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Eight mole percent yttria stabilized zirconia powders by organic precursor route

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Abstract

An organic precursor-mixing route has been developed for preparation of 8 mol% yttria stabilized zirconia (8YSZ) ceramics. Polymeric salt of succinic acid with yttrium and zirconium has been prepared separately by treating sodium succinate with yttrium chloride and zirconyl chloride followed by washing with water and drying at 120 °C. Thorough mixing of the two salts in stoichiometric proportions by planetary ball milling followed by calcination at 850 °C resulted in a precursor powder containing nanocrystalline (~40 nm) monoclinic zirconia, tetragonal YSZ, cubic YSZ and yttria. Compacts prepared after deagglomeration of powder by planetary ball milling produce 8YSZ ceramics having density 99.3% TD on sintering at 1550 °C for 2 h.

Keywords: C. Ionic conductivity; Solid oxide fuel cell; Yttria stabilized zirconia; Organic precursor

1. Introduction

Eight mole percent yttria stabilized zirconia (YSZ) is well known electrolyte material for electrochemical devices such as oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFC) owing to its satisfactory oxide ion conductivity at high temperature and relatively low cost [1–5]. YSZ is also used for the preparation of Ni-YSZ cermet anode for SOFC [6–9]. The YSZ ceramic material for the electrochemical devices has to be dense and impervious to gases. Wet chemical methods have been used for the preparation of homogeneous fine ceramic powders which are sinterable at low temperature and provide better mechanical strength and functional properties. A number of wet chemical processes [10–19] such as sol–gel, co-precipitation, hydrothermal, spray drying, spray pyrolysis, freeze drying, combustion synthesis, auto-ignition, polymer precursor synthesis and oxalate precipitation route have been reported for the preparation of yttria-doped zirconia powder. However, most of the above reports focus on tetragonal (3–5 mol% yttria stabilized zirconia) phase for structural applications.

Organic precursor technique is an attractive route for synthesis of pure and homogeneous nanocrystalline ceramic powders. In organic precursor route, formation of hard agglomerates during calcinations is expected to be low as the metal atom in the precursor is surrounded by organic moieties. These organic moieties shield the primary oxide particles formed during initial stages of calcination from the neighboring primary oxide particles. Ceramic powder synthesis from polymeric precursors based on dicarboxylic acids would be an attractive method. Further, it is easy to handle the polymeric carboxylate precipitate containing both organic and inorganic part in the same molecules during the processing stage compared to the gelatinous hydroxide precipitates obtained in other co-precipitation techniques. Also, there is scope for tailor making the structure of metal containing polymer. In the present work, preparation of polymeric salts of zirconium and yttrium with succinic acid from their homogeneous solutions and subsequent conversion of the polymeric salts to yttria stabilized zirconia has been attempted.

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2. Experimental

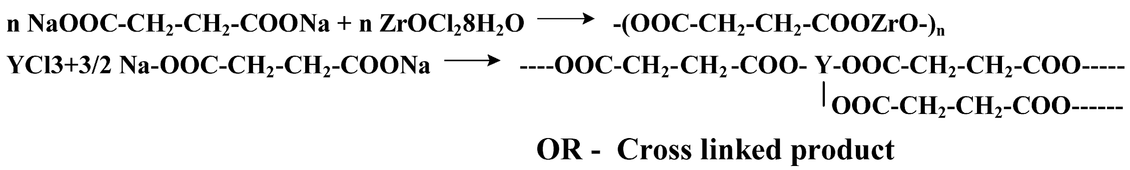
Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, 99.99%) and yttria (Y_2O_3, 99.99%) were procured from Indian Rare Earth Ltd. Sodium succinate (CDH, 99.99%, India) and hydrochloric acid (Merck, India) used were of analytical reagent grade. Deionized water was used for preparation of the solutions. Yttrium chloride solution was prepared by dissolving the yttria powder in hydrochloric acid solution.

