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Proton conductivity of potassium doped barium zirconates

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ABSTRACT

Potassium doped barium zirconates have been synthesized by solid state reactions. It was found that the solubility limit of potassium on *A*-sites is between 5% and 10%. Introducing extra potassium leads to the formation of second phase or YSZ impurities. The water uptake of barium zirconates was increased even with 5% doping of potassium at the *A*-site. The sintering conditions and conductivity can be improved significantly by adding 1 wt% ZnO during material synthesis. The maximum solubility for yttrium at *B*-sites is around 15 at% after introducing 1 wt% zinc. The conductivity of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ at 600 °C is 2.2×10^{-3} S/cm in wet 5% H_2. The activation energies for bulk and grain boundary are 0.29(2), 0.79(2) eV in wet 5% H_2 and 0.31(1), 0.74(3) eV in dry 5% H_2. A power density of 7.7 mW/cm^2 at 718 °C was observed when a 1 mm thick $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet was used as electrolyte and platinum electrodes.

1. Introduction

Proton conducting ceramics have a wide range of possible applications such as gas sensors, hydrogen pumps and membrane reactors, etc. [1]. Their potential application as electrolytes in fuel cells were considered as a promising way to reduce greenhouse gas emissions [2]. Perovskite oxides based on $SrCeO_3$ have been recognized to exhibit predominant proton conduction under hydrogen containing atmosphere at elevated temperatures many years ago [3]. Thereafter numerous perovskite oxides with similar compositions have been synthesized and investigated such as $CaZrO_3$ [4–6] and $BaCeO_3$ [7–10]. Their chemical compositions could be written as $AB_{1-x}M_xO_{3-\delta}$, where M is some trivalent element such as a rare earth and δ is the oxygen deficiency per perovskite unit cell. Among the perovskite oxides investigated, cerate-based oxides generally present the highest conductivity but suffer from decomposition under atmospheres containing CO_2 or H_2O below 500 °C [11,12]. Great efforts have been devoted to partially substitute cerium with zirconium or by the introduction of other elements such as Gd, Nd or Co in the hope to improve the stability [13–16]. It has been found that the stability of these partially replaced cerates depends strongly on the zirconium content [14], in other words, complete replacement of cerium for zirconium is expected to exhibit the highest stability under atmospheres containing CO_2 and H_2O therefore allowing hydrocarbon fuels to be utilized. Although zirconates such as doped $BaZrO_3$ demonstrate similar conducting behavior to cerates in terms of formation and mobility of protonic charge carriers [17], their conductivity is usually one order of magnitude lower than cerates [1]. This is attributed to the highly refractory properties of zirconates with low rates of grain growth under typical sintering conditions which limit the overall proton transport [17]. This explanation has been confirmed by annealing the zirconates at a high temperature (~2200 °C) where the grain boundary conductivity was improved by nearly two orders of magnitude [18]. However, high temperature sintering should be avoided due to loss of barium at high temperature which is one factor that leads to a diminished conductivity [19]. Besides, from a technological point of view, high sintering temperatures introduce difficulties and unfavorable cost in manufacturing the materials since other auxiliary materials such as electrodes in fuel cells can hardly sustain such a high temperatures, never mind the likelihood of interfacial reaction [20]. Introducing zinc oxide into the *B*-sites is an efficient way in improving sintering conditions while conductivity is still unsatisfactory compared with cerates. On the other hand, proton conductivity of perovskite oxides was found to be strongly affected by the basicity of the constituent oxides due to its dominant influence on water uptake capacity [21], introducing highly basic alkaline oxides should improve the conductivity. Alkaline ions are more preferable to be doped at *A*-sites where crystal structure could be maintained. Patnaik et al. [22] did some fundamental work on *A*-site potassium doped barium zirconates, they found that the *A*-site potassium doped barium zirconates showed a significantly higher conductivity than *A*-site undoped barium zirconates where the yttrium dopant

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contents on *B*-site are approximately equal. However, some impurities (ZrO_2) remained in their samples and pure *A*-site potassium doped barium zirconates were not synthesized successfully in their work. One possible reason is that the limit for potassium doping at *A*-site is lower than 10%. In this paper, samples in series $Ba_{1-x}K_xZr_{1-y}Y_yO_{3-\delta}$ ($x \le 0.15$, $y \le 0.2$) with and without zinc doping have been synthesized. The conductivity of the samples in different atmospheres has also been investigated.

2. Experimental

2.1. Material synthesis

All samples were synthesized by conventional solid state reaction methods. Calculated amounts of $BaCO_3$, ZrO_2, Y_2O_3, K_2CO_3, ZnO were mixed according to the desired compositions. The oxides were preheated at 500 °C prior to weighing in order to remove the adsorbed water and gases. The mixtures were then planetary ball milled in a zirconia container with zirconia balls in the presence of acetone to ensure thorough mixing. The finely ground materials were fired at 1400 °C for 10 h with intermediate grindings. For samples without zinc, the fired powders were subsequently ground using a mortar and pestle before pressing into pellets under a pressure of 500 MPa. The pellets were fired at 1450 °C again for another 10 h before conductivity measurements. For samples with zinc, the precursors (apart from zinc) according to the formula were mixed and pre-fired at 1100 °C to decompose the carbonates then a calculated amount of zinc oxide was mixed together with as-fired powders, ball-milled for 30 min and pressed into pellets in a diameter of 13 mm before firing at 1300 °C for 10 h.

