SOL GEL PROCESS FOR THE PREPARATION OF SOLID ELECTROLYTE MATERIAL

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The reality that fossil fuels are running out is driving the development of fuel cells. These fuel cells offer attractive and alternative energy sources because of high conversion efficiency, low pollution, light weight, and high power density. In this article, status of fuel cells and ceramic fuel cells have been discussed with particular emphasis on stabilized zirconia widely used as solid electrolyte material in solid oxide fuel cells (SOFCs) due to its high oxygen ion conductivity. The study is also focused on low cost process for synthesis of 12mol% yttria stabilized zirconia (12YSZ) powder from the zirconia sol prepared by hydrothermal treatment of zirconium nitrate solution with an aqueous electrolyte extraction by organic extractant. The 12YSZ powder found to be pure white crystalline. 12YSZ calcined powder were sintered at 1200ºC for 1-6 hours durations. Phase, purity, crystallinity and morphology of 12YSZ were examined by differential thermal analysis (DTA), thermogravimetry (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. SEM indicated the size range 0.2 - 5 micron. The results revealed that the product material (pellet) can be sintered into uniformly size fine grained ceramic of > 98% theoretical density around 1200ºC for 6 hours as compared to the pellet sintered for 1 hour at the same temperature.

Keywords: Yittria stablized zirconia, Solid electrolyte, Fuel cell, Solid oxide fuel cells

1. Introduction

In modern era the fuel cells are going to become a common energy source as compared with conventional power generation methods. Fuel cell is a device that electrochemically converts the chemical energy of a fuel and an oxidant to electrical energy. The fuel and oxidant are typically stored outside of the fuel cell and transferred into the fuel cell as the reactants are consumed. In a fuel cell, hydrogen and oxygen are converted into electricity with heat and water as by-products [1-3]. There are 5 major types of fuel cells, differentiated from one another by their electrolyte: Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), (Proton Exchange Membrane Fuel Cells (PEMFC), Molten Carbonate Fuel Cells (MCFC) and Solid Oxide Fuel Cells (SOFCs) [4-6]. While all five fuel cell types are based upon the same underlying electrochemical principles, they all operate at different temperature regimes, incorporate different materials and often differ in terms of their fuel tolerance and performance characteristics, as shown in Table 1. The structure, availability of materials, performance, applications, initial and running costs, advantages and disadvantages of fuel cells have been reviewed in the literature [7-11]. However, solid-oxide fuel cells are found more efficient and less expensive per kilowatt of power in comparison to other fuel cells. The most attractive characteristic of the SOFC is its clean and efficient production of electricity from a variety of fuels [12]. Solid oxide fuel cells have attracted a great deal of interest in recent years as potential sources of electrical energy due to their light weight, high efficiencies and environmental advantages. SOFCs offer several potential advantages over other fuel cell systems because of high operating temperature (1200 to 1830ºF or 650 to 1000ºC) gives flexibility in the choice of fuel, and in particular allows the possibility of running the cell directly on natural gas or other hydrocarbon fuels, internally reforming the fuel within the fuel cell. The SOFC is the ideal device for small-scale application offering tremendous potential for clean and economic production of electrical power as well as higher efficiencies through improved heat utilization [13].

SOFC is a ceramic device that converts the chemical energy of a fuel gas and an oxidant gas directly to electrical energy without combustion as an intermediate step. A SOFC is made up of four layers, three of which are ceramic i.e., an oxide electrolyte sandwiched between an anode and a cathode. Fuel is fed to the anode, undergoes an oxidation reaction, and releases electrons to the external circuit. Oxidant is fed to the cathode,

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Table 1.   Characteristics of fuel cells.

Constituents and Conditions	Types of Fuel Cell			
	Polymer Electrolyte Membrane (PEM)	Phosphoric Acid	Molten Carbonate	Solid Oxide
Electrolyte	Ion Exchange Membrane	Phosphoric Acid	Alkali Carbonates Mixture	Yttria Stabilized Zirconia
Operating Temp. °C	80	200	650	1,000
Charge Carrier	H^+	H^+	CO_3^{2-}	O^{2-}
Electrolyte State	Solid	Immobilized Liquid	Immobilized Liquid	Solid
Cell Hardware	Carbon or Metal Based	Graphite Based	Stainless Steel	Ceramic
Catalyst	Platinum	Platinum	Nickel	Perovskites
Cogeneration Heat	None	Low Quality	High	High
% Fuel Cell Efficiency	<40	40-45	50-60	50-60

