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Subcontract No: DE-FG26-03NT41915**U.S-DOE-I [National Energy Technology Laboratory](#)****Title of the Project****Dense Membranes for Anode Supported all Perovskite IT-SOFCs**

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Abstract:

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Dense Membranes for Anode Supported all Perovskite IT-SOFCs

Innovative wet chemical synthetic techniques were employed to obtain highly ionic conducting dense perovskites, mixed conducting porous perovskites, and electronically conducting perovskite membranes to be as electrolyte, cathode, anode, and interconnect for assembling all perovskite IT-SOFC system. Processing conditions were optimized to obtain well sintered LSM, LSF, LSCF, LNF, and LCF for SOFC cell and stacks working at 600-800 °C. Series of nanocrystalline bulk and thin films of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$, $\text{LaSr}_{0.2}\text{Fe}_{0.8}\text{O}_3$, $\text{LaSr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$, $\text{La}_{0.8}\text{Ni}_{0.7}\text{Fe}_{0.3}\text{O}_3$, $\text{LaCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ were prepared at very low temperatures and characterized using XRD, SEM, HRTEM, XPS, EXAFS, and EIS techniques. The influence of preparation techniques on the microstructure, grain-size and consequently on the electrical transport properties were investigated. Processing conditions, sintering temperature (1200-1500°C) and time severely affected the grain size (< 0.1 µm to 10 µm) and the resistance in all grain-boundary (3 kΩ to 175 kΩ). Through investigations of A and B site doping in perovskite materials, we have reduced cathode-electrolyte interfacial resistance, will be very effective for the SOFCs operating $\approx 750^\circ\text{C}$.

Epitaxial films of LiFeNiO_3 , for SOFCs cathode were deposited on LaAl_2O_3 , MgO, and YSZ single crystals by pulsed laser deposition (PLD) method, and characterized using advanced spectroelectrochemical techniques. The film orientations depend on the substrate planes. Surface morphology of the films also depends on the substrate orientations. These films showed different electrode properties depending on the orientations.

The porous characteristic of the electrode materials are achieved by the combination of combustion and microwave sintering using SiC as susceptor (1200-1400 °C). Concurrently, the other oxygen ionic/protonic conducting oxides (perovskites, pyrochlores, and apatites) were also prepared, characterized and understood the role in the development of reduced temperature SOFCs.

In this HBCU/MI –research and educational project, we have emphasized the need to expand research opportunities for talented undergraduate and graduate African American students and junior faculty in the field of power sources based on nanoscience. We have paired the selected three undergraduate and two graduate students with full time research staff (PDF), for experimental measurements and discussions via preparing students to present the work in regional, national and international conferences. These students on an average made one presentation per year out side the SUBR campus. The effort in this project yielded 7 publications in refereed journals and about 15 in conference proceedings including NETL annual review meetings. Further, we have initiated a collaborative research and educational outreach project entitled “Center for Hydrogen Energy and Advanced Power [CHEAP]” with University of West Indies-St. Augustine, Trinidad & Tobago (T &T).

Executive Summary

The U.S–DOD –NETL has provided \$188,000 to Southern University A&M College (SUBR), over the three year period to train selected African American undergraduate, and graduate students for developing dense perovskite membranes to be used as components in the fabrication of all perovskite anode supported IT-SOFC. Innovative wet chemical and thin film deposition techniques were used to fabricate the different cell components, such as dense electrolyte, porous cathode, anode and interconnect in this project. The influence of preparation techniques on the microstructure, grain-size and consequently on the electrical transport properties of the ABO_3 structured materials used as electrode and electrolytes in all perovskite IT-SOFC were investigated.

Nano-crystalline dense $La_{1-x}M_xGa_{1-y}N_yO_{3\pm\delta}$ ($M = Sr$; $x = -0.10$ to 0.15 ; $N = Mg$; $y = -0.10$ to 0.15) (LSGM) as electrolyte, porous $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3\pm\delta}$ (LSCF) or $LaNi_{1-x}Fe_xO_{3\pm\delta}$ ($x=0-0.5$) (LNF) as cathode, $La_{0.8}Sr_{0.2}Cr_{0.7}Mn_{0.3}O_{3\pm\delta}$ (LSCM) as anode and $LaCrO_3$ or substituted $LaCrO_3$ as interconnect were synthesized by various wet chemical methods. The effect of wet chemical methods especially sonochemical, and regenerative sol-gel in processing large quantities of nano-crystalline perovskites with multi-element substitutions at A- and B-sites to achieve physico-chemical compatibility for fabricating zero emission all perovskite IT-SOFCs are reported. Multilayered thin films were deposited on single crystalline substrates using pulsed laser deposition (PLD) techniques.

It is reported for the first time the Sr- and Mg-doped $LaGaO_3$ ($La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-0.5(x+y)}$, LSGM) was regenerated to aqueous solution. LSGM with comparable quality to other solution route was synthesized by sol-gel route from the regenerated solution. The LSGM solid was dissolved in hot doubly distilled water which pH was adjusted in the range of 0.5 to 1.0. To 50 ml of the solution, 10 g of citric acid and 5 ml of glycerol were added and dissolved to form the regenerated solution for LSGM. $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM-2015) and

LaGaO₃ were prepared through both the regenerative sol-gel (RSG) and conventional solid-state route at 1400°C. The LSGM pellets prepared by the both ways were compared in their X-ray diffraction (XRD), scanning electron micrography (SEM) and electrochemical impedance spectroscopy (EIS) measurements. The RSG route LSGM-2015 exhibited conductivity $\sigma_t = 0.066$ S/cm and 0.029 S/cm at 800°C and 700°C respectively, and activation energy $E_b = 0.97$ eV, $E_{gb} = 1.03$ eV and $E_t = 1.01$ eV for bulk, grain-boundary and whole material, respectively. Series of La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815} pellets were prepared by the RSG method in different sintering temperature (1200-1500°C) and time. The sintering temperature severely affected the grain size (< 0.1 μ m to 10 μ m) and the resistance in all grain-boundary (3 k Ω to 175 k Ω).

Simultaneously, we have investigated the following perovskites:

- LaCr_{1-x}M_xO₃, M= Mn, Mg, Co, Fe, x=0.1 were prepared as interconnect materials and catalytic applications. Phase stability and structural transformation due to substitution on Cr site were investigated. Glycine nitrate method is used to prepare these materials.
- LaNi_{1-x}Fe_xO₃, x= 0.1 –0.9 were prepared by glycine nitrate method and these nanoscale powders were used to deposit thin films on single crystalline substrates.

Among Ni-cermets, Ni-YSZ is the state-of-the-art materials for the anode in SOFC which is the fuel electrode. But sulphur impurity present in different gaseous fuels, depending on its concentration, is highly poisonous to the stability and electrochemical performance of the Ni catalyst in the cermet anodes. Thus in this study the microstructural stability of Ni-YSZ, Ni-CGO and Ni-LSGM cermet are studied in the intermediate temperature range of SOFC operation. Thermodynamic modelling studies of Ni-S-O-H quaternary system was performed for the calculation of the thermodynamic stability and sulphur-tolerance limit of Ni in the gaseous atmosphere made up of H, O and S.

Novel wet-chemical methods of synthesis have been adopted to synthesize nano-crystalline CeO_2 and Gd-substituted compositions aiming to explore an efficient oxide ion conducting solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications. Nano-crystalline CeO_2 powders were synthesized by combustion method using redox mixture of ceric ammonium nitrate or cerium nitrate and maleic acid or 1,3-dimethylurea and compared with high surface area CeO_2 powders prepared by hydrothermal technique with microwave precipitated precursor from aqueous solutions of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and urea. The grain size achieved by the hydrothermal technique is ~ 7 nm which is smaller than that of commercial nano CeO_2 powders. Conventional or microwave sintering was used to prepare dense $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ pellets from the ceria powders made of redox mixture of cerium nitrate, 1,3-dimethylurea (DMU) and Gd_2O_3 as the starting ingredients. The samples were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and ac impedance spectroscopy. The ionic conductivity measured for the pellet sintered at 1400°C is 1×10^{-2} and 2.4×10^{-2} S/cm at 700°C and 800°C respectively.