2.2. Materials characterization and conductivity measurements

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a Cu*K*α1 source ($\lambda = 1.54056$ Å). The step size for data collection was 0.02° with a collection time 10 s at each step. Vaseline was used to mount the sample in the holder. X-POW software was used to perform least square refinement of the lattice parameters of the samples. Thermal analysis was carried out on a Rheometric Scientific TG 1000M+ and TA instruments with heating and cooling rate of 5 °C/min under flowing dry Ar, dry and wet 5% H_2/Ar (humidified in water at 20 °C) at a rate of 20 mL/min. The microstructure of pellets was inspected by scanning electron microscope (SEM) on a JEOL 5600 SEM with a Mica energy dispersive X-ray spectroscopy (EDS) analysis system. EDS on cross-section of a $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet was carried out at a voltage of 20 kV and spot size of 45. Sample for EDS analysis was prepared by mechanical breaking without further treatment. An Agilent 7500a inductively coupled plasma mass spectroscopy (ICP-MS) with laser ablation was used for surface element analysis.

Conductivity was investigated by a.c. impedance method over the frequency range from 1 MHz to 0.1 Hz at 100 mV r.m.s. using a Schlumberger Solartron 1255 Frequency Response Analyzer coupled with a 1287 Electrochemical Interface controlled by Zplot electrochemical impedance software. Pellets obtained above were coated with conductive platinum paste on both sides serving as electrodes and were then fired at 900 °C to ensure good ohmic contact. Measurements were performed from 200 to 850 °C on cooling under ambient air, wet 5% H_2/Ar (humidified at 20 °C in water), dry 5% H_2/Ar (desiccated at 20 °C in 98% H_2SO_4). Accordingly, the steam vapor pressures are 8.4×10^{-4}, 3.0×10^{-2} and 1.3×10^{-6} atm for air, wet and dry 5% H_2, respectively [23]. Pellets were maintained at 850 °C for at least 12 h in each atmosphere and impedance data were collected at 50 °C steps after 1 h dwell at each step for equilibrium.

3. Results and discussions

3.1. Phase composition

X-ray powder diffraction was carried out on each of prepared samples; XRD patterns for samples without zinc are shown in Fig. 1. Single phase perovskite oxides were formed on doping 5% potassium onto the *A*-site and 10% yttrium onto *B*-site; a second perovskite-like phase and YSZ (yttrium stabilized zirconium) appeared when 10% or more potassium was introduced, implying the upper limit of solid solution formation on *A*-sites for potassium is between 5% and 10%. This could be a reason why Patnaik et al. did not obtain a pure potassium doped $BaZrO_3$, where more than 10% potassium was used [22]. The unit cell parameter of $Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-\delta}$ (4.2075(6) Å) is close to the reported value for $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ [24] (4.2044 Å) which is plausible due to the similar average ionic radius of Ba^{2+} (1.60 Å) and K^+ (1.60 Å) at 12 coordinates [25]. However, the experimental density of $Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-\delta}$ pellets fired at 1450 °C only reached 60% of its theoretical density (calculated using lattice parameters from XRD data) due to the refractory properties of barium zirconates. Dense pellets were not obtained even when the sintering temperature was increased to 1600 °C indicating that potassium oxide is not an efficient sintering aid for barium zirconates.

3.2. Thermogravimetric and water uptake studies

Thermogravimetric studies were carried out by recording the weight change against temperature in different atmospheres (dry and wet 5% H_2 (humidified at 20 °C)). Samples for TG studies were pre-treated in dry Ar at 900 °C for 5 h to eliminate water and the temperature was controlled from 900 to 20 °C at a cooling rate of 5 °C/min. Fig. 2 shows the weight changes in different atmospheres. In dry 5% H_2, the as-prepared sample shows a weight change $<0.25\%$ from 900 to 20 °C. This weight change can

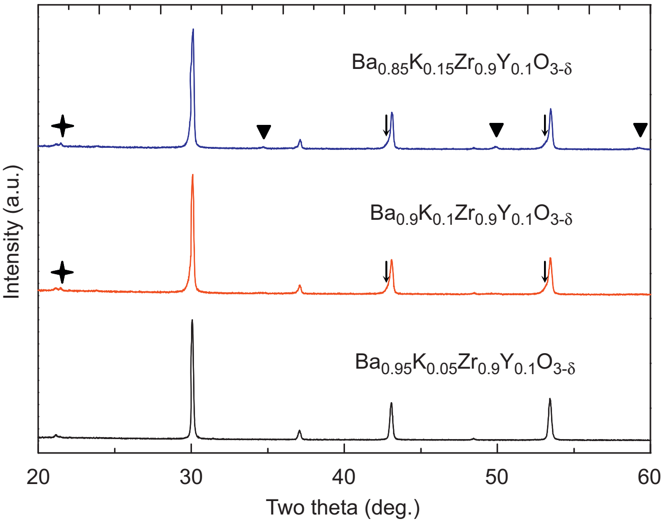

Fig. 1. X-ray diffraction patterns of samples prepared: ✦, vaseline peak; ▼, YSZ peaks; ↓, second phase.