accepts electrons from the external circuit, and undergoes a reduction reaction. The electrons flow from the anode to the cathode produce direct-current electricity, as shown in Figure 1 [1]. The solid electrolyte conducts ions between the two electrodes. Under typical operation conditions (with hydrogen fuel and oxygen oxidant), a single cell produces less than 1 volt. Thus, practical SOFCs are not operated as single units; rather they are connected in electrical series to build voltage. A series of cells is referred to as a stack. A component, variously called an interconnect or bipolar separator, connect the anode of one cell to the cathode of the next in a stack, as shown in Figure 2 [4]. SOFC stack can be configured in series, parallel, and both series and parallel or as single cell depending on the particular application. The type of materials and structure of components of SOFCs depend essentially on the fuel cell operating conditions, mainly the temperature and the physical state of the reactant, the fuel and the oxidants. Most often solid electrolyte is made from yttria stabilized zirconia (YSZ), i.e. ZrO_2 doped with a sufficient amount of Y_2O_3 to stabilize it in a cubic crystalline structure which gives the highest oxygen conductivity.

Zirconia (ZrO_2) is a white crystalline insoluble fine ceramic oxide. The most important zirconium mineral from which the oxide and other zirconium compounds are produced is zircon (ZrO_2-SiO_2), found in beach sands in Australia, India, and the United States. Another source of zirconia is the impure oxide of zirconium called baddeleyite or brazilite. This mineral, occurring principally in Brazil, contains from 70 to 90% ZrO_2. The chief impurities are silica, iron oxide, titanium oxide, and alumina. The chemically purified compound is about 99% ZrO_2. The crystal form of baddeleyite (natural zirconium oxide), which is monoclinic, is stable at normal temperatures and this stability is maintained upto about 1000°C. At higher temperatures, the stable crystalline form is tetragonal. When pure zirconia is heated to temperatures above 1000°C and recooled, it not only undergoes large volume changes with temperature but also may not even return to its original dimensions. Pure zirconia under standard conditions forms monoclinic phase (m-ZrO_2). With increasing temperature [14-15] it transforms respectively to the tetragonal (t-ZrO_2) and then cubic and with increasing pressure to ortho-rhombic polymorphs [16] .The phase behaviour of monoclinic zirconia has been described in literature [4,16]. Phases for pure zirconia may differ from one another, however, depending upon the crystalline form of starting material; six different forms of ZrO_2 have been described in the literature [17-24]. Work of the National Bureau of Standards
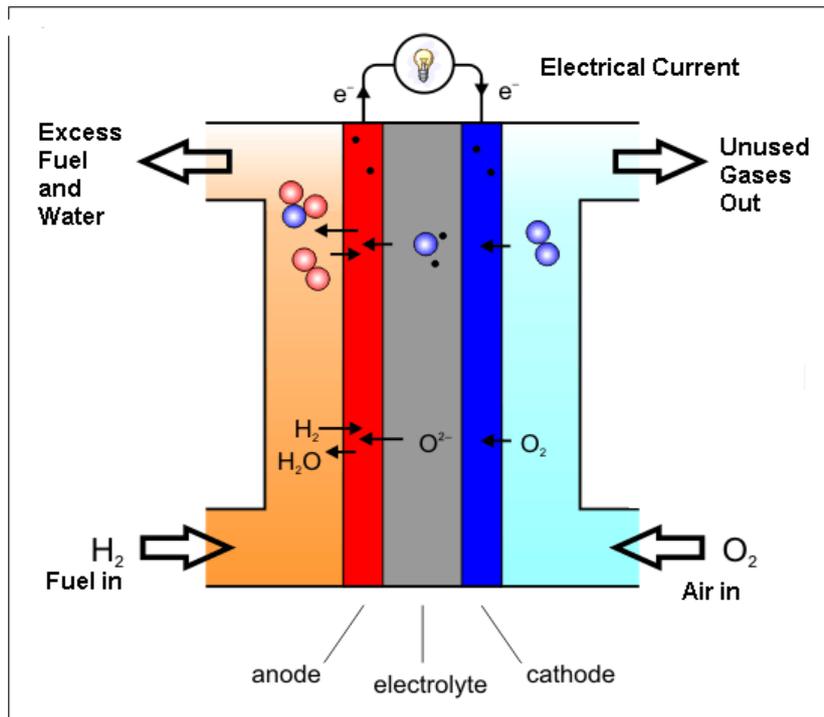
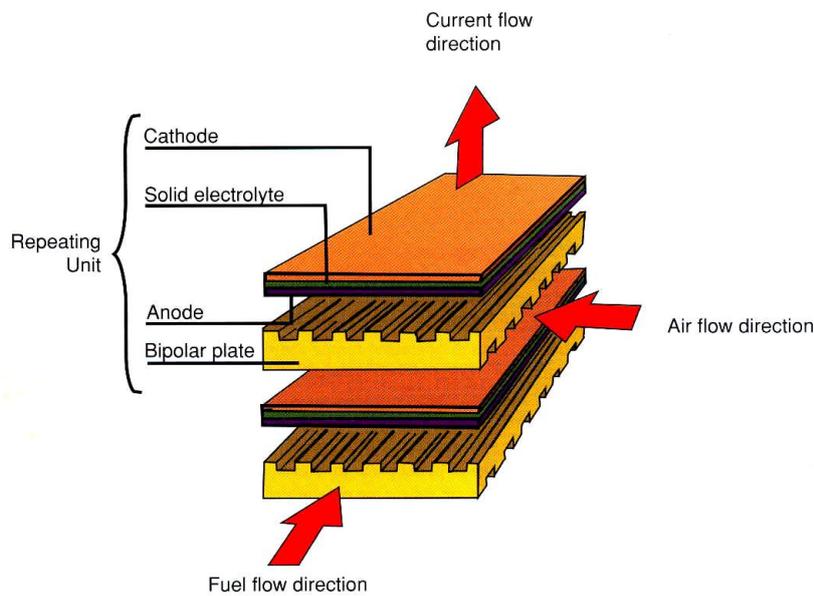Figure. 1. Schematic diagram of solid oxide fuel cell operation [3,5].