Attempts were made to prepare proton-conducting perovskites of $\text{SrCe}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Dy, Eu, Er, Tb, } x=0.1$) by using sonochemical and hydrothermal technique followed by microwave sintering processes. These compositions were prepared characterized by XRD, TEM, SEM and electrical conductivity of the pellets was measured. The interest of low temperature proton conducting electrolyte is to replace the well known oxide ion conducting solid electrolyte in SOFCs, thereby reducing the operating temperature of SOFC to lower temperature (i.e $400\text{--}600^\circ\text{C}$) and named it as PC-SOFC (proton conducting-solid oxide fuel cell). SrCeO_3 , $\text{SrCe}_{1-x}\text{M}_x\text{O}_3$ compositions were synthesized by sonochemical treatment followed hydrothermal method and sintering is done by microwave heating. CeO_2 hydrated gel was obtained from Ce(IV) ammonium

nitrate and mixed with $\text{Sr}(\text{OH})_2$ and sonicated for 30 min., then the reactants were subjected to hydrothermal treatment at 150°C for 4 h. SrCeO_3 was found to form orthorhombic perovskite above 1200°C of heat-treatment. The powders were characterized by XRD, TEM, and EIS techniques. The effect of ball milling was also studied on sintering of the pellets. The 10% substitution of dysprosium at Ce site does not form single phase. Instead Sr_2CeO_4 is formed along with SrCeO_3 . Similarly, Eu, Er (10 % and 90 %Ce) were also attempted to substitute at Ce site; however, $\text{SrCe}_{1-x}\text{M}_x\text{O}_3$ ($x=0.10$) does not take up 10 % substitution. The electrical conductivity measurements were carried out on the single phase pellets by ac impedance techniques. The crystal structure and phase stability of perovskites as well as apatites were investigated with respect to substitution of various iso-valent and alivalent ions to determine the % of solubility in the crystal lattice of perovskites.

Sonochemical technique (power of ultra sonic probe 750 watt) combined with hydrothermal treatment of precursors for the preparation of calcium hydroxy apatites (Ca-HAp) was used for the first time. Hydroxy apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Ca-HAp) is a bio-ceramic and is an alternative candidate for stainless steel and titanium based materials being used for replacement of fractured bones. In this study an attempt is made to synthesize nano-composites of Ca-HAp with varying Ca to PO_4 ratio and alkaline earth (Ba, Sr and Mg) doping at Ca-site of the HAp by using sonochemical, hydrothermal followed by microwave sintering. The powders obtained in all these routes were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) .The formation of single phase of HAp was confirmed by XRD analysis. XRD peak broadening and TEM examination of the powders confirmed the nano-crystalline nature of the powders. The hydrothermal method (autoclave heated at 150°C) of synthesis yielded single-phase powders without further heat-treatment. The urea combustion method needed heat-treatment of the pre-cursor at $400\text{--}800^\circ\text{C}$. The sonochemically treated starting materials before proceeding to hydrothermal treatment yielded needle shaped HAp. The needle shaped nano-rods may be of

great importance to fabricate high strength bone material. Electrical transport properties of these compositions were carried out by ac impedance technique. The conductivity of CHAp is observed to be 0.05mS/cm at 500⁰C. The measurement of various properties of $\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6(\text{OH})_2$, $\text{CaMg}_5(\text{PO}_4)_6(\text{OH})_2$, $\text{CaBa}_5(\text{PO}_4)_6(\text{OH})_2$ compositions is to be carried out to find its suitability to justify its use as biomaterials for vertebrates. The presence of protons in the lattice has been investigated by proton NMR and FT-IR spectroscopy measurements. The structural and transport properties were correlated with the natural human bone powder measured under identical experimental conditions. The ordering mechanism of hydroxy groups in hydroxy-apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, which is the major constituent of mammalian bones and tooth enamel has been discussed. Apart from its use as biomaterials, Ca-HAp may be a candidate for future proton conductors for proton conducting ceramic fuel cell application as well as the composite electrolyte in the direct methanol fuel cells.

TiO_2 + CaHAp composite was prepared by using water soluble Titanium bis-ammonium lactato dihydroxide (TALH) as precursor for TiO_2 by using sonochemical precipitation technique for the first time. The surface microstructure, crystallite size and phase stability of the compositions were investigated and compared with the natural bone powders. The properties like electrical conductivity, crystal structure, compositions of artificial bone (CaHAp) were studied and compared with the natural bone material. The comparison found to be excellent indicating the efficiency of the preparation techniques. The typical value of conductivity measured is $0.091 \times 10^{-6} \text{ Scm}^{-1}$ at 25⁰C and $19.26 \times 10^{-6} \text{ Scm}^{-1}$ at 850⁰C with an applied frequency of 100 kHz. The conductivity increases on increasing frequency and temperature and reaches 0.05mS/cm at 500⁰C. Various electrode and electrolyte material compositions were prepared and characterized by XRD, SEM, XPS and electron microprobe.

The preparation of dense electrolyte films for most electrochemical devices is a crucial technological process. Net shape technology is a new approach, which uses a combination of colloidal suspensions and polymer

precursor techniques, to obtain the dense electrolyte layers. It allows the overlapping of the thickness range from 1 to 10 μm in which other preparation techniques experience difficulties. Net shape processing is a low temperature technology (preparation temperature can be as low as 400 oC) and it eliminates shrinkage of the film during the densification stage, so chemical reactions between the substrate and the film can be minimized. In this study two types of dense substrates were used to confirm these features of the net shape technology: single crystal sapphire and platinum foil. It was shown that dense electrolytes obtained on both types of substrates at the temperatures as low as 400°C. Moreover, further higher annealing temperature does not produce either shrinkage or cracking of the film. Electrical properties of films were measured in plane (on sapphire) and through the film (on platinum) using impedance spectroscopy and two-probe DC methods.

Figure 1 show the schematic of all perovskite anode supported planar SOFC system, under progress at the Solid State Ionics Laboratory in the Southern University.

To utilize the NG assertively for sustainable development and growth of the region, there is an urgent need to explore distributed energy sources fuelled by NG that can provide customers with reliable, local energy supplies while

lowering the emissions of air pollutants. In this scenario, the renewable energy technology for power generation that is in the verge of commercialization is the fuel cell technology for both stationary, and transportation applications. Very recently, Dr. Ramsey Saunders of University of West Indies, Trinidad, and Dr. Bobba of Southern University, Baton Rouge, USA proposed to establish a national center for research excellence for promoting hydrogen economy entitled "Center for Hydrogen Energy and Advanced Power [CHEAP]" for conducting study, research, consultancy, organizing seminars and conferences in areas of fuel cells and hydrogen, and establishing a model decentralized 10-50 KW NG fuelled solid oxide fuel cell (SOFC) power plant in T&T jointly with the T&T NG Company. All activities of the centre will move from materials research for component and cell development, production, and formulating strategies for developing decentralized power generation source that can be highly efficient, clean, quiet, scalable, reliable, and potentially cheap. Such power packs will become popular for energizing the medium, and business complexes (malls), hospitals, centralized office complexes, airports, educational institutions, residential complexes, and remote villages in T&T. Global market analysts expect that the overall market for fuel cell technology could reach \$95 billion by the year 2010. The vision of this industrial/academic R &D CHEAP is to prepare T&T for grabbing the market share that belong to decentralized power based on NG.

In this research and educational (R&E) project, we have emphasized the need to expand research opportunities for talented undergraduate and graduate African American students and junior faculty in the field of power sources based on nanoscience and nanotechnology. We have paired the selected undergraduate and graduate students with the PDFs closely, and involved the undergraduate students through experimental sessions and discussions via preparing students to present the work in regional, national and international conferences. Every student supported in this project attempted to do at least one presentation per year out side the SUBR campus. The students selected for this

program have been primarily from the Physics, Chemistry, Mechanical Engineering and or Electrical Engineering disciplines. The effort in this project yielded 10 publications in the refereed journals and over 12 conference papers. During the life of this R&E project, the students participating in this project are involved in either DOE or DOD funded projects on energy conversion and storage devices. The PI and his team have published overall 30 papers in the refereed journals and several in conferences at this project site during the life of this US-DOE-NETL-HBCU/MI project. Three graduate students supported from this project graduated and earned employment in the private sector. Three undergraduate students are about complete their degree requirements and planning to pursue graduate education. For infrastructure enhancement, the impedance analyzer, and microwave furnace were acquired. It is important to mention here, that this project also suffered some extent during the recent Katrina in the State of Louisiana.

