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Chemical synthesis and properties of $La_{1.9}Ba_{0.1}Mo_{1.9}Mn_{0.1}O_9$ as electrolyte for IT-SOFCs

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Abstract: The highly phase-pure electrolyte materials with composition $La_{1.9}Ba_{0.1}Mo_{1.9}Mn_{0.1}O_9$ (LBMMO) was prepared by the sol-gel auto-combustion method for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The details of gel's auto-combustion, phase evolution, sintering, thermal expansion and electrochemical performance of LBMMO were investigated by means of thermo-gravimetry (TG), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), thermal expansion curve (TEC) and complex impedance spectra. The results showed that the highly phase-pure electrolyte LBMMO could be obtained after calcining at 600 °C. The sample sintered at 900 °C for 4 h in air exhibited a better sinterability, and the relative density of LBMMO was higher than 96%. The electrical conductivities of the sample were 6.7×10^{-3} and 25.9×10^{-3} S/cm at 700 and 800 °C in air, respectively. Results also showed that LBMMO had moderate thermal expansion (α=16.3×10^{-6} K^{-1}, between room temperature and 800 °C) and an electrical activation energy equal to 1.32 eV).

Keywords: electrolyte; electrical conductivity; $La_2Mo_2O_9$; sol-gel; rare earths

Solid oxide fuel cells (SOFCs) are considered as promising systems for efficient, environmental friendly, and reliable electrical energy production. Research and development of SOFCs have received much attention recently[1,2]. A general SOFCs stack may be composed of five main components: a porous anode, oxygen ion conducting electrolyte, mixed conducting cathode, sealing materials and interconnect. The electrolyte must be an oxide ion conductor with negligible electronic contribution and must be dense to prevent gas mixing. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte in SOFCs, which requires operating temperature in the range 800–1000 °C[1–5]. However, the high temperature will lead to a series of complicated material problems such as high-temperature gas seal, thermal expansion mismatch and interface reaction between components in SOFCs. The above-mentioned problems could be solved when the operating temperature reduces to an intermediate-temperature region (600–800 °C)[3,4]. Therefore it is necessary to develop an electrolyte exhibiting a sufficient oxide ionic conductivity at 600–800 °C. Alternative oxide-ion conductors have been reported over the last few years, including doped CeO_2 with fluorite-type structure[5,6], doped $LaGaO_3$ with perovskite structure[7,8], doped lanthanum silicates with apatite-type structure[9], and $La_2Mo_2O_9$ based materials (LAMOX)[10–13]. According to the report by Laccore et al., $La_2Mo_2O_9$ exhibits relatively high oxide ionic conductivity as high as 0.06 S/cm at 800 °C，and is comparable to that of yttria-stabilized zirconia (YSZ) at high temperatures[12,13]. So LAMOX is expected to be candidates for the electrolyte of the SOFCs operated at an intermediate temperature range of 600–800 °C.

However, pure $La_2Mo_2O_9$ presents some limitations for its potential application as solid electrolyte due to a phase transition that causes a drastic drop in the conductivity below 580 °C. In order to stabilize the β-polymorph, several series of compounds have been investigated, substituting La^{3+} with Bi^{3+}, Ca^{2+}, Ba^{2+}, K^+, Y^{3+} and rare-earth elements, whereas Mo^{6+} has been substituted with Cr^{6+}, V^{5+}, Nb^{5+}, Ti^{4+}, Mn^{4+}, and W^{6+} [12–20].

In this work, La and Mo sites were partially substituted with Ba and Mn, respectively. The nano-crystalline $La_{1.9}Ba_{0.1}Mo_{1.9}Mn_{0.1}O_9$ (LBMMO) powder has been successfully prepared by sol-gel auto-combustion method using a combination of citric acid firstly. The synthesis process, the characterization and the sintering properties of the nano-sized LBMMO powder were reported.

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1 Experimental

1.1 Synthesis of LBMMO powder

LBMMO powder was prepared in the laboratory by sol-gel auto-combustion method. $La(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3)_3$, $MnSO_4{\cdot}H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, all in analytical grades, were used as the metal sources. Citric acid with purity higher than 99.5% was used as the chelants. The molar ratio of citric acid to metal ions in this study was fixed at 2:1. In this method, stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3)_3$, $MnSO_4{\cdot}H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved in distilled water and an aqueous solution of citric acid was added with constant stirring until a homogenous solution was achieved. After this stage, a proper amount of NH_4NO_3 was added into the solutions, the molar ratio (R) of NO_3^- to metal ion (La^{3+}, Ba^{3+}, Mo^{6+} and Mn^{4+}) was varied at 5:1. The prepared solution was then heated to 80 °C to obtain viscous solution (sol) and continuously heated at the same temperature until to obtain the gel state precursor sample. The gel in the glass beaker was heated on a hot-plate until self-sustaining combustion to form the ashen powder products. The ashen powder was then calcined at 600 °C for 2 h in air to obtain highly phase-pure LBMMO powder. The flowchart of synthesis of samples by the sol-gel auto-combustion method is shown in Fig. 1.