Figure 2.   SOFC cell stack of bipolar flat plate [4].

[15-16] has shown that a cubic solid solution, rich in zirconia, can be formed by firing the oxide with certain other refractory oxides, and that, in some cases, this cubic form is stable at high temperatures. The formation of a stable cubic form was accomplished most effectively by the addition of (a) 11.5 and 15 % of Y_2O_3 and heating at 1700°C or higher; (b) 8 and 15 % of MgO and heating at 1500°C or higher; and (c) 5, 6, 8, and 15 % of CaO and heating at 1550°C or higher respectively. Addition of CaO is most widely used commercially, not only because CaO is cheap but also because the cubic form remains stable at all temperatures whereas the MgO stabilized form may revert to the monoclinic structure at low temperature. Completely

stabilized zirconia (cubic fluorite form) has high but uniform thermal expansion. The partially stabilized product, on the other hand, has only moderately high thermal expansion, but this expansion is not uniform since it is counteracted at high temperatures by the contraction of monoclinic material. Zirconia is superior in strength, toughness, ion conductivity, and chemical durability, etc., and it is one of the oxides, which has attracted attention as raw materials for ceramics. Zirconia in its pure form is chemically inert but is a poor ceramic because of a mechanically damaging phase transformation that occurs in its crystal structure when it is cooled after firing. The polymorphic stability of zirconia over a broad temperature range is very important. It is well known that during a heating process, zirconia will undergo a phase transformation process. Zirconia shows three polymorph phases with increasing temperature e.g., monoclinic upto ~1170°C, tetragonal upto ~ 2370°C and cubic symmetry upto the melting temperature, at ~2706°C under atmospheric pressure. These transformations process in three stages.

$$\text{Monoclinic} \xrightarrow{900-1000\,^{o}C} \text{Tetragonal} \xrightarrow{2370\,^{o}C}$$

$$\text{Cubic} \longrightarrow \text{Liquid}$$
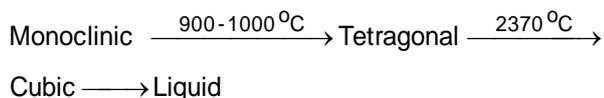
The crystal structure of ZrO_2 is cubic at high temperatures, transforming to tetragonal at intermediate temperatures and to monoclinic crystal form at lower temperatures, while cooling through a temperature of about 1150°C. At lower temperature, this phase transformation is accompanied by an expansion in volume of 3-4%, similar to the volume increase that occurs when water freezes. The change in volume associated with this transformation makes the usage of pure zirconia in many applications impossible. Addition of some oxides such as, CaO, MgO and Y_2O_3 into the zirconia structure in a certain degree results in a solid solution, which is a cubic form and has no phase transformation during heating and cooling. This solid solution material is termed as stabilized zirconia, a valuable refractory. Stabilized zirconia is used as solid electrolyte in solid oxide fuel cells due to its high oxygen ion conductivity [21-25]. The function of oxide electrolyte is to conduct oxygen ions between anode and cathode. The electrolyte carries the ions produced at one electrode to the other electrode to balance the charge from the electron flow and completed the electrical circuit in the SOFC [26-27]. Some other ZrO_2-M_2O_3 systems