UNDERGRADUATE, GRADUATE, AND SENIOR RESEARCH ASSOCIATES AT THIS HBCU-SITE

UNDERGRADUATE STUDENTS

2004-2005

- 1) Koutney Jackson [Electrical Engineering]
- 2) Selisha Mitchel [Engineering]
- 3) Jonthan Dooley [Chemistry]

2005-2006

- 1) Marlon Lemond [Engineering]
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- 3) Wiechang Zhao M.S Physics
- 4) Samrat Ghosh Ph.D., Physics
- 5) Hrudananda Jena Ph.D., Materials Science
- 6) Gunasekaran

**PUBLICATIONS IN REFEREED JOURNALS AND CONFERENCE
PROCEEDING BOOKS [2004-2007]**

1. Innovative processing of dense LSGM electrolytes for IT-SOFC's, B. Rambabu, Samrat Ghosh, Weichang Zhao and H. Jena, Journal of Power Sources, 159 (2006) 21-28
2. Novel wet-chemical synthesis and characterization of nanocrystalline CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ as solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications, B. Rambabu, Samrat Ghosh and Hrudananda Jena, J. Mater. Sci. (2006) 41:7530-7536
3. An exploratory study on solution assisted synthetic routes to prepare nano-crystalline $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{NyO}_3$ (M=Sr, N=Mn, Mg) for IT-SOFC applications. Hrudananda Jena and B. Rambabu, Mater. Chem. Phys (2007), vol 101, 21-22.
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6. Microstructural evaluation of sonochemically prepared $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.7}\text{Mn}_{0.3}\text{O}_{3\pm\delta}$ (LSCM) as anode, B. Rambabu, and H. Jena, submitted for publication, Ionics, 2007
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Innovative processing of dense LSGM electrolytes for IT-SOFC's

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Abstract

This paper reports for the first time the attempted synthesis of SrO- and MgO-doped LaGaO_3 ($\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-0.5(x+y)}$, LSGM) perovskite by an aqueous 'regenerative' solution route. This novel technique enabled recycling of the undesired product and subsequently yielded product with much better phase purity and density than that obtained from the solid-state route. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015) and LaGaO_3 were prepared using both the regenerative sol-gel (RSG) and conventional solid-state route at 1400°C . Series of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ (LSGM-2017) pellets were also prepared by the RSG method at different sintering temperature (1200 – 1500°C) and time. The effect of conventional and microwave sintering of samples obtained from both solid-state and regenerative route was also investigated. Microwave heating was carried out using SiC as a microwave susceptor. The LSGM pellets prepared by using different synthetic methods were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and pellet density was determined by pycnometry. The LSGM-2015 prepared by RSG route exhibited conductivity $\sigma_t = 0.066$ and 0.029 S cm^{-1} at 800 and 700°C , respectively, and activation energy of the bulk, grain-boundary, and total are $E_b = 0.97 \text{ eV}$, $E_{gb} = 1.03 \text{ eV}$ and $E_t = 1.01 \text{ eV}$, respectively. The sintering temperature severely affected the grain size (<0.1 – $10 \mu\text{m}$) and also the grain-boundary resistance (3 – $175 \text{ k}\Omega$). The unique aspect of this RSG technique is that the final product can be recycled which makes the process cost effective and time saving compared to the solid-state ceramic technique and this technique would allow optimization of processing parameters in a cost effective and time saving manner for obtaining well sintered LSGM as an electrolyte for IT-SOFC's.

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Keywords: Strontium- and magnesium-doped lanthanum gallate (LSGM); Intermediate temperature solid oxide fuel cells (IT-SOFC); Regeneration; Sol-gel synthesis; Crystal growth; Impedance spectroscopy

1. Introduction

In the search for new electrolyte materials, the perovskite-based systems (ABO_3) have been considered as alternative options, particularly because ABO_3 can take on a number of different structures, and can be doped with aliovalent cations on both the A and B sites. They can also accommodate very large concentrations of anion vacancies into their structures. Within the past few years, the $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-0.5(x+y)}$ has been attracting considerable attentions as very promising alternate electrolyte materials for intermediate temperature solid oxide fuel cells (IT-SOFC) [1–4]. It presents stable, high and almost pure oxide-ion conductivity over a broad range of oxygen partial pressure at operating temperatures equal or below 800°C [5]. To produce submicron LSGM powders for high-quality

membrane fabrication, the combustion technique via aqueous solutions is usually preferred to the conventional solid-state mixed-oxide method. The solution route provides many advantages, for example, molecular homogeneous precursors, reduced sintering temperature for obtaining dense ceramics, and controllability of uniform superfine grain size [6–12].

However, single phase LSGM with high sintered density is not easy to obtain by conventional solid-state technique. One of the requisites for application as SOFC electrolytes is high sinterability. The extent of sintering depends on the mode of synthesis. The solid-state route results in hard agglomerates and coarser grains which inhibit sintering to obtain dense electrolyte materials. The ball milling of hard agglomerates may cause contamination from the milling and grinding medium. Solution technique, provided homogeneity at molecular level is maintained at all levels of processing, will enable synthesis of these oxides at lower temperature and consequent higher densification. Since solution techniques results in soft agglomerates, ball milling if employed will cause no contamination. Water is a benign solvent and preferable for large scale synthesis.

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Therefore, development of aqueous solution techniques which make use of cheaper precursors will be of great advantage. Since gallium precursors are expensive, therefore, for determination of optimum synthetic conditions necessary for obtaining the desired product with improved properties, recycling of LSGM samples will prove to be cost effective.

For any sol–gel synthesis, phase purity and sintered density of a product depends on the nature of the gel under identical charring conditions. To obtain a phase pure material with high sintered density under less extreme conditions, therefore, several synthetic trials need to be performed which would involve optimization of several gelling parameters such as concentration of the precursor solution, concentration of citric acid, citric acid–glycerol ratio and so forth. Usually in other synthetic approaches for LSGM, this optimization process starts right from the initial step which is weighing of lanthanum, strontium, gallium and magnesium precursors. These leads to preparation of several samples. The advantage of our regenerative sol–gel synthesis lies in recycling of the same product until a better product is obtained in terms of phase purity and sintered density. This makes the process time saving compared to the solid-state ceramic technique. In the regenerative solution technique, the first synthetic trial entails both solid-state ceramic and solution route, whereas the subsequent trials are only solution based. Hence the weighing of individual precursors, their milling and calcination are circumvented which saves time because LSGM obtained in the first trial even if it is not the desired phase can be dissolved in a hot acidic solution to yield a clear solution. This now becomes the precursor solution for the subsequent synthetic trial in which the perovskite LSGM will be regenerated. There are reports of solution synthesis of LSGM in which gallium precursors used were either costly gallium metal or hygroscopic $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ which requires careful estimation prior to every synthetic process. On the other hand, in our regenerative solution technique, the final product is a combined precursor of Ga, La, Sr and Mg for the subsequent synthetic trial. The combined precursor may not be phase pure but the stoichiometric ratio of the constituents is always retained throughout the synthetic trials. Depending on the particulate properties of the regenerated LSGM, this solid-solution–solid transformation process can be repeated until the processing parameters are optimized.

Recently sol–gel synthesis and microwave sintering of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.825}$ ($x+y>0.35$) has been reported using costly gallium metal as a precursor [13]. Highly sintered mixed phase sample was obtained by microwave processing at 1500°C for 10 min. To the best of our knowledge there are no reports on recycling of old LSGM samples to obtain new samples of same composition but with different properties. In view of increasing importance to produce dense LSGM ceramics on a large scale with better phase purity at lower temperatures for use as electrolytes, an investigation was carried out to study the effect of conventional and microwave assisted sintering of the recycled LSGM samples obtained from RSG route which is a combination of solid-state reaction and Pechini-type method. This paper reports for the first time an attempt by RSG technique to prepare LSGM ceramic of composition $(\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-0.5(x+y)})$, $x=0.2$, $y=0.15$ – 0.17 , LSGM-2015 and 2017) and investiga-

tion of the effect of conventional and microwave assisted sintering using SiC as a microwave susceptor. LSGM pellets made by the two methods were compared based on their X-ray diffraction (XRD), scanning electron micrography (SEM) and electrochemical impedance spectroscopy (EIS) measurements. The LSGM obtained by RSG method has shown improved properties than the one made by the solid-state method.

2. Experiment

Stoichiometric amounts of La_2O_3 , SrCO_3 , Ga_2O_3 and MgO were ground and heated at 1200°C for 24 h, then ground and heated at 1400°C for 24 h to form the solid-state LSGM precursor. A portion of the solid-state precursor was dissolved in hot doubly distilled water whose pH was adjusted in the range of 0.5–1.0. To 50 ml of the solution, 10 g of citric acid and 5 ml of glycerol were added and dissolved. The resulting solution was introduced into a domestic microwave oven (2.45 GHz; 700 W) and concentrated at maximum power for 10 min to yield a dark brown crisp resin. The resin was calcinated in a muffle furnace at 900°C for 6 h to form the regenerative sol–gel precursor, a kind of soft white powder. The solid-state and RSG precursors were pressed under 230 MPa at room temperature into pellets about 1.4 cm thick and 11 cm in diameter. The pellets were sintered in another furnace (Carbolite RHF 1600) at temperature range of 1200 – 1500°C . A flow chart for the regenerative sol–gel process is shown in Fig. 1.