Flow chart for the preparation of 8 mol% yttria stabilized zirconia powder is shown in Fig. 1. Aqueous solution containing 0.3 mol/l of sodium succinate was prepared. The solution was heated to 70 °C in a water bath. Polymeric zirconyl succinate and yttrium succinate were prepared separately by drop wise addition of aqueous solution of zirconium oxychloride (0.3 mol/l) and yttrium chloride (0.3 mol/l) into the bath of sodium succinate solution with continuous stirring. The temperature of the bath was maintained at 70 °C throughout the precipitation process. The precipitates were washed several times with deionized water to remove the chloride ions and then filtered and dried the residue at 120 °C. The zirconium and yttrium content in the polymeric zirconyl succinate and yttrium succinate precipitate were determined from thermo gravimetric analysis (Set-Sys 16, France).

For preparation of 8 mol% YSZ, required amount of the polymeric zirconyl succinate and yttrium succinate in stoichiometric proportion were intimately mixed by planetary milling for 10 h in methanol medium using zirconia grinding media. The mixed precipitate was calcined at 850 °C for 2 h for complete burn out of the organics. The calcined powder was further deagglomerated about 30 h by planetary ball milling in methanol medium using zirconia grinding media. Mole percentage of zirconia in the YSZ powder was measured by X-ray fluorescence spectroscopy (Oxford MDX 1000, UK). The surface area of the YSZ powder was measured by BET method (Sorptomatic 1990, Thermo Finnigan, Italy). Crystallite size in the powder particles was measured by Transmission Electron Microscope (Philips USA). X-ray diffraction (Philips-XRD PW 2770 /00, Holland) analysis of the powders calcined at various temperatures has been carried out. Pellets were prepared by pressing the powder at 50 MPa pressure in a hardened steel die. The pellets were sintered at temperature in the range of 1450–1600 °C for 2 h. Heating rate used was 5 °C/min up to 1250 °C and, thereafter, 3 °C/min up to the sintering temperature. Density of the sintered samples was measured using Archimedes principle. Microstructure of the sintered sample was observed on a fractured surface using scanning electron microscope (LEO 1455, UK). Conductivity of the sintered YSZ pellets was measured by ac impedance analyzer (PM 6304, Programmable automatic RCL meter) at a frequency of 1 kHz.

3. Results and discussion

Zirconium oxychloride and yttrium chloride react with sodium succinate to form polymeric zirconyl succinate and yttrium succinate as shown in reaction given below. The yield of the polymeric zirconium succinate and the polymeric yttrium succinate obtained in the present experimental conditions were 98.84% and 96.95%, respectively.



$$n\ NaOOC\text{-}CH_2\text{-}CH_2\text{-}COONa + n\ ZrCl_28H_2O \longrightarrow \text{-}(OOC\text{-}CH_2\text{-}CH_2\text{-}COOZrO\text{-})_n$$

$$YCl3+3/2\ Na\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COONa \longrightarrow \text{----}OOC\text{-}CH_2\text{-}CH_2\text{-}COO\text{-}\ \underset{|\,OOC\text{-}CH_2\text{-}CH_2\text{-}COO\text{------}}{Y}\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COO\text{-----}$$

OR - Cross linked product

Usually co-precipitation of polymeric organic precursors from homogeneous solutions is used for preparation of binary oxides [10–12]. When homogenous solution containing both zirconium and yttrium ions in the molar proportions required for 8 mol% YSZ was added in to a bath of sodium succinate solution there was formation of a white precipitate at 70 °C. The oxide powder obtained by calcination of this precipitate showed the presence of only 3.2 mol% yttrium instead of 8 mol% when estimated using XRF spectroscopy. This indicates that complete conversion of zirconium and yttrium present in the solution in to polymeric zirconyl succinate and polymeric yttrium succinate by co-precipitation is difficult. Therefore, attempts were made to prepare the polymeric zirconyl succinate and yttrium succinate separately followed by mixing them in required proportions by planetary milling for the preparation of 8 mol% yttria stabilized zirconia.