(where M is ytterbium, scandium, neodymium, samarium or gadolinium) have also shown stabilized solid solutions in a certain M_2O_3 range [28-29]. The minimum amount of M_2O_3 necessary to stabilized ZrO_2 in cubic structures is close to the composition which gives the highest conductivity (approximately 8 mol% for Yb_2O_3, 10 mol% for Sc_2O_3, 15 mol% for Nd_2O_3, 10 mol% for Sm_2O_3, and 10 mol% for Gd_2O_3 [30-31].

The aim of the present work is to look at some basic structure of fuel cell, solid oxide fuel cell and also the most economical sol-gel emulsion and hydrothermal processes for the synthesis of 12mol% yttria stabilized zirconia ultra fine powder.

2.   Experimental

Zirconium nitrate (B.D.H.), Yttrium nitrate 99% (Fluka), Ethylene diamine tetra acetic acid (EDTA) disodium salt (B.D.H.), ammonia and nitric acid used were of A.R. quality. Sodium hydroxide used was extra pure. Denitration of zirconium nitrate was performed using amberlite LA-2 (Fluka). Demineralized water (DMW) was used for preparing solutions. Zirconium nitrate was dissolved in DMW and the solution was precipitated with ammonia solution to hydrolyze zirconium. The precipitate was washed, dried and dissolved in minimum quantity of nitric acid to get zirconium solution. Zirconia sol was prepared by autoclaving the zirconium solution free of acid at 180-225°C for 15 minutes to five hours. The calculated amount of yttrium nitrate was added to the zirconia sol according to its volume in order to get 12mol % yttria stabilized zirconia, which was milky-white sol.

2.1.   Preparation of 12 mol%Y_2O_3 stabilized ZrO_2 powder

Yttria stabilized zirconia (YSZ) powder was prepared by dehydration of aqueous sol of 12mol% yttria doped zirconia using dehydrating agent along with small quantity of surfactant as described else where [32]. The powder was allowed to remain in hot column for 30 minutes and then dried in air overnight at 110°C. The powder was calcined at 600°C for 1 hour. Synthesized powder was characterized using different analytical techniques such as differential thermal analysis (DTA), thermogravimetric (TG), and X-ray diffraction (XRD).

2.2.   Sintering

Yttria stabilized zirconia calcined powder was mixed with 2wt.% polyvinyl alcohol as binder material. The pellets were made using uni-axial

Table 2. Effect of different time duration on sintering density of 12 mol% yttria stabilized zirconia pellet.