The sol–gel precursor was ground, milled with PVA as a binder and uniaxially pressed into 11 mm dia pellets under a load of 3 t. For microwave sintering, one of the pellets was kept inside an alumina thermal insulator box (inner dimensions $12\text{ cm} \times 7\text{ cm} \times 10\text{ cm}$) containing SiC as microwave susceptors. This alumina box was then placed in a microwave oven (Panasonic, 2.45 GHz, 1200 W) equipped with a platinum sheathed thermocouple and interfaced with a programmable temperature controller (ThermWave Mod. III, Research Microwave Systems, LLC). The tip of the thermocouple was positioned an inch above the sample pellet mounted between SiC susceptors. Tap water was circulated to prevent overheating of the microwave. On exposure to microwaves at 100% power, the temperature inside the alumina box rose rapidly and reached 1200°C in 30 min and was maintained at that temperature for another 30 min. After heating was over, the alumina box was carefully removed from the oven and allowed to cool in air. To study the effect of different sintering process on phase purity and density, another pellet from the same sol–gel precursor was conventionally heated in air. The temperature of the furnace (Carbolite RHF 1600) was raised at 5°C min^{-1} from room temperature to 1400°C where it was held for 8 h and allowed to cool down to room temperature at 5°C min^{-1} . In order to compare the phase purity and density of the sintered samples obtained from various precursors, a pellet from the ceramic precursor was also conventionally heated in air under the same conditions as above.

The LSGM samples were characterized by XRD, SEM and EIS. The XRD data were taken at room temperature by a

Fig. 1. Flow chart for the regenerative sol-gel process.

Siemens/Bruker D5000 diffractometer using $\text{Cu K}\alpha$ as the incident X-ray. The SEM data were obtained by a JEOL 6300F microscope using 3–5 kV as the accelerating voltages of the electron beam. The EIS measurement (HP-4192A, 5 Hz–13 MHz) of the LSGM-2015 of both solid-state and RSG methods was taken in air at temperature range of 250–850 °C. The two electrodes were made by applying platinum paste to the two sides of the pellet and firing at 980 °C for 30 min. The EIS measurement of the LSGM-2017 prepared in different sintering condition was taken in air at temperature range of 250–500 °C by using Ag-paste made electrodes.

3. Results and discussion

3.1. Comparison of LSGM synthesized by regenerative sol-gel route and solid-state route

LSGM oxides are traditionally recycled through the solid-state method by grinding, pressing and re-sintering. In our experiment, we found the LSGM solid can be dissolved in aqueous solution, and LSGM pellet can be synthesized through

Fig. 2. XRD spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015): (a) solid-state route precursor; (b) solid-state route pellet starting from the ground powders of (a); (c) regenerative sol-gel route precursor; (d) regenerative sol-gel pellet.

the sol-gel route from the solution. In this way, LSGM can be regenerated also through a solution route, which in general leads to LSGM oxide of superior quality than the solid-state route. To evaluate the physico-chemical properties of LSGM by RSG method, we reproduced LSGM-2015 and LaGaO_3 pellets through both the sol-gel route and the solid-state route starting from the same LSGM-2015 (or LaGaO_3) solid and sintered under the same conditions.

The XRD data in Fig. 2(a) shows the LSGM-2015 precursor obtained by the solid-state reaction (1200 °C for 24 h and 1400 °C for 24 h) has three impurity phases, mainly LaSrGaO_4 and $\text{LaSrGa}_3\text{O}_7$. The peak at $2\theta = 42.2^\circ$ might be from the residue of MgO which is one of the starting oxide material and has very high melting point (2852 °C). The XRD in Fig. 2(b) indicates the recycled LSGM-2015 by solid-state reaction show similar amounts of secondary phases LaSrGaO_4 , $\text{LaSrGa}_3\text{O}_7$ and possible MgO. It was noted that the increased number of sintering cycles did not effectively reduce the secondary phases in the solid-state route LSGM-2015 at 1400 °C. Therefore, to achieve single phase LSGM starting from solid-state oxide mixtures, higher temperature of sintering ($\sim 1500^\circ\text{C}$) is usually needed [3,12]. Fig. 2(d) shows the formation of pure phase LSGM-2015 at a reduced sintering temperature of 1400 °C by the RSG route. The weak peak near 30.5° is doubted to be a real peak because of its very low counts and may not be assigned to possible impurity phases. The LSGM-2015 precursor (RSG) powders heated at 900 °C and used for pellet pressing were examined by XRD as shown in Fig. 2(c). The broadened peaks in Fig. 2(c) indicate the prevalence of many metastable nanocrystalline phases which are the atomic mixture of cations to the thermodynamically stable LSGM phase.

The SEM micrographs in Fig. 3 exhibit the microscopic surface morphologies of the LSGM precursors and pellets. Fig. 3(a) shows the microstructure of LSGM-2015 pellet obtained from

Fig. 3. SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015) and LaGaO_3 : (a) solid-state route precursor of LSGM-2015; (b) regenerative sol-gel (RSG) route precursor of LSGM-2015; (c) solid-state route pellet of LSGM-2015; (d) RSG pellet of LSGM-2015; (e) solid-state route pellet of LaGaO_3 ; (f) RSG pellet of LaGaO_3 .

the LSGM-2015 precursor prepared by solid-state reaction route and heated at $1200^\circ\text{C}/24\text{ h}$. The picture in Fig. 3(b) shows the regenerative sol-gel LSGM-2015 precursor heated at 900°C . Although the two precursors show similar microscopic morphologies in the SEM micrograph, their internal crystallization phases are quite different indicated by the XRD in Fig. 2(a) and (c). Fig. 3(a) show the SEM micrograph of LSGM-2015 pelletized and sintered at 1200°C for 24 h (density = 4.29 g cm^{-3} , colour = white). The grain size observed in this micrograph is $\sim 100\text{ }\mu\text{m}$ with large number of voids with no uniform distributions of grains. The pellet re-sintered at $1400^\circ\text{C}/32\text{ h}$ shows coalescing of grains and closing of voids and intergranular spaces leading to pore-free microstructure with a grain size distribution of $5\text{--}10\text{ }\mu\text{m}$ (Fig. 3(c)). The compact microstructure

is further verified from the density measurement (5.25 g cm^{-3} , creamish colour). On the contrary, the SEM micrograph of the pellet obtained from the regenerative sol-gel precursor shown in Fig. 3(d) has highly compact microstructure (5.85 g cm^{-3} , creamish) compared to Fig. 3(b) and (c). The grains are in close contact to each other with distinct grain-boundaries. Ninety percent of the grains are in the range of $1\text{--}5\text{ }\mu\text{m}$. It is noticeable for the similarities in microstructures and grain sizes between the LSGM-2015 and the undoped LaGaO_3 shown in Fig. 3(c) and (e) and in Fig. 3(d) and (f), respectively. Like the LSGM-2015, the reproduced LaGaO_3 through the solid-state route also has plenty of cavities occupying high percentage of the material volume (Fig. 3(e)), but the reproduced LaGaO_3 through the RSG route has compact microstructure (6.46 g cm^{-3} , brown) (Fig. 3(f)).

The similar grain sizes for the LSGM-2015 and LaGaO_3 shown in Fig. 3(c) and (e), respectively, as well as in Fig. 3(d) and (f), indicate the two materials have similar diffusion coefficients even though they have different compositions. The XRD and SEM results in Figs. 2 and 3 have shown the sintering temperature of 1400°C is high enough for the RSG route to obtain satisfactory dense and single phase LSGM-2015, but not for the solid-state route.

