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Synthesis, processing and characterization of nasicon solid electrolytes for CO_2 sensing applications

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Abstract

Precursor powders of nasicon solid electrolytes were synthesized by both the colloidal method (CM) and sol–gel method (SGM) and characterized. The phase evolution of the sensor materials and sintered microstructures was analyzed by X-ray diffraction technique (XRD) and scanning electron microscopy (SEM). Zirconia-free nasicon phase was formed at relatively low temperature from the sol–gel precursor powder. Sintered pellets produced from calcined sol–gel powder exhibited single-phase (homogenous) microstructure while a silica-rich glass phase was present at the grain boundaries in the pellets sintered from calcined colloidal powders. Disc-shaped sensor elements were fabricated via uniaxial pressing of the calcined powders and subsequently sintered at 1150 °C for the CM powders and 1200 °C for the SGM powders, respectively. Platinum electrode was applied to the sensor elements to produce potentiometric/electrochemical carbon dioxide gas sensors. The electrical response of the sensors to CO_2 was investigated at various operating temperatures and CO_2 concentrations. Sensors made from sol–gel derived materials displayed better sensing response to CO_2 gas at higher testing temperature as compared to sensors made from the colloidal powders.

Keywords: Nasicon; Calcination; Sintering; Grain boundaries; Sensors

1. Introduction

In recent years, growing interest in environmental problems has resulted in a need for monitoring sensors for controlling industrial process of discharging carbon dioxide gas into the atmosphere. Among the materials used for CO_2 sensors such as solid electrolytes [1–7], mixed oxide capacitors [8] and polymers with carbonate solution [9], solid electrolyte-type CO_2 sensors are of particular interest because of their low-cost, high-sensitivity and simple element structure. Nasicon ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 \leq x \leq 3$) seems to be one of the most promising sensor materials because of its high ionic conductivity at a relatively low temperature and high chemical stability due to its microstructure [5–7,10–14]. As first reported by Goodenough et al. [15,16], nasicon ($x = 2$) consists of a three-dimensional skeletal network of PO_4 tetrahedra corner-sharing ZrO_6 octahedra with the Na^+ ions occupying a large octahedral site in the interstitial space. Each ZrO_6 octahedra is connected to six PO_4 tetrahedra, while each tetrahedron is linked to four octahedra [16]. This three-dimensional network is stabilized by electrons from mobile alkali ions in a three-dimensionally linked interstitial space. As indicated by Hong and co-workers [16], H_2O and Na_2O may occupy the interstitial space and block alkali-ion transport, which reduces the ion conductivity. In order to minimize this plaguing effect, some effort [17–21] has been made to obtain homogeneous nasicon precursor powder with different components mixed at a nanometer even molecular scale, thereby allowing further processing to yield a uniform microstructure with well-defined grains of small amount of defects as well as less grain boundary phases.

Extensive studies have also been conducted on various electrode materials such as binary carbonate electrode [6,13,14,20,22], Na_2SnO_3/SnO_2 and $Na_2Ti_6O_{13}/TiO_2$ [4,23,24], and other perovskite-type oxides [25] for CO_2 nasicon sensors, aiming to improve the sensitivity and stability. For Li_2CO_3–$BaCO_3$ binary carbonate electrode system, the nasicon electrochemical sensor may be outlined as follows [12]:

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(SE) (−) CO_2, O_2, Pt|$BaCO_3$/Li_2CO_3|nasicon|Pt, O_2, CO_2 (+) (RE)

The overall reaction may be written as:

$$Li_2CO_3 + BaCO_3 = 2Li_2O + BaO + 2CO_2 \quad (1)$$

The following Nernstian equation can be derived:

$$E = A - \frac{RT}{2F} \ln P_{CO_2} \quad (2)$$

where A is a constant related with temperature and the activities of the electrode materials and T is the testing temperature. It can be seen that EMF is decided by the CO_2 partial pressure when the temperature and oxygen partial pressure are maintained constant.

In the present work, a sol–gel method (SGM) was used to synthesize precursor powders of nasicon solid electrolyte, which was compared with nasicon prepared by a colloidal method (CM) [18]. The phase evolution of the synthesized precursor powders under thermal treatments was investigated. Sintered pellets from the green bodies formed by uniaxial pressing were used to fabricate CO_2 sensors. The electrical response of the sensors to CO_2 was investigated at various temperatures and CO_2 concentrations. The influence of microstructure and electrode materials on the CO_2 sensing characteristics of the sensors was investigated.

2. Experimental procedure

Detailed information concerning the synthesis, sintering and microstructure of nasicons prepared by the CM has been reported previously [18,19]. The results show zirconia-free Hong-type nasicon powder can be synthesized by the CM below 1000 °C in the composition range of $x = 1.5$–2.2. The colloidal method developed in this lab before was used to prepare the nasicon precursor powder with $x = 2$ for studying its CO_2 gas sensing characteristics in the present work.