Sr. No.	Pelletization load (MPa)	Duration (Hours)	Green density (gm.cm^{-3})	Sintered density (gm.cm^{-3})	Theoretical density (%)
YSZ1	170.9	1	2.6	5.22	94.41
YSZ2	154.5	4	2.58	5.23	95.52
YSZ3	185.5	6	2.82	5.45	98.52
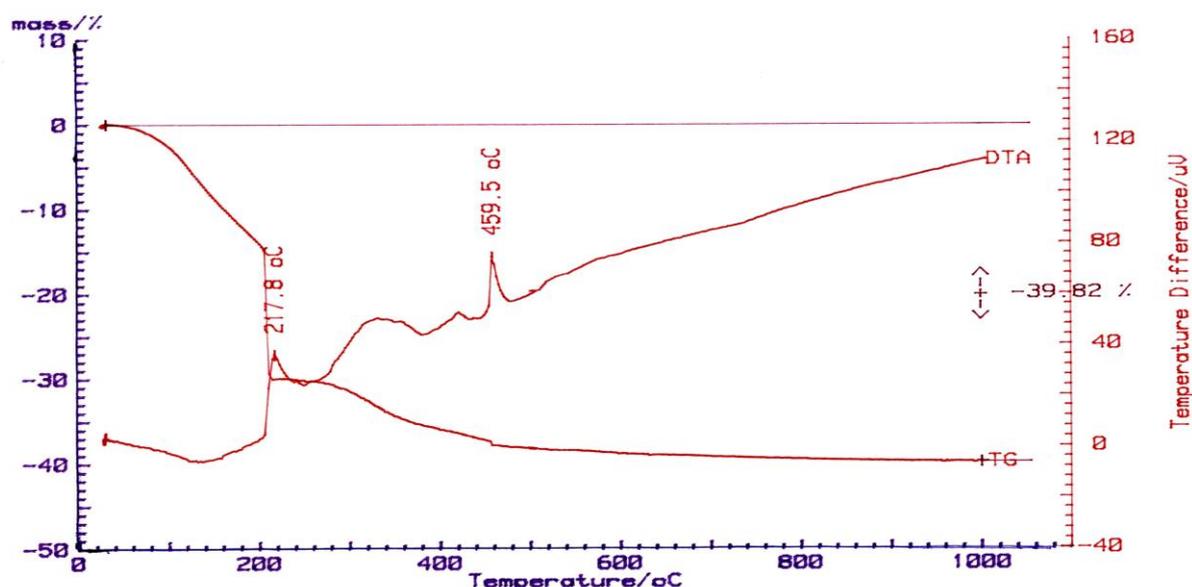
Figure 3: TG/DTA curves for dried powder of 12mol% Y_2O_3 -stabilized zirconia.

hydraulic press of load capacity 14 tons. The binder was removed by heating the pellets at 400°C for 4 hours. The heating rate was kept low to avoid cracking of the pellets. The pellets were sintered at 1200°C for different time durations. Morphology of the sintered material was measured by scanning electron microscopy (SEM). Samples were mounted in a brass support and coated with a thin layer of evaporated gold. The chemical analysis was performed by wet chemical methods and inductively coupled plasma (ICP) emission techniques.

3.   Results and Discussion

Fuel cells are energy converters, not a new energy sources. They will be part of a sustainable energy solution only if they can compete with other conversion technologies. This includes system parameters, fuels and applications. We need fuel cells for available fuels. Natural gas and oil-derived liquid hydrocarbons will be around for many years. However, their use will be restricted by costs, environmental concerns or even political reasons. Sustainable hydrocarbons like bio-methane, bio-ethanol and bio-methanol from organic waste, wood or farming are already replacing fuels of fossil origin. Hydrocarbon fuels will be more important forever and fuel cells will be capable of directly converting these fuels into electricity. Currently, the greatest disadvantage of fuel cell technology is the cost. Additional problems include operational temperature compatibility concerns, susceptibility to environmental poisons, and durability under start/stop cycling. Solid oxide fuel cell technology is under development for a broad range of power generation applications. One advantage of solid oxide fuel cell compared with other type of fuel cells is the flexibility of fuel choices. Natural gas which constitutes mainly methane is an interesting fuel because of the already available infrastructure to produce, store and transport in contrast to pure hydrogen.

Recently, worldwide interest in the development of commercially viable SOFCs R&D work is going on now in the direction of lower-temperature SOFC (600ºC) in order to decrease the material degradation and facilitate the use of low cost metallic components which will enable the use of metallic materials with better mechanical properties and thermal conductivity [33].

12 mol% yttria doped zircon ceramic powder was obtained from the hydrothermal treatment of zirconia sol and sol-gel hexanol emulsion technique. The product material was found pure white and crystalline. Traditionally, the ultrafine yttria or calcia stabilized zirconia has been used as solid electrolyte material for SOFCs. It is observed that the sol-gel emulsion route is most suitable for preparation of pure, stoichiometric, dense, equiaxed and mondispersed particles of 12YSZ. These oxide materials can also be prepared through sol-gel combustion, spray pyrolysis and hydrothermal techniques [34-36]. The synthesized powder was sintered at 1200ºC for different time durations. Results in Table 2 reflect increase in sintered density with the increase of sintering duration and also pelletization load (Mpa). The 98%, theoretical density was achieved when the pellet was sintered for 6 hour at 1200ºC as compared to the pellet sintered for 1 hour at same

temperature. The sintering time and temperature was found to be very important related to the microstructure and properties.