The TGA-DSC plot of the polymeric zirconyl succinate and yttrium succinate is given in Fig. 2a and b. The polymeric zirconyl succinate decomposes in four stages. Weight loss of about 2% observed at temperature below 120 °C is due to loss of absorbed moisture. Weight loss of nearly 18% observed in the temperature range of 120–350 °C is due to decarboxylation reactions. Burn out of the remaining organic moieties was completed at a temperature of 830 °C leaving a residue of 55% zirconia. Exothermic peaks were observed in the TGA-DSC plot corresponding to all decompositions except moisture loss. Exothermic peak observed at 930 °C in the DSC is due to crystallization of zirconia. However, the polymeric yttrium succinate decomposes in three stages and the weight loss of nearly 10% observed up to 200 °C could be due to loss of moisture and decarboxylation. A strong exothermic decomposition observed in the temperature range of 380–490 °C is due to burn out of the organic materials. A weight loss of 46% was observed in this temperature range. Burn out of the organics was complete in the third stage in the

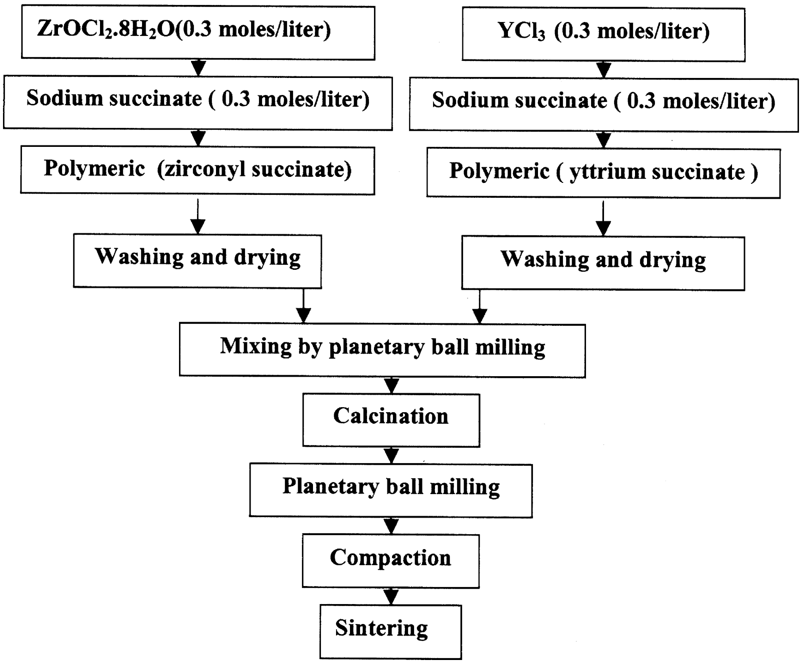


Fig. 1. Flow chart for the preparation of 8 mol% YSZ powder.

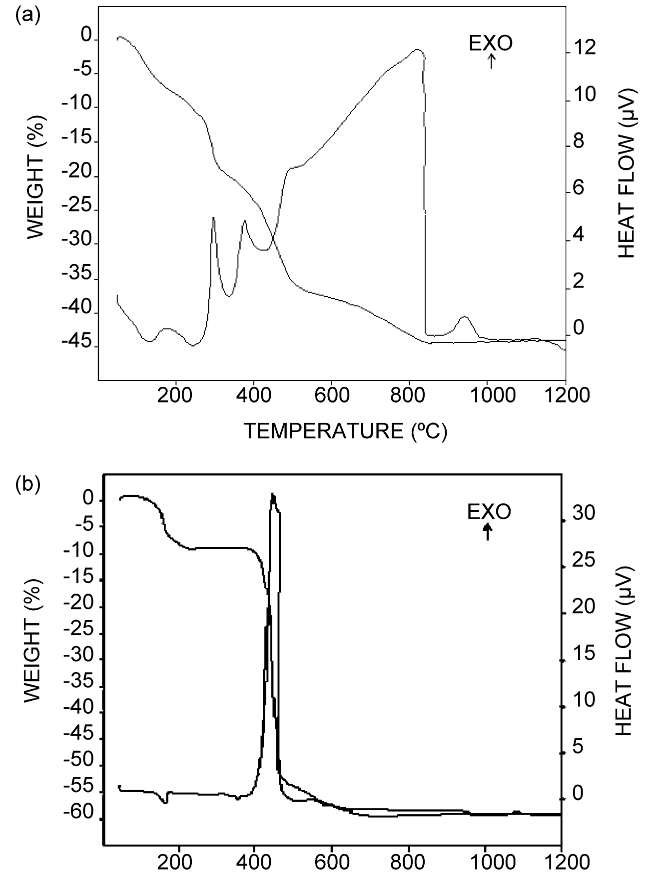


Fig. 2. TGA-DSC plots of the polymeric (a) zirconyl succinate and (b) yttrium succinate.

temperature range of 490–630 °C leaving a residue of 41% yttrium oxide.