Fig. 4 illustrates the impedance spectroscopy measurement of the LSGM-2015 pellets synthesized by using both the regenerative sol–gel route and solid-state route. The resistances in all bulk and in all grain-boundary (R_b and R_{gb}) of the pellets were estimated from the real axis intercepts of the depressed semicircles based upon the equivalent series circuit of two R – C parallel circuits. The first depressed semicircle near the origin corresponds to the bulk resistance and the second corresponds to the grain-boundary resistance. The first real axis intercept offers the R_b and the second offers the sum of R_b and R_{gb} . The resistances were unified by multiplying the ratio of area to thickness of the measured pellets. Although we got the resistances, because volume fractions of the bulk and grain-boundary are unknown,

it involves complex techniques to calculate the bulk and grain-boundary conductivities. The Arrhenius relations of the bulk and the grain-boundary resistances in Fig. 4(a) indicate the grain-boundary resistance is almost equal to the bulk resistance. Based on the Arrhenius relation of $T/R \propto \exp(-E/k_B T)$, we estimated the activation energies for the oxide-ion conduction across the whole pellet ($E_t = 1.01$ eV), the bulk part ($E_b = 0.97$ eV), and the grain-boundary part ($E_{gb} = 1.03$ eV) by fitting the slopes of the curves in Fig. 4(a). The Arrhenius relation of the total conductivities in Fig. 4(b) indicates the regenerative sol–gel LSGM-2015 has a higher temperature-dependent conductivity than that of the solid-state route LSGM-2015. At 800 and 700°C , the solid-state route LSGM-2015 has a conductivity $\sigma_t \approx 0.056$ and 0.025 S cm^{-1} , respectively, and the RSG-LSGM-2015 has a conductivity $\sigma_t \approx 0.066$ and 0.029 S cm^{-1} , respectively, which is 16–18% more than the solid-state LSGM-2015 conductivity and is comparable to the conductivity of conventional sol–gel route LSGM starting from liquid-mixing of salt solutions (refer to [6], $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$, $\sigma_t \approx 0.065$ and 0.034 S cm^{-1} at 800 and 700°C , respectively).

Fig. 4. Impedance spectroscopy of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015): (a) Arrhenius relation for conductivities of the solid-state route and regenerative sol–gel route LSGM-2015; (b) Arrhenius relation for bulk and grain-boundary resistances of regenerative sol–gel LSGM-2015.

Fig. 5. XRD spectra of regenerative sol–gel route $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$: (a) first cycle of sintering for 8 h; (b) second cycle of sintering for 8 h (total 16 h).

Fig. 6. SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$: (a–e) first cycle of sintering for 8 h; (f–j) second cycle of sintering for 8 h (total 16 h).

Fig. 7. Complex plane plot of impedance spectroscopy measured in air when the samples are at 325 °C.

3.2. Effects of sintering conditions on LSGM properties

A group of RSG synthesized LSGM-2017 pellets was sintered at five different temperatures, from 1200 to 1500 °C, for 8 h each, and subsequently sintered 8 h. Fig. 5 shows no secondary phase in XRD pattern on the samples sintered at temperature above 1400 °C. The XRD spectra indicate the RSG synthesized LSGM-2017 pellets crystallize in the stable simple-cubic phase at temperature range of 1200–1500 °C. Further, increasing sintering time for 8 h has no effect on the phase formation.

The SEM micrograph in Fig. 6 show the microstructure of LSGM-2017 sintered under different conditions. The grain size is found to be affected severely by the sintering temperature, i.e. higher temperature resulted in bigger average grain size (Fig. 6(a)–(e)). The further sintering helped to diminish those cavities (Fig. 6(a) and (f)), the second cycle of 8 h sintering provided increased grain sizes, (Fig. 6(a)–(e) and (f)–(j)). The grains size of the samples sintered at 1200 °C are very small and most of them are in sub micrometer scale. Whereas the samples prepared by conventional solid-state method did not produce such small LSGM grains with cubic phase. The average grain size of the sample sintered at 1500 °C is $\sim 10 \mu\text{m}$. The XRD peaks in Fig. 5 for sample of 1500 °C are not as sharp as those for samples of 1400 and 1450 °C. This observation can be attributed to the melting leading to deformation of the pellet sintered at 1500 °C. There are many interesting wrinkles on the grain surface of the sample of 1500 °C, as shown in Fig. 6(e) and (j). The above phenomena suggest there might be many defects in the grains caused by energetic diffusion at the high temperature of 1500 °C.

Fig. 7 displays the complex-plane impedance spectroscopy measured at 325 °C of the LSGM-2017 samples sintered at different temperatures for 8 h. The samples have similar bulk resistances in the range of 15–30 k Ω , but very diverse grain-boundary resistances from 3 to 175 k Ω . The grain-boundary resistance values are in the inverse order of the sintering temperature. Referring to the SEM pictures in Fig. 6(a)–(e), the sample of 1200 °C has the smallest grains, thus the highest percentage of grain-boundary region, hence the biggest grain-boundary resistance. The sample sintered at 1500 °C has the largest grains, i.e. the smallest grain-boundary region, therefore, smallest grain-boundary resistance in the impedance measurement. Fig. 8 shows the Arrhenius relations for total conductivities, bulk and grain-boundary resistances for the samples sintered at different

Fig. 8. Arrhenius relation from impedance spectroscopy measurement for regenerative sol-gel route $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$: (a) total conductivity; (b) bulk resistance; (c) grain-boundary resistance.

temperature. There is no significant difference in total conductivities (Fig. 8(a)) of the three samples of 1400, 1450 and 1500 °C. The sample of 1400 °C exhibited the best conductivity. Fig. 8(b) and (c) show the bulk resistances are very close to each other, however, their grain-boundary resistances are quite different. The grain sizes affect severely the grain-boundary resistances compared to the bulk resistance.

4. Conclusion

In summary, the Sr- and Mg-doped and undoped LaGaO₃ oxides can be regenerated through solution route by dissolving the solids in aqueous solution. It is a cost effective way for in-lab or industry synthesis of large amount of LSGM materials which consume expansive gallium containing precursors and also a convenient way to tailor the exact composition by adding solution of certain cation ingredient. The LSGM prepared through the RSG route has higher quality (phase purity, compact microstructure and electrical conductivity) than the solid-state route. The sintering temperature affects the average grain size severely, while the sintering time has little effect on the grain size. The impedance spectra reveal that the smaller the average grain size, the higher grain-boundary resistance; but the bulk resistance almost kept stable and did not change as monotonically along with the grain size as the grain-boundary resistance did.

In conclusion in this paper, we say the merit of regenerative solution technique is the transformation of inhomogeneous system into a homogeneous system. Secondly, the recyclability of the product makes the regenerative solution process cost effective and time saving compared to the solid-state ceramic technique for preparation of phase pure and dense LSGM electrolytes. The process can be repeated till a RSG technique can be extended to other members of the LSGM series. It is well known that performance of SOFC at intermediate temperatures

is enhanced if the electrolytes can be used in the form of thin films. The regenerative solution technique may enable deposition of thin dense films of LSGM on porous anode/cathode substrates by spray pyrolysis, dip or spin coating.

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Novel wet-chemical synthesis and characterization of nanocrystalline CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ as solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications

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Abstract Novel wet-chemical methods of synthesis have been adopted to synthesize nano-crystalline CeO_2 and Gd-substituted compositions aiming to explore an efficient oxide ion conducting solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications. Nano-crystalline CeO_2 powders were synthesized by combustion method using redox mixture of ceric ammonium nitrate or cerium nitrate and maleic acid or 1,3-dimethylurea and compared with high surface area CeO_2 powders prepared by hydrothermal technique with microwave precipitated precursor from aqueous solutions of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and urea. The grain size achieved by the hydrothermal technique is ~ 7 nm which is smaller than that of commercial nano CeO_2 powders. Conventional or microwave sintering was used to prepare dense $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ pellets from the ceria powders made of redox mixture of cerium nitrate, 1,3-dimethylurea (DMU) and Gd_2O_3 as the starting ingredients. The samples were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and ac impedance spectroscopy. The ionic conductivity measured for the pellet sintered at 1400°C is 1×10^{-2} and 2.4×10^{-2} S/cm at 700°C and 800°C respectively.

Introduction

Fluorite structured Ceria (CeO_2) has many applications as oxygen sensor [1], auto exhaust catalysts [2], polishing agents [3], sunscreens [4], and electrolyte materials for intermediate temperature solid oxide fuel cell (IT-SOFC) [5, 6]. Although yttria stabilized zirconia (YSZ) is still the favored electrolyte materials; ceria is considered alternative electrolyte material and could operate at lower temperatures ($500\text{--}700^\circ\text{C}$). The ionic conductivity of ceria is approximately an order of magnitude greater than that of YSZ for comparable doping condition and especially when its nano-crystalline nature is retained. However, CeO_2 is not a pure ionic conductor but has electronic conduction too, at elevated temperatures and electronic conduction gets enhanced in reducing atmospheres. IT-SOFC stacks operating at reduced temperature offer many exiting advantages, for example, increased material durability and reduced overall cost. They allow the use of gaskets that will permit greater design flexibility for the stack configuration, and allow the metal-supported positive-electrolyte-negative (PEN) structures, which will withstand the rapid temperature cycles during operation of small stacks [7–9].