Thermal techniques (TG/DTA) are being used to provide complementary information on the dehydration and decomposition process of various guest molecules that interact with the intermediate phases obtained during transformation of amorphous and gels into crystalline materials. Figure 3 shows TG/DTA curves for dried powder of 12YSZ ceramic powder. Exothermic peaks at 217.8 and 459.5 ºC were found with total weight loss 39.82% upto 800 ºC and no other thermal effects were observed above the 800 ºC The exothermic peak at 460ºC may be due to crystalline nature of zirconia. Figure 4 shows scanning electron micrograph of 12YSZ pellet sintered at 1200ºC for 6 hours. Good uniformity in crystallite size is apparent. The particles are long and semispherical with size in range 0.2-5 micron. There are many aspects, such as composition, impurity, particle size and specific surface area must be taken into account, when one chooses a right zirconia or stabilized zirconia for his specific applications. Understanding of preparation processes, physical properties and phase transformation of zirconia and stabilized zirconia will definitely be advantageous for the users. This
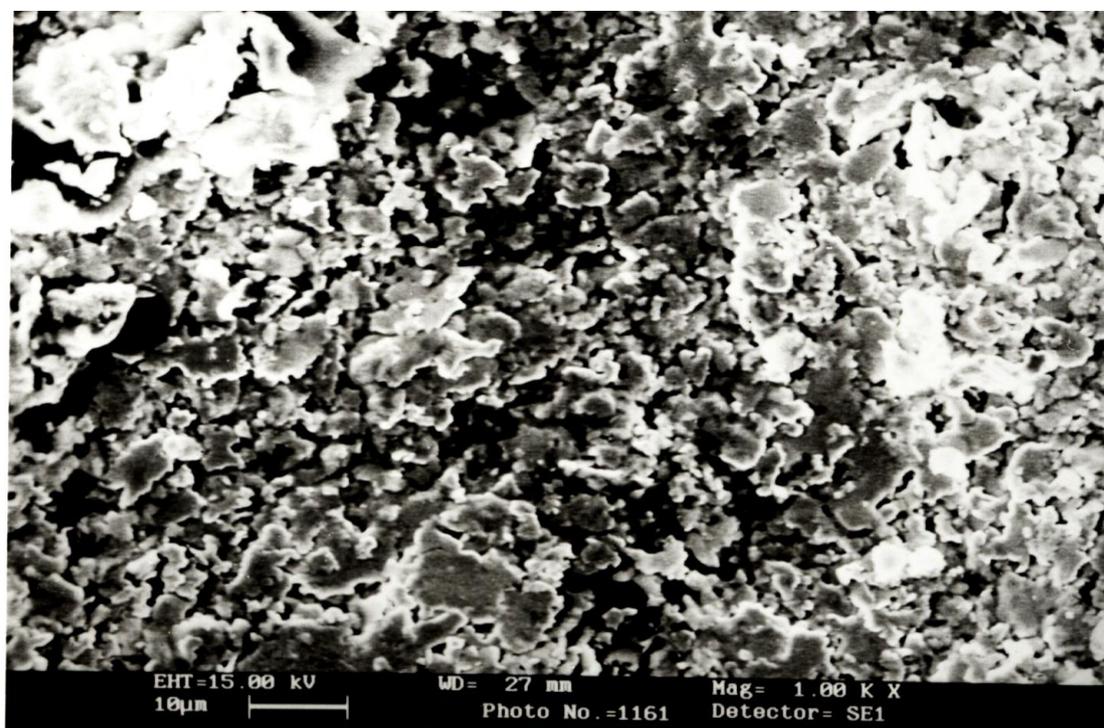

Figure 4.   Scanning electron micrograph of 12mol% Y_2O_3 -stabilized zirconia ceramic powder calcined at 600 ºC for 6 hours.

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article briefly discuss these aspects and gives reader some basic understanding of fuel cells, SOFCs, solid electrolyte, zirconia and yttria stabilized zirconia. The physico-chemical characteristics, structural and textural properties of 12YSZ powder i.e., phase analysis, micro-structure, surface area, porosity, particle size and particle size distribution measurements are in development stages and will be accessible in the next issue.

3. Conclusions

- Some basic features of fuel cell, components of SOFCs, and preparation of solid electrolyte e.g., yttria stabilized zirconia used in SOFC have been discussed.

- Sol-gel and hydrothermal treatment of zirconium salts and dehydration with organic aqueous extractant produce fine dense and agglomerates free 12YSZ powder.

- The product material is sintered into uniformly size fine grained ceramics of > 98% theoretical density around 1200°C .

- Sol-gel process has advantages like good homogeneity, ease of compositional control, low temperature processing and versatile shaping over other techniques.

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