The batch calculation of polymeric zirconyl succinate and yttrium succinate for preparation of 8 mol% yttria stabilized zirconia was based on the TGA data. The amount of yttrium in the powder obtained after calcination of the polymeric zirconium succinate and polymeric yttrium succinate mixture was confirmed as 8 mol% by X-ray fluorescence spectroscopy. XRD spectrum of the powder showed peaks corresponding to

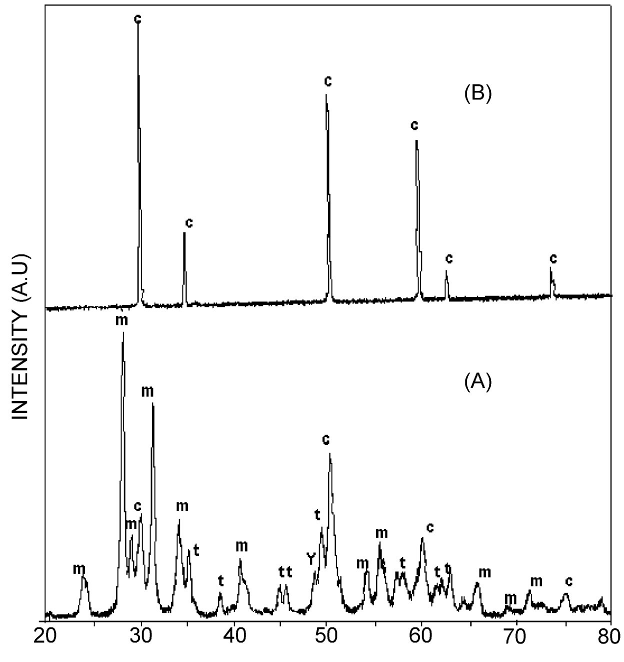


Fig. 3. XRD pattern of the YSZ powder calcined at (A) 850 °C and (B) 1250 °C.

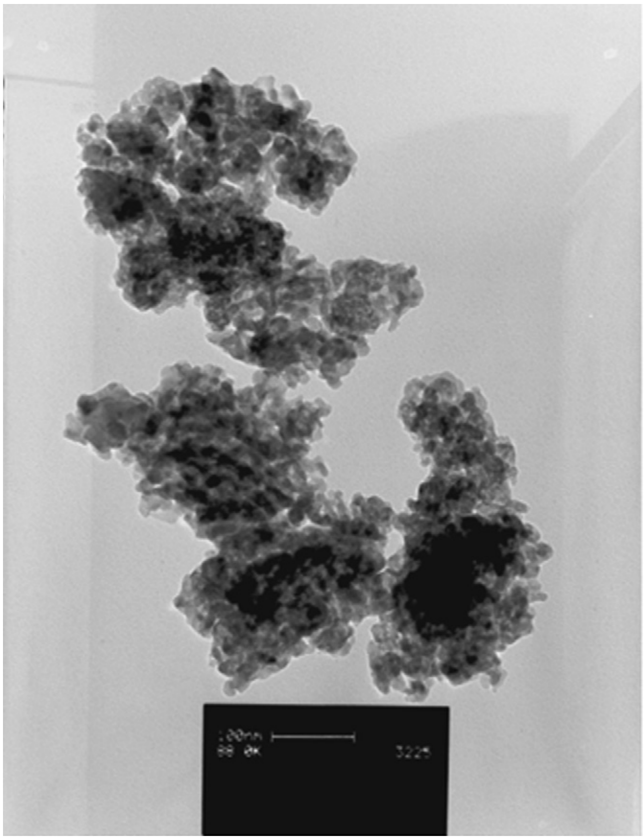


Fig. 4. TEM image of the YSZ powder calcined at 850 °C.

cubic yttria stabilized zirconia, tetragonal yttria stabilized zirconia, monoclinic zirconia and free yttria. This indicates that the whole yttria in the system has not gone in to solid solution during calcination at 850 °C. It has been observed that phase formation of pure cubic yttria stabilized zirconia was formed after calcination of the powder at a minimum temperature of 1250 °C for 2 h which is few hundred degrees celsius lower than the phase formation temperature of the conventional and other non-conventional process. XRD spectrum of the powder calcined at 850 °C and 1250 °C is shown in Fig. 3. The deagglomerated powder showed high surface area of 38.4 m^2/g.