Ceria is highly refractory oxide and difficult to sinter without sintering aids. However, nano-crystalline ceria can be densified at much lower temperature because of high surface energy of the nanoparticles [10–13]. Many solution based techniques were used to obtain the nanocrystalline ceria powders, such as hydrothermal technique [14], mimic alkoxide technique [15], micro-emulsion technique [16], sol-gel technique [17], precipitation technique [18], glycine-nitrate combustion technique [19], hydrazine technique [20], and spray

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hydrolysis [21]. In the past, nanocrystalline CeO_2 powders have been prepared by using urea and hexamethylenetetramine-based precipitation [17, 18]. In these experiments precipitation was carried out by conventional heating of the precursor solution at 80 °C. Since microwave heating is rapid and uniform, homogeneous nucleation and agglomerate-free precipitation is expected when the precursor solution is heated by microwaves. In this work emphasis has been given on the preparation of uniform nano-crystalline ceria powders at 200 °C, by hydrothermal treatment of microwave precipitated precursor from aqueous solution of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and urea. Nanocrystalline CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders were also prepared by solution combustion technique using different kinds of starting reagents for comparison. The ceria powders prepared in this study were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), and diffuse reflectance spectroscopy (DRS), and compared with commercial nanocrystalline ceria powders. Combustion synthesized $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders were made to dense pellets by using a resistance-heating furnace at 1400 °C and 1550 °C; and microwave sintering at 1200 °C. The microstructure of the sintered pellets were examined by scanning electron microscopy (SEM), and their electrical conductivity

was measured by ac impedance spectroscopy (EIS). The results of the experimental observations are discussed in this paper.

Experimental

Synthesis

In this study, CeO_2 nanocrystalline powders were prepared by solution combustion and hydrothermal techniques. Starting from four kinds of solution mixtures, the CeO_2 powders were synthesized by the solution combustion route. The four kinds of starting solution were: (a) redox mixture of ceric ammonium nitrate (CAN) and maleic acid; (b) redox mixture of cerium nitrate and maleic acid; (c) redox mixture of ceric ammonium nitrate (CAN) and 1,3-dimethylurea (DMU); and (d) redox mixture of cerium nitrate and 1,3-dimethylurea (DMU). Assuming complete combustion of the redox mixture, the theoretical equation for the formation of CeO_2 may be written as follows:

- $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 + 2(\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}) \rightarrow \text{CeO}_2 + 4\text{N}_2 + 8\text{CO}_2 + 8\text{H}_2\text{O};$
- $4\text{Ce}(\text{NO}_3)_3 + 5(\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}) + \text{O}_2 \rightarrow 4\text{CeO}_2 + 6\text{N}_2 + 20\text{CO}_2 + 10\text{H}_2\text{O};$

Fig. 1 Flowcharts to synthesize the nanocrystalline ceria powders: (a) combustion technique to prepare the CeO_2 powders; (b) combustion technique to prepare the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders; and (c) hydrothermal treatment of microwave precipitated precursor

A typical solution combustion process can be described considering the case (a) as given above as an example: 10 g of CAN were taken in a 250 mL petri-dish dissolved in minimum amount of water, 4.234 g of maleic acid was added to this solution. The redox mixture of CAN and maleic acid was slightly heated on the hot plate to completely dissolve the reactants. Then the petridish was introduced into a preheated furnace (600 °C). The solution boiled and frothed leading to self propagating-type combustion after a few seconds. The product was bright yellow in color. The details of the procedure are given in the flowchart (Fig. 1a).

The hydrothermal technique has more processing steps than the solution combustion technique. The aqueous solution of 10 g of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and 16 g of urea was heated in a domestic microwave (2.45 GHz, 700Watts) at maximum power for 3 min. No turbidity was observed. When this solution was kept under ambient conditions in an open beaker without stirring for an hour, turbidity was observed. The solid settled down when the turbid solution was kept standing under ambient conditions in an open beaker without stirring overnight. The solution was centrifuged. The microwave reheating at maximum power of the transparent yellow supernatant in open beaker did not result in any significant turbidity. The pale yellow slimy residue obtained from centrifugation was transferred to a teflon container in a steel lined autoclave and hydrothermally treated at 200 °C for 48 h. The product obtained was spongy, swollen and voluminous. It easily separated from the teflon container. The product smelled of little ammonia. The product was rinsed with double distilled water and dried overnight in oven at 60 °C. The product obtained was shrunk in volume. It was ground and the color is lighter than the commercial nano-active CeO_2 . The detailed steps of the process are given in the flowchart (Fig. 1b). Gd-doped ceria was also prepared by solution combustion technique using redox mixture of cerium nitrate, 1,3-dimethylurea (DMU) and Gd_2O_3 . The details are shown as a flowchart in Fig. 1(c). The ceria powders were pelletized under 230 MPa at room temperature into pellets of 1.2 mm thick and 11 mm diameter. The pellets were sintered in resistance heating furnace (Carbolite RHF 1600) at 1400 °C and 1550 °C for 12 h, or sintered in a microwave oven (Panasonic, 2.45 GHz, 1200 W) at 1200 °C for 60 min. The

microwave oven was equipped with a thermocouple and a programmable temperature controller (ThermWave Mod.III, Research Microwave Systems LLC).

Characterization

The powder and pellet samples were characterized by XRD, transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and ac impedance spectroscopy (EIS). The XRD data were obtained at room temperature by a Siemens/Bruker D5000 diffractometer using CuK_α as the incident X-ray. The TEM was taken by a JEOL 2010 High-resolution Transmission Electron Microscope (HRTEM). The DRS was scanned by a CARY 500 Scan UV-Vis-NIR spectrophotometer. The SEM was taken by a JEOL 6300F microscope using 3–5 kV as the accelerating voltages of the electron beam. The EIS was measured by HP-4192A LF Impedance Analyzer (5–13 MHz) in air at temperature range of 200–900 °C. The two electrodes were formed by applying platinum paste to the two sides of the pellet and firing at temperature 980 °C for 30 min or silver paste firing at 500 °C for 30 min.

Results and discussion

XRD of the ceria powders and pellets

The X-ray diffraction of the ceria powders and pellets are shown in Fig. 2. The broad peaks in Fig. 2(a) indicate the ceria powders are nanocrystalline. The XRD pattern of CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders synthesized in this work (Fig. 2(a)) have quite similar XRD pattern as that of the commercial powders (NanoActive Cerium Oxide, NanoScale Materials, Inc.), this indicates that their crystal structure is same and their grain sizes are of same order of magnitude. The crystallite size of the particles were also measured by using Scherrer formula; $t = 0.9\lambda/B\cos\theta$, Where, t = Average crystallite size, λ = wavelength of X-rays, θ = the position of the reflection in XRD pattern in degrees, B = integral breadth of a reflection (in radians 2θ) located at 2θ and often calculated by using a solid reference standard, i.e $B^2 = B_s^2 - B_r^2$. The particle size measured from TEM and XRD confirms the nanocrystalline nature of the particles. The XRD patterns of the ceria pellets prepared from the laboratory-made undoped and doped ceria powders are shown in Fig. 2(b). In Fig. 2(b) the peaks are very sharp indicating well crystalline nature of the material compared

Fig. 2 XRD of (a) nanocrystalline ceria powders and (b) ceria pellets

to those in Fig. 2(a) and there is no impurity peak shown except for the microwave-sintered pellet. The XRD data confirms that conventional (resistance heating) sintering produces well crystalline and phase pure CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ pellets.

TEM of the ceria powder

In Fig. 3(a–d) TEM and electron diffraction pattern of the ceria powders synthesized by different routes and different compositions has been shown. The undoped ceria in Fig. 3(a–c) have mean grain-size ~ 5 nm, and the doped ceria in Fig. 3d has a bigger mean grain-size ~ 20 nm. It is noticeable that the electron diffraction patterns in Fig. 3c are similar to the pattern of the commercial ceria powder in Fig. 3a.

The similar smooth diffraction rings in Fig. 3c indicate that the ceria prepared in the laboratory through the hydrothermal synthesis has similar grain homogeneity as the commercial ones. The dark diffraction spots scattered along the rings in Fig. 3b and 3d reflect the presence of some big grain in the powders and the grain evenness is not as perfect as the ones in Fig. 3a and c.