1.2 Characterization

The thermal analysis was done using thermo-gravimetric analysis (TG) techniques with a heating rate of 10 °C/min in air environment to study the different reaction steps and temperatures of the LBMMO precursor gel. The phase identification of the as-synthesized products was recorded by X-ray diffractometer (XRD) with Cu Kα radiation (λ=0.15406 nm).

The obtained LBMMO powder was mixed with an appropriate amount of 5 wt.% polyvinyl alcohol as the binder, and granulated using a 180-mesh sieve, after which the granulated powder was uniaxially pressed into pellets and cylinders at 100 MPa for electrical conductivity and thermal expansion measurements and finally were sintered at different temperatures. The relative density of the sintered samples was obtained by Archimedes method in water.

The morphology and microstructure of sintered sample were observed with a scanning electron microscope. Ionic conductivity of the sintered pellet was obtained by a Solartron 1260 impedance analyzer. The pellets were coated uniformly with silver paste on both sides and then fired at 700 ºC for 10 min in the muffle furnace, data were collected in the 0.1 Hz–1 MHz frequency range, every 50 ºC from 400 to 800 ºC in air and registered impedance spectra were analyzed using Zsimpwin software. The thermal expansion property was researched by dilatometer in air from room temperature to 800 ºC and heating rate was 5 ºC/min.

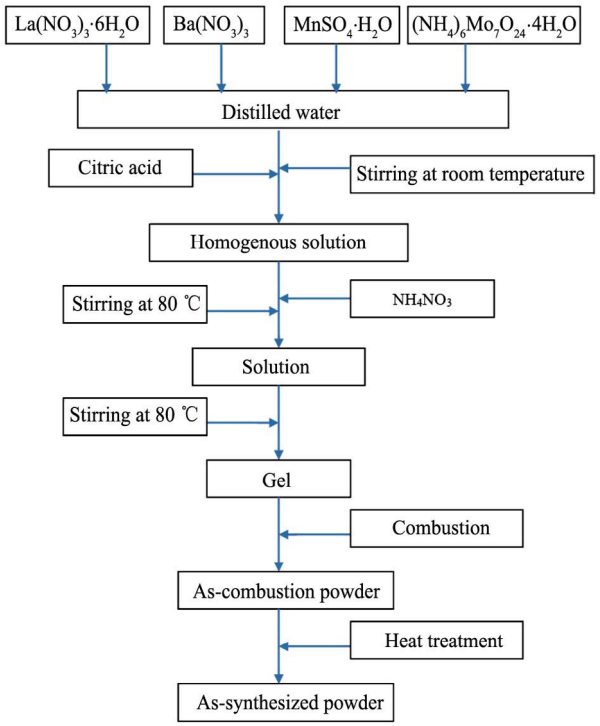

Fig. 1 Flowchart of synthesis process of LBMMO powder

2 Results and discussion

2.1 Thermal analysis

Fig. 2 is the TG curve of LBMMO dried gel. The weight loss (~30%) in the temperature range of 25–240 °C corresponds to the removal of the physical absorbed and structural water in the gel precursor. The weight loss (~35%) in the temperature range of 240–450 °C corresponds to the combustion of inorganic and organic constituents of the precursor. Almost no loss was observed above 450 °C on TG curve, implying only the presence of crystalline LBMMO. It was further confirmed by XRD studies.

2.2 XRD phase structure analysis

Fig. 3 shows the XRD pattern of the as-synthesized LBMMO solid solutions powder prepared by the sol-gel

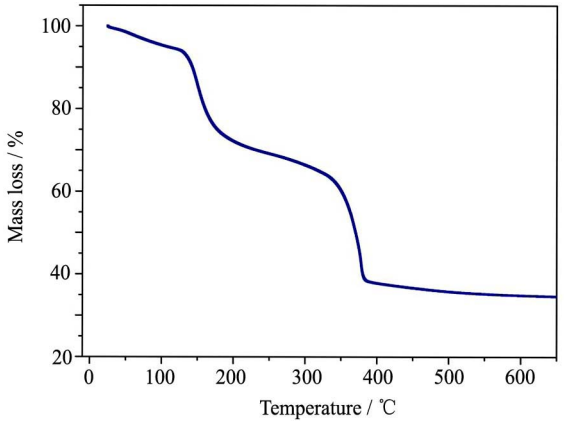

Fig. 2 TG analysis of the dried gel