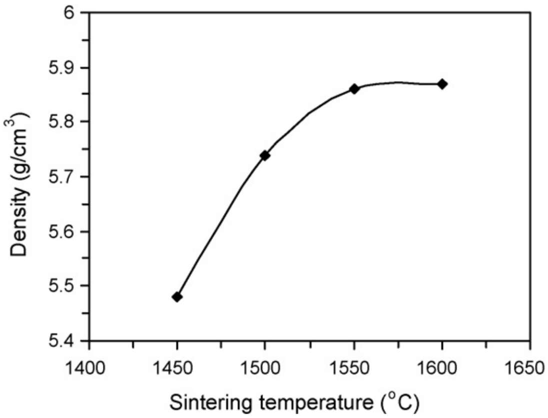


Fig. 5. Density variation with increasing sintering temperature of the YSZ powder compacts.

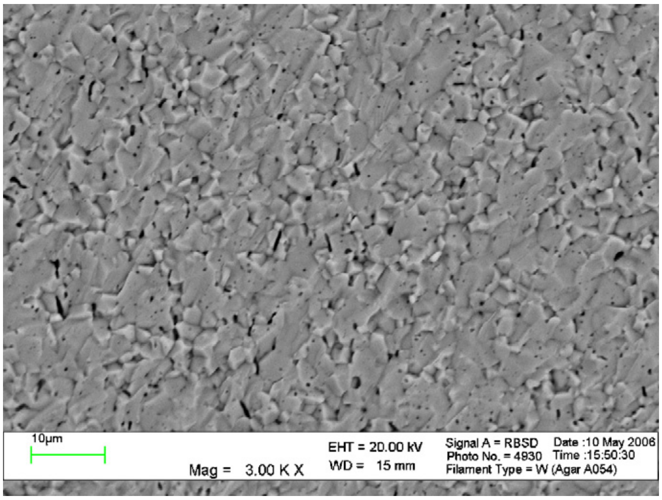


Fig. 6. SEM image of fractured surface of the sintered YSZ ceramic.

The particles are aggregates of nanocrystallites as evidenced from TEM analysis and the average crystallite size observed is 20 nm. (Fig. 4)

It is well known that ceramic powder particles form hard agglomerates and become coarse during calcination at higher temperature. Though phase pure cubic yttria stabilized zirconia is formed at 1250 °C, the powder calcined at 850 °C is used for preparation of sintered ceramics. Fig. 5 shows the variation of sintered density as a function of sintering temperature for the compacts. Density increased with sintering temperature up to 1550 °C and thereafter remains constant. Maximum sintered density of 5. 90 g/cm^3 (99.3%TD) was achieved at 1550 °C. Fig. 6 shows SEM photomicrograph of fractured surface of the sintered YSZ ceramic. The microstructure showed intergranular fracture. Isolated micro pores were observed within the YSZ grains. The conductivity of the sintered YSZ measured was 0.098 S/cm^2 at 1000 °C which is very close to the conductivity of 8YSZ ceramics prepared by different processing routes reported in the literature [1,2].

4. Conclusions

Eight mole percent yttria stabilized zirconia (8YSZ) ceramic has been prepared by an organic precursor mixing route. An intimate mixture of polymeric zirconyl succinate and yttrium succinate in stoichiometric proportion, on calcination at 850 °C, produced a powder containing mixture of nanocrystalline (∼40 nm) monoclinic zirconia, tetragonal YSZ, cubic YSZ and yttria which on sintering at 1550 °C for 2 h gave 8YSZ ceramic with density which is 99.3% of TD. Microstructure of the sintered ceramic showed isolated micro pores within the YSZ grains. The sintered YSZ ceramic showed an ionic conductivity of 0.098 S/cm^2 at 1000 °C at 1 KHz.

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