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Nano Crystalline Thin-Film Electrolyte For Solid Oxide Fuel Cell Application: A Brief Review

Sandhya.k
Chithra Priya N.S.
Dr. Deepthi. N. Rajendran
Department of Physics, Govt. College for Women, TVPM, Kerala, India

Shabeer T. K
Department of Electronics, Malabar College of advanced studies, Vengara, Kerala

***Abstract:** The growing energy needs of modern world demand more advancement in the efficiency of energy systems. Solid oxide fuel cells (SOFC) play a major role in the clean energy technology due to its high efficiency, fuel flexibility and low pollution. Electrolyte is one of the key components of SOFC. CeO_2 -based solid electrolytes, which have high oxygen ion transport, are one of the main candidates as electrolyte for SOFC. Nano structured CeO_2 -based solid electrolytes have enhanced physical and electrical properties which help to improve the performance of the SOFC. Several research groups are working in the field to improve the properties of solid electrolytes. Thin film technology is also utilized to improve the performance of SOFC. This paper reviews thin film deposition techniques and current research on nanocrystalline thin film electrolyte.*

***Keywords:** Solid Oxide Fuel Cell, Electrolyte IT-SOFC.*

I. INTRODUCTION

Fuel cell is an electrochemical device which converts chemical energy of a fuel gas directly into electrical energy with high efficiency. Fuel cells are classified according to the nature of the electrolyte used, geometry of the construction and temperature of operation [1]. Among the different types of fuel cells, SOFC attracted great attention since it is a solid state device and operates at elevated temperature [2].

Solid Oxide Fuel cell is characterized by having a solid ceramic electrolyte which is usually a metallic oxide, hence the name ceramic fuel cell. SOFCs are built up with three solid elements an anode, an electrolyte and a cathode [3]. The relatively high operating temperature of SOFC allow for highly efficient conversion to power internal reforming and high quality by heat for cogeneration. But the high temperature of operation limits the selection of materials, degrades its performance and increase the cost for production. So there is a need for lowering the operating temperature down to 500-600^{0}c. However at lower temperatures, electronic conductivity and electrode kinetics decreases significiantly. The performance losses associated with a low operating temperature can be compensated by developing thin film electrolyte with lower ohmic resistance[4].

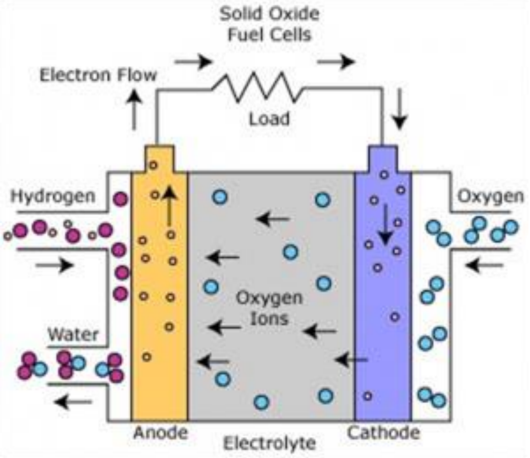

Figure 1: Schematic diagram of solid oxide fuel cell (SOFC)

II. THIN FILM DEPOSITION TECHNIQUES

At present, thin films are found numerous applications such as in portable electronic devices like, laptops, personal digital assistants (PDAs) and scanners [5]. The size of the electrolyte produced by powder processing or by thick film techniques, such as tape-casting is in the range 10-200 µm thick [6]. Thin film method are favorable to decrease SOFC operating temperatures from 1000 ◦C to about 500 ◦C and to reduce the costs of the system. Thin film technology offers following advantages : (i) the decreased film thickness, being 100 to 1000 nm, lowers the ohmic losses across the fuel cell, (ii) the processing allows sintering temperatures below 1000 ◦C or even no sintering at all and (iii) the possibility exists to manipulate the electrical conductivity by controlling the nanocrystalline microstructure of a thin film[7]. Nano crystalline oxides material exhibit unusual electrical conductivities and thermal stabilities due to their high amount of grain boundaries with respect to grain area. The choice of an appropriate thin film deposition technique is strongly influenced by the material to be deposited and the desired film quality and available budget. Research is being carried out to develop thin film electrolytes in order to lower the ohmic resistance losses in the electrolyte and thereby lower the operation temperature of the SOFC[8].Various thin film deposition techniques such as Physical vapor deposition (PVD),Chemical vapor deposition (CVD) and Spray deposition methods is being studied as a potential way to address these issues. PVD techniques have the common feature that atoms are brought to the gas phase through a physical process from a solid or molten target [9]. CVD is a chemical process in which one or more gaseous precursors form a solid material by means of an activation process. The advantages of the CVD technique consist of producing uniform, pure, reproducible and adherent films at low or high rates. It is useful in the deposition of coating in sites difficult to reach by other deposition techniques [10]. PLD is a physical method of thin film deposition in which a pulsed laser beam, usually of wavelength in the UV range, is employed to the target composed of the desired thin film material, which is subsequently deposited onto a substrate. PLD has attracted much attention over the last 20 years, as it enables fabrication of multi-component stoichiometric films from a single target[11]. Spray Pyrolysis is a method which involve the generation of fine aerosol of a liquid precursor solution, which is then directed towards a heated substrate surface with or without the aid of an external electric field. Depending on the substrate temperature and precursor used, the droplets evaporate or decompose completely before reaching the substrate, resulting in a process resembling to CVD or the liquid is deposited without evaporation. The different spray techniques are mainly distinguished by the method of atomization, which can be accomplished by means of pressurized gas or application of a high electric field to the solution surface at the spray nozzle. In Pressurized gas spray deposition (PSD), atomization of the precursor is achieved by a pressurized carrier gas, e.g. air. The spin- and dip-coating processes are widely utilized to produce thin ceramic coatings on a variety of substrate materials [12]. Thin film deposition with spin-coating consists of applying a precursor solution on one side of a rapidly rotating substrate whereas during the dip-coating process the substrate is partly or fully immersed in the precursor solution with both sides and then withdrawn from the liquid[13].

