. La_2O_3 (SHOWA, Reagent grade), GeO_2 (Kojundo Chemical Lab., Reagent grade), MnO_2 (Alfa, Reagent grade), NiO (Alfa, Reagent grade), Fe_2O_3 (SHOWA, Reagent grade), and TiO_2 (SHOWA, Reagent grade) with a purity exceeding 99.9% were used as raw materials. To ensure the removal of absorbed water and oxygen, the La_2O_3 powders were pre-heat-treated at 1000 °C for 2 h. Oxides based on the formulations of $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$, $La_{9.5}Ge_{5.5}Mn_{0.5}O_{26}$, $La_{9.5}Ge_{5.5}Ni_{0.5}O_{25.75}$, and $La_{9.5}Ge_{5.5}Ti_{0.5}O_{26.25}$ were mixed and milled in methyl alcohol solution using zirconia balls and polyethylene jars for 4 h and then dried overnight in an oven at 90 °C. After drying, the powders were calcined at 1100 °C for 6 h (heating rate = 5 °Cmin^{-1}), re-milled in methyl alcohol for 4 h, and oven-dried at 90 °C overnight. For phase identification, X-ray diffraction (XRD, Siemens D5000) analysis was performed on the calcined powders to verify the phases. The calcined powders were subsequently mixed with a 5 wt% binder of 15 wt%-PVA solution and pressed into disc-shaped compacts in a diameter of 25 mm under a uniaxial pressure of 0.9 tons cm^{-2}. The compacts were then heat treated at 550 °C for 4 h to eliminate PVA and sintered at different temperatures for 4 h (heating rate = 5 °Cmin^{-1}). Liquid displacement method was used to measure the densities of the specimens.

Conductivity versus temperature was evaluated by a standard four-probe method (Keithley 2400) in air at temperatures ranging from 25 to 800 °C. Scanning electron microscopy (SEM, Hitachi S4700) studies on the as-sintered and the fracture surfaces of the discs were accomplished. Compositions and chemical bonding states in the films were determined by X-ray photoelectron spectroscopy (XPS). Prior to the XPS analysis, the samples were sputter-etched with Ar$^+$ ions for 5 min to remove the top surface contaminants. Dilatometrical analysis (NETZSCH 402C) of the dense ceramics was performed at a heating rate of 5 °Cmin^{-1} in order to determine the coefficient of thermal expansion.

Commercially available materials, including $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC; Fuel Cell Materials, USA; $d_{50} = 0.53$ μm and BET surface area = 6.2 m^{2}g^{-1}), $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF: Fuel Cell Materials, USA; $d_{50} = 0.99$ μm and BET surface area = 5.4 m^{2}g^{-1}), and NiO ($d_{50} = 0.8$ μm and BET surface area = 3.4 m^{2}g^{-1}; Fuel Cell Materials, USA), were used to build SOFC in the study. The electrolyte-supported SOFC single cells—25 mm in diameter and 0.4 mm in thickness—consisted of a $La_{9.5}Ge_{5.5}M_{0.5}O_{26\pm\delta}$ electrolyte layer, a NiO–SDC composite anode layer at a ratio of 60 wt%/40 wt%, and a LSCF–SDC composite cathode layer at a ratio of 60 wt%/40 wt%. The electrode pastes were prepared by mixing the NiO–SDC and LSCF–SDC mixtures respectively with a suitable amount of ethyl cellulose (binder) and terpineol (solvent). The sintered $La_{9.5}Ge_{5.5}M_{0.5}O_{26\pm\delta}$ ceramics were polished down to approximately 0.4 mm in thickness for use as electrolyte substrates. The NiO–SDC anode layer was first screen-printed on one side of the substrate in an area of 8 mm × 8 mm and then fired at 1350 °C for 2 h (heating rate = 2 °Cmin^{-1}). The LSCF–SDC cathode paste was then screen-printed on the opposite surface of the substrate, followed by firing at 1000 °C for 2 h. The electrochemical performance of the single cells was examined by a commercially available ProboStat (NorECs, Norway). Detailed information of the electrochemical test is available in a previous paper [33]. SEM studies on the fracture surface of the single cells after electrochemical measurement were performed to examine the microstructure.

3. Results and discussion

In this study, the $La_{9.5}Ge_{6.0}O_{26.25}$ ceramic was doped with Fe, Mn, Ni, and Ti ions to explore the possibility of lowering its densification temperature. The apparent densities of the $La_{9.5}Ge_{5.5}Mn_{0.5}O_{26}$, $La_{9.5}Ge_{5.5}Ti_{0.5}O_{26.25}$, $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$, and $La_{9.5}Ge_{5.5}Ni_{0.5}O_{25.75}$ ceramics versus sintering temperature are shown in Fig. 1. The densification temperatures of the transition metal-doped apatites appeared to vary significantly and strongly correlate with the dopants. The density of the $La_{9.5}Ge_{5.5}Mn_{0.5}O_{26}$ ceramics escalated with sintering temperature and reached a sintered density of 6.14 g cm^{-3} at 1550 °C. Less than 1.06% weight loss was recorded during the sintering of the ceramics. Further increase in the sintering temperature to reach maximum densification was not attempted as the sample experienced partial melting on the surface as the temperature approached 1600 °C. The sintered density of the $La_{9.5}Ge_{5.5}Ti_{0.5}O_{26.25}$ ceramics was found to achieve its maximum value of 5.83 g cm^{-3} at 1400 °C and the associated weight loss during sintering read 0.68%. The sintered density was found to degrade as the sintering temperature exceeded 1400 °C, and partial melting of the samples was observed as the sintering temperature reached 1450 °C. Similar to its $La_{9.5}Ge_{5.5}Ti_{0.5}O_{26.25}$ counterpart with a lower sintering temperature, the $La_{9.5}Ge_{5.5}Fe_{0.5}O_{26}$ ceramics reached maximum densification (5.86 g cm^{-3}) at the sintering temperature of 1400 °C with a weight loss of 0.81%. The sintered density tended to plummet when the sintering temperature rose above 1400 °C due to trapped porosities. For the $La_{9.5}Ge_{5.5}Ni_{0.5}O_{25.75}$ ceramics, a maximum sintered density of 6.02 g cm^{-3} was acquired at the sintering temperature of 1450 °C, the weight loss emerged to be 0.60%, and the density experienced a light decline at