Diffuse reflectance spectra (DRS) of the ceria powder

In Fig. 4 the diffuse reflectance spectra of the undoped and doped ceria synthesized through different routes has been shown. For ceria powders synthesized through the conventional solution route as shown in Fig. 1a exhibited similar DRS patterns as the commercial one, ref. Fig. 4I(a), (b), (c) and (e) for CeO_2 , and Fig. 4II(b) for $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$. However, the powders synthesized through the hydrothermal route in Fig. 1c has an obvious blue shift comparing to the commercial one as shown in Fig. 4(I)-(d) and (f). The ultraviolet absorption is commonly believed a direct charge-transfer transition between O-2p and Ce-4f bands. Due to the quantum size effect, the blue shift is inversely proportional to the nearly square of the particle diameter [22]. In this case, the blue shift of the hydrothermally synthesized ceria in Fig. 4-I-(d) indicates that the ceria synthesized in this work has a smaller mean grain size than the commercial ceria in Fig. 4-I-(e).

SEM of the ceria pellets

Some pellets were made from the nano-crystalline ceria powders. The scanning electron microscopy pictures of the ceria pellets are shown in Fig. 5(a)–(d). Fig. 5(a) and (b) show the sintering temperature effect on the grain size of the doped ceria. The mean grain size of pellet sintered at temperature 1550°C ($\sim 7\ \mu\text{m}$) is about seven times bigger than the one sintered at 1400°C ($\sim 1\ \mu\text{m}$). We also sintered the pellet by using microwave, as shown in Fig. 5(c). The pellet was sintered under microwave at 1200°C for 60 min. The mean grain size is about $0.2\ \mu\text{m}$, which is very small comparing to the upper two conventionally sintered pellets. We also made an undoped ceria pellet sintered at 1550°C as shown in Fig. 5(d). It is noticeable that the grain size is very big, up to $100\ \mu\text{m}$. The mean grain size is about ten times bigger than that of the Gd-doped ceria pellet sintered at the same temperature (comparing Fig. 5(d) to 5(b)).

Fig. 3 TEM of the nanocrystalline ceria powders

Fig. 4 Ultraviolet-Visible diffuse reflectance spectra

Fig. 5 SEM of the ceria pellets

Impedance spectroscopy (EIS) of the ceria pellets

We measured the conductivities of the Gd-doped pellets by ac impedance spectroscopy in air. The transport number is nearly equal to one in air or an inert atmosphere [23]. The Arrhenius relations of conductivity versus temperature are shown in Fig. 6. All the three samples display similar conductivities and Arrhenius slope. Although the grain size of the microwave sintered ceria is as small as submicrometer, the sample (Fig. 6(c)) shows similar conductivity as the conventional sintered and bigger grained $\text{Ce}_{0.8}$

$\text{Gd}_{0.2}\text{O}_{1.9}$ (Fig. 6(a) and (b)). The sample has higher conductivity than the other two samples in the lower temperature region below 600 °C. The sample sintered at 1400 °C has a higher conductivity (1.0×10^{-2} S/cm at 700 °C and 2.4×10^{-2} S/cm at 800 °C) than the sample sintered at 1550 °C, even though the sample has smaller grain or bigger grain-boundary region. It shows the grain-boundary region has negligible contributions to the total resistance of these pellets.

Conclusion

Uniformly nano-grained ceria powders were synthesized at 200 °C by hydrothermal treatment of microwave precipitated precursor from aqueous solution of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and urea. The average grain size (~5 nm) of hydrothermally treated ceria powders is smaller than that of commercial nano-grained ceria (~7 nm) evident from the TEM and DRS studies. The obvious blue-shift in the DRS plot is believed to be caused by smaller nanoscale grain size.

Dense CeO_2 and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ pellets were prepared from the nanocrystalline powders. The pellets sintered by conventional furnace (resistance heating) at 1400 °C and 1500 °C were well-crystallized phase pure. The sample sintered at 1400 °C has ionic conductivities of 1.0×10^{-2} S/cm at 700 °C and 2.4×10^{-2} S/cm at 800 °C. The pellets sintered by microwave oven

Fig. 6 Arrhenius relations of the Ceria pellets

at 1200 °C have submicrometer grain size and secondary phase, which needs higher sintering temperature to achieve better crystallization.

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An exploratory study on solution assisted synthetic routes to prepare nano-crystalline $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$ ($\text{M} = \text{Sr}, \square$; $\text{N} = \text{Mn}, \text{Mg}$) for IT-SOFC applications

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Abstract

Nano-crystalline $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$ ($\text{M} = \text{Sr}; \square$ (vacancy), $x = -0.10$ to 0.15 ; $\text{N} = \text{Mn}, \text{Mg}$; $y = -0.10$ to 0.15) compositions were synthesized by various wet chemical methods. The La- or Ga-deficient compositions are attempted to avoid substitution of aliovalent cations which can facilitate the formation of single phase at relatively low temperature by restoring the nano-crystalline nature of the powders. The wet chemical methods like metal–carboxylate gel decomposition, hydroxide co-precipitation and regenerative sol–gel process followed by microwave sintering in a very short interval time (30 min) of the powders were attempted at $\sim 1200^\circ\text{C}$. The powders were characterized by various techniques like XRD, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The grain size measured was ~ 22 nm range. The electrical conductivities of the compositions were measured by ac and dc techniques. The conductivity of a sintered pellet was found to be ~ 0.01 – 0.21 S cm^{-1} at 550 – 1000°C range, respectively. The influence of process parameters on the properties of the materials based on experimental observations and literature data is discussed. The advantages of nano-crystalline nature of the powders over microcrystalline powders synthesized by the conventional methods of preparation were brought out. The effect of wet chemical methods especially regenerative sol–gel in producing nano-crystalline perovskites with multi-element substitutions at A- and B-sites (of ABO_3) to achieve physico-chemical compatibility for fabricating zero emission all perovskite IT-SOFCs has been reported.

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1. Introduction

There are many obstacles that have to be solved to operate SOFCs at intermediate temperatures, including the performance of electrolyte and electrodes. Lowering the operating temperature is possible with the use of alternative materials, appropriate cell design and manufacturing routes. In the search for dense electrolyte materials, the perovskite-based systems (ABO_3) have been considered as alternative options, particularly because ABO_3 can take on a number of different structures, and can be doped with aliovalent cations on the A- and B-sites [1–12]. They can also accommodate very large concentrations of anion vacancies in some cases cation vacancies into their structures [6]. LaGaO_3 -based perovskite type oxides, in particular Sr- and Mg-doped LaGaO_3 (LSGM), exhibit high oxide

ion conductivity [1–3]. The exceptional structural and chemical compatibility of LSGM electrolyte with $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.9}\text{M}_{0.1}\text{O}_3$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Mn}$) perovskite-based cathode has been studied by Huang et al. [4]. Effects of Co doping to Ga-site of a LaGaO_3 -based perovskite on the oxide ion conductivity was investigated by Ishihara et al. [8]. Oxide ion conductivity increased by doping with Co and it was found that usage of a LaGaO_3 -based perovskite type oxide doped with Sr for the A-site and Co and Mg for the B-site ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_3$ denoted as LSGMC), for the electrolyte of the fuel cell gave a notably large power density at an intermediate temperature of 873 K on a cell using H_2 and O_2 as fuel and oxidant, respectively [8]. Some studies have been reported on the suitability of Ni, Gd-doped CeO_2 cermet as anode with LSGM electrolyte for IT-SOFC [13]. However, Mg, Ca, Sr, Mn, Fe, Co and Ni substituted LaCrO_3 -based perovskite has also been investigated by Sfeir [14] as alternative anodes to Ni-YSZ cermet. Therefore, SOFC with all components made of perovskite is a viable alternative to operate the device at relatively low temperatures ($<800^\circ\text{C}$). By selecting materials

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Fig. 1. Schematic of solid oxide fuel cell with oxide ion conducting electrolyte.

having same crystal structure may help achieving the thermo-physical (thermal expansion, etc.) and chemical compatibility, which will enhance the life of the SOFC device (Fig. 1).

The term perovskite was derived from the atomic arrangement first found in the rare mineral CaTiO_3 [15,16]. The cubic perovskite is referred to as ideal perovskite, and has a unit cell edge of $\sim 4 \text{ \AA}$ containing one ABX_3 formula unit, where the A-site cations are typically larger than the B-site cations and similar in size to the X-site anions. A typical structure is shown in Figs. 2 and 3. Perovskites are of particular interest in advanced materials science because of their stability and the fact that a wide range of properties can be obtained by substituting A and B cations with suitable aliovalent ions in the crystal lattice. Perovskites constitute a large group of materials of technological importance in various fields [17,18]. The versatile crystal structure of perovskites is the key to their fascinating properties. Perovskites stabilize in various crystal systems. The crystal structure of ideal perovskite is cubic, but most of the known perovskites stabilize in orthorhombic, rhombohedral or tetragonal systems. Recently, Mitchell [15] has described in detail the structural aspects of various perovskites. Perovskites (ABX_3) belonging to cubic symmetry, space group $Pm\bar{3}m$ ($P4/m\bar{3}2/m$ #221). In order to have contact between the ions ($R_A + R_O$) should be equal to $\sqrt{2}(R_B + R_O)$, where R_A , R_B and R_O are the respective ionic radii. Goldschmidt [19] defined a tolerance factor, t , to define the limits of stability of the structure.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

The perovskite structure is stable within the range $0.7 < t < 1.00$ with t lying between 0.8 and 0.9 in most cases. The necessity for octahedral coordination by oxygen sets a limit of $0.51 \text{ \AA}$ on the size of the B cation in oxide systems, since any ion smaller than

this does not achieve optimum B–O separation and stabilizes a structure with lower coordination. The tolerance factor and the minimum size of the B ion set a lower bound of $0.90 \text{ \AA}$ on the size of the A cation.