The precursor powder of NASICON was prepared by sol–gel method as shown in Fig. 1. The silica sol was prepared according to the following mole ratio: TEOS (tetraethylorthosilicate):EtOH:HNO_3:H_2O = 1:5:0.025:1 and heated up to 70 °C under stirring; $Zr(OC_4H_9)_3$ was dissolved in ethanol, the solution was added into the silica sol slowly. The mixture sol was kept at 70 °C under stirring. The $NaNO_3$ and $NH_4H_2PO_4$ were, respectively, dissolved in ethanol and were subsequently mixed. This mixture solution of the $NaNO_3$ and $NH_4H_2PO_4$ was added slowly with rapid stirring into the hot mixture sol (70 °C) of silica and zirconia. Gelation and precipitation took place and relatively concentrated cream-like slurry was obtained. The heater was turned off, the slurry was kept inside the fume hood and the stirring was maintained until it was too concentrated to be stirred. After 12-h drying, the obtained cake-like material was ground and dried in an oven at 80 °C for 4 h. The resulting nasicon precursor powder was ready for further experiments.

Phase evolution studies were conducted on the SGM precursor powders calcined at temperatures of 700, 900, 1000, 1100 and 1200 °C for 2 h. An X-ray diffractometer (XRD, Rigaku Miniflex Model 1GC2) was used to identify the phase compositions of the calcined powders. Sintering studies were conducted using precursor powders calcined at 900 °C for 2 h, then milled for 24 h in *iso*-propanol using zirconia balls in a Teflon jar. Green discs of the milled SGM powders were formed using a uniaxial press. The sintering was carried out at 1200 °C for 2 h with a heating rate of 3 °C/min. Some of the discs (S_1) were buried in coarse nasicon powders while the others (S_2) were exposed to air during the sintering.

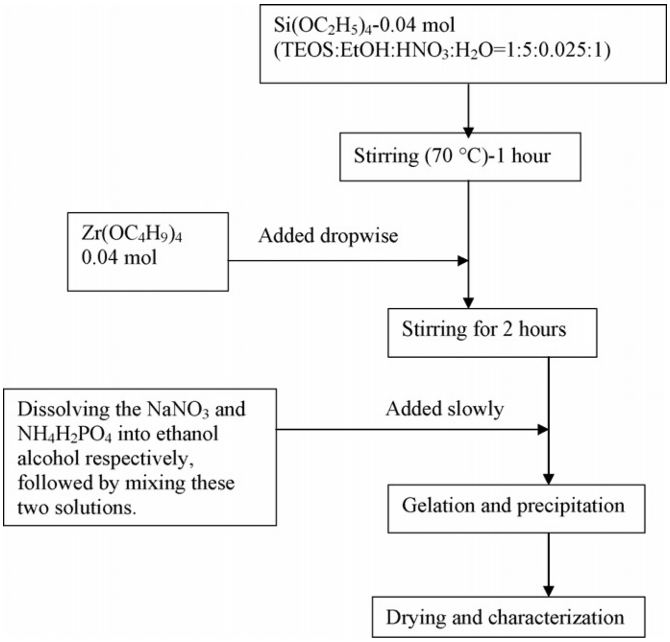

Fig. 1. Flowchart for the synthesis of a nasicon precursor by a sol–gel method.

Phase evolution studies were also conducted on the calcined CM precursor powders. The sintering of the CM green discs was carried out at 1150 °C for 2 h with a heating rate of 3 °C/min.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Netzsch STA 449 C, Jupiter) were used to characterize the behavior of the CM and SGM precursor powders under thermal treatment.

XRD analyses were also performed on three sintered sample surfaces; the first is raw surface of S_1 sample; the second is raw surface of S_2 sample and the third is polished surface of S_2 sample (using abrasive papers, the depth of the surface layer polished is about 0.1 mm). The sintered SGM sample for microstructure analysis by scanning electron microscopy (SEM, Philips ZL-30 with a LaB_6 filament) via energy dispersive spectrometry (EDS) were first polished with various grades of sand papers (400 mesh down to 1200 mesh) and then polished with diamond paste (6 down to 1 μm). The polished sample was thermally etched for 30 min at a temperature 5–10% lower than the sintering temperature before carbon film was deposited on the sample prior to SEM and EDS analyses.

The sintered pellets prepared from both CM powders and SGM powders were first polished on both sides into discs 10 mm in diameter and 1 mm in thickness. Then platinum electrodes were applied initially as a paste brushed onto both sides of the pellets and then thermally treated at 950 °C for 30 min. Platinum mesh and auxiliary phase were attached as follows: a small