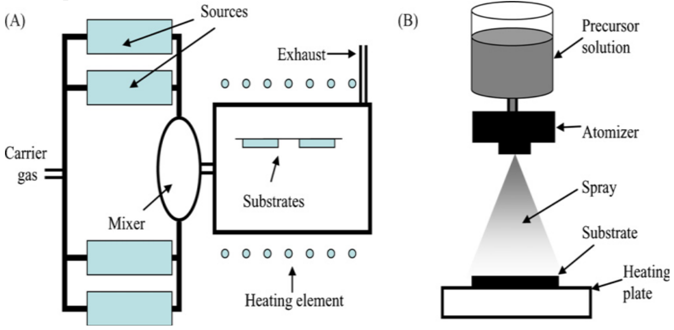

Figure 2: A. Schematic diagram of a generic CVD Reactor. (B). Schematic diagram of Generic Spray Process

III. THIN FILM ELECTROLYTES

A. YTTRIA STABILIZED ZIRCONIA (YSZ)

An electrolyte is the heart of a SOFC unit. Various electrolyte materials are used to study the microstructure and electrical conductivity characteristics of SOFC thin film electrolyte materials [14]. Among them, YSZ is most often used due to their unique combination properties such as high chemical and thermal stability and pure ionic conductivity up to 1000 ˚C.One problem associated with lowering the temperature is the increase of the YSZ electrolyte resistivity. This can be overcome by lowering the electrolyte resistance either by decreasing the electrolyte thickness or with alternative materials of higher ionic conductivity at lower temperatures. SOFCs based on thin electrolytes have already been tested and exhibited excellent electrochemical performances [15]. Zirconia has high dielectric constant which is the reason for being used as gate dielectric in metal oxide semiconducting field effect transistors (MOSFETs) instead of SiO_2.Thick and thin films of zirconia has a wide range of application such as overcoats for thin film media of magnetic recording discs and buffer layers in processing of high-temperature (HTP) superconducting thin film devices[16].YSZ thin films are produced by a wide variety of methods such as (i) plasma spraying; (ii) RF-magnetron sputtering and ion beam assisted deposition[17]; (iii) pulsed laser deposition[18]; (iv) sol_ gel techniques[19]; (v) electrochemical deposition[20], ; and (vi) chemical vapor deposition (CVD)[21] . CVD has been widely used for fabricating microelectronics. YSZ thin films were prepared by doping Y_2O_3 in the zirconia lattice using different deposition techniques such as Chemical Vapour Deposition(CVD), Pressurized gas spray deposition (PSD), Pulsed Laser Deposition (PLD), Physical vapor deposition (PVD) techniques, Spin and dip Coating[23]. The electrical and microstructural properties of YSZ thin film prepared were investigated. There is a variation in the activation energy of electrical conductivity between 0.9 eV and 1.3 eV for YSZ thin films depending on the level of doping and the microstructure [24]. The electrical properties of YSZ thin film with a constant film thickness and a constant average grain size deposited by CVD technique on different substrates was studied. Electrical properties were affected due to the mismatch of thermal coefficient between the substrate and the YSZ thin film. Electrical properties mainly depend on the amount of stress present in a thin film [25]. In otherwords, the lowest activation energy of 0.9eV was measured for the thin film having largest compressive stress, and the highest activation energy of 1.3 eV was measured for the thin film with the lowest compressive stress [26]. Difference in thin film quality was observed in YSZ thin film electrolytes produced by different deposition techniques. YSZ film produced by PLD and CVD results in columnar thin films, whereas spin coating and PSD results in non-columnar microstructures [27].YSZ electrolyte shows 3.5 times lower conductivity than the microcrystalline samples such as scandia-stabilized zirconia (SSZ), CGO, LSGM or bismuth vanadium copper oxide (BIMEVOX) [28]. The lower conductivity for SOFC operation is compensated by a low ohmic resistance of thinner electrolyte. But there is a less-than-linear relationship between electrolyte thickness and electrolyte resistance in an SOFC. The resistance of thin film electrolytes is expected to be lower due to geometrical reasons. Therefore excessive thinning of the electrolyte has a low impact on the electrolyte resistance.