The structure and properties of perovskites can be engineered/tailored by suitably adopting a preparation route [6,16]. The preparation techniques used for the synthesis of perovskites include mainly solid-state reaction and wet chemical methods. The solid-state reaction routes are time consuming and

Fig. 2. The ideal ABX_3 perovskite structure showing the octahedral and cubo-octahedral coordination of the B- and A-site cations, respectively (here $B = \text{Ti}$; $A = \text{Ba}$; $X = \text{O}$).

Fig. 3. Clinographic projection of the unit cell of ABX_3 perovskite in the B-cell setting depicting eight BX_6 octahedra enclosing the A-site cation.

produce microcrystalline materials often with heterogeneous phases on heat-treatment at elevated temperatures. To overcome heterogeneity especially when synthesizing multi-element substituted compositions and to achieve nano-crystalline phase pure powder, solution-based precursor techniques is a pre-requisite. The well-known solution-based techniques are: (i) hydroxide/carbonate/oxalate co-precipitation, (ii) metal-carboxylate gel decomposition and (iii) urea, tartarate, citrate combustion to name a few. The solution-based techniques provide homogeneous mixing in atomic scale and allow the reactants to form product at relatively low temperatures. The metal nitrate-carboxylic acid complexes help in bringing all the reactant ions into a single complex, which decomposes at a specific temperature facilitating the formation of the product.

Among the solution-based routes, dissolving the used $LaGaO_3$ and its doped compositions for recycling the expensive gallium via regenerative sol-gel technique is a new approach which utilizes used gallium compounds instead of pure Ga metal for the reaction precursor. This regenerative sol-gel (RSG) technique has been used for preparation of $Ln_4[Ga_{2(1-x)}Ge_{2x}O_{7+x}\square_{1-x}O_2]$ ($Ln=La, Nd, Gd; x \leq 0.4$) by Chesnaud et al. [20]. Regenerative sol-gel synthesis has also adopted by Bobba et al. [21] to synthesize a few selected rare-earth gallates and its doped compositions. The RSG technique improves the sintering behaviour of the material. Solution precursor via regenerative sol-gel or microwave assisted synthesis can yield homogeneous products with lower processing costs and desired material properties. The solution-based techniques generally yield nano-materials that are useful for the compactness and better-sintered density, which ultimately improves the property of the material. The other aspect which has been emphasized in this article is the preparation of cation-deficient perovskites ($x \leq 0.1$ or $y \leq 0.1$) in the parent $La_{1-x}M_xGa_{1-y}N_yO_{3\pm\delta}$ ($M=Sr; \square, x=-0.10$ to 0.15 ; $N=Mn, Mg; y=-0.10$ to 0.15) lattice to avoid Sr^{2+} substi-

tution at La-sublattice. Though substitution of Sr^{2+} produces charge compensating oxygen vacancies in the crystal lattice of $La_{1-x}Sr_xGaO_3$, the material requires high temperature sintering to dissolve phases like $SrLaGaO_4$ and $LaSrGa_3O_7$ [22] to form a phase pure material. The high temperature heat-treatment led to the loss of nano-crystalline nature of the material. In this paper novel exploratory preparation methods have been described to achieve nano-crystalline rare-earth gallates and aliovalent or iso-valent ion substituted or La-deficient compositions. The influence of regenerative sol-gel route followed by microwave sintering of the products is reported for the first time on $La_{1-x}M_xGa_{1-y}N_yO_{3\pm\delta}$ ($M=Sr; \square$ (vacancy), $x=-0.10$ to 0.15 ; $N=Mn, Ni; y=-0.10$ to 0.15) compositions. The material properties of the products obtained by using other wet chemical methods were compared with the products obtained from RSG. The suitability of regenerative sol-gel and other wet chemical techniques to prepare multi-element substituted perovskites for intermediate temperature solid oxide fuel cell has been discussed.

2. Experimental

2.1. Metal-carboxylates gel decomposition method

Metal nitrate solutions were prepared by dissolving pre-calcined La_2O_3 (at 1000 K for 4 h), Ga and Mn metal powders in 1:1 HNO_3 . The nitrate solution of reactants (i.e. $La(NO_3)_3 \cdot xH_2O$ and $Ga(NO_3)_3 \cdot xH_2O$) were mixed and boiled for 10 min. The concentration of tartaric acid added was three times the mole ratio of $La(NO_3)_3$ and $Ga(NO_3)_3$ (i.e. $La(NO_3)_3:Ga(NO_3)_3:(CHOHCOOH)_2 = 1:1:3$ proportion). The mixed solution was heated on a hot plate (373 K) for 1 h. A cream coloured fluffy mass was obtained with the evolution of brown fumes from the solution mixture. Similar procedure was employed to prepare $LaGaO_3$ and doped compositions by adding sucrose solution, keeping the above mole ratio.

2.2. Co-precipitation of hydroxides

Stoichiometric amounts of La_2O_3 and Ga metal were dissolved in 1:1 HNO_3 . The nitrate solutions of La and Ga were mixed and boiled for 5 min. The solution was diluted and the pH of the solution was brought to 7 by adding NaOH solution. The white precipitate formed was allowed to settle down; then the precipitate was filtered and washed with boiled distilled water till the precipitate was free from sodium. The washed white precipitate was heated at 973, 1273 or 1623 K for 4 h in air. The powders were examined by XRD.

2.3. Regenerative sol-gel synthesis

The regenerative sol-gel method of synthesis uses re-dissolution of the used materials as starting ingredients instead of individual reactants obtained from their respective elements or compounds. Stoichiometric amounts of La_2O_3 , $SrCO_3$, Ga_2O_3 and MgO were taken ground and mixed, pelletized and heat-treated at 1473 K for 24 h. A portion of the product was ground repelletized and again heated at 1673 K for 24 h (this is taken as precursor for regenerative sol-gel synthesis henceforth named as CP1). A known quantity (4.0 gm) of ceramic precursor (CP1) was dissolved in hot doubly distilled water whose pH was adjusted to 0.5–1.0 range. Citric acid ($COOH-CH_2-COH(COOH)-CH_2-COOH$) and glycerol ($HOCH_2-OHCH-CH_2OH$) in 2:1 molar ratio were added to the nitrate solution of CP1. The resulting solution was introduced into a domestic microwave oven equipped with a platinum-sheathed thermocouple and a temperature controller at maximum power (2.45 GHz; 700 W) for 10 min. No turbidity or precipitate was observed at any stage of processing. Microwave treatment transformed the solution first into a gel and then into a dark brown crisp resin. The resin was pulverized, transferred to a porcelain container and introduced into

Fig. 4. Showing the steps followed for the regenerative sol-gel synthesis for the preparation of $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$.

a muffle furnace (Thermolyne, Furnace 6000) for charring and calcination. The temperature of the furnace was raised at $10^\circ\text{C min}^{-1}$ from room temperature to 900°C where it was held for 6 h and allowed to cool down to room temperature at $10^\circ\text{C min}^{-1}$. The product obtained is referred to as sol-gel precursor, SP1. The sol-gel precursor (SP1) was ground, milled with PVA as a binder and uniaxially pressed into 11 mm diameter pellets under a load of 3 tonnes. Some of the pellets were heated in a microwave and others were conventionally heated. One of the pellets was rapidly heated in a microwave at 1200°C for 30 min is referred as SP2. The pellet referred as SP2 is further heated for 30 min in microwave and designated as SP3. The sol-gel precursor (SP1) was ground pelletized and heated conventionally in air at 1400°C for 8 h; the final product is designated as SP4. The pellet CP1 was ground repelletized and conventionally heated in air at 1400°C for 8 h (cumulative 32 h) is designated as CP2. The details of the regenerative sol-gel process for the preparation of $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$ compositions are given as a flow sheet (Fig. 4).

2.4. Characterization of the powders