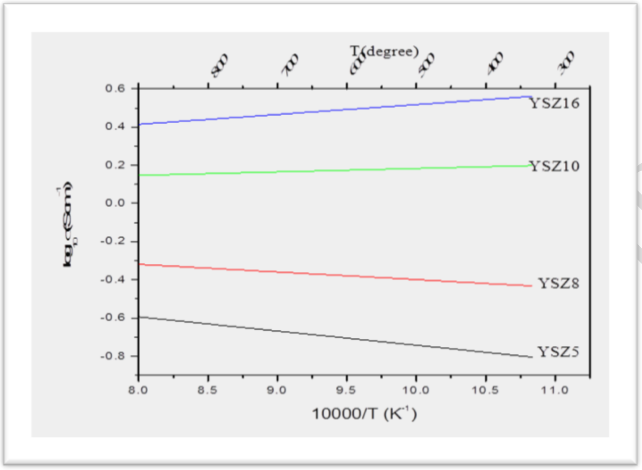

Figure 3: Ionic Conductivity of different percentage of Yttria stabilized zirconia at 700^{0}c

B. CERIA GADOLINIA OXIDE (CGO*)*

Among the highly conductive electrolytes, Gadolinium doped ceria oxide (CGO) became more popular due to its high mechanical strength and good thermal stability. CGO is a so called "mixed ionic-electronic conductor" with ionic and electronic conductivity at low oxygen partial pressures and temperatures higher than 800°C. It is, therefore, mainly used for intermediate- to low-temperature SOFC operation where ionic conductivity prevails [29].Gadolinium doped ceria oxide (CGO) thin films was deposited by PLD, spin-coating and PSD. Effect of different thin film preparation methods and different substrates and the corresponding microstrain within the CGO (or YSZ) thin films was studied. It was observed that the total conductivity of CGO at 700^{0}C varies for both high and low micro strain and found to be 5-1.25 times smaller than the ionic conductivity of microcrystalline CGO [29]. The activation energy of total conductivity found to be 0.95-1.05 eV for CGO film deposited onto different substrate such as Polycrystalline Al_2O_3 and Quartz by PVD techniques [30]. CGO film deposited onto a sapphire substrate by PSD with a film thickness 200-400 nm. It was found that the activation energy of ionic conductivity increased from 0.68 eV to 0.93 eV for a microstrain decrease of 2.09% to 0.32%. CGO film deposited onto a sapphire substrate by spin coating reported that the activation energy increased from 1 eV to 1.3 eV for a microstrain decrease from 1.5% to 0.02% [31]. CGO thin film deposited on different substrate using different thin film deposition methods leads to different initial stresses and the corresponding microstrain will be different. The electrolyte thickness has to be carefully chosen due to their mixed ionic electronic conductivity in CGO. If the electrolyte is too thin, the electronic conductivity will prevail and depress the cell performance [32].

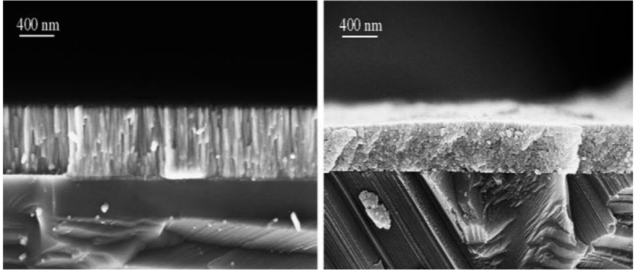

Figure 4: Cross- section micrographs of (A) CGO deposited by PLD showing columnar microstructure and (B) CGO deposited by PSD with isotropic microstructure

IV. CONCLUSION

Several factors such as process complexity, choice of materials, large area coating, equipments and process costs has to be taken into consideration in the industrial fabrication of thin film. SOFC performance can be improved by exploring new approaches (such as nanotechnology) for the development of electrolyte for LTSOFC. Synthesis of nanomaterials and nanostructures are the essential aspects of nanotechnology. Studies on physical properties and applications of new nanomaterials are possible only when materials are made available with desired size, morphology, crystal structure and chemical composition. The change of the electrical properties with the microstructure (i.e. ratio of grain: grain boundary area) and microstrain for thin film electrolyte is to be observed. The nanocrystalline thin film electrolytes conductivity with respect to microcrystalline samples and the resistance of thin film electrolytes is to be studied. Thus the development of any new material will have good application potential if it can be deposited in thin film form with the same properties are foreseen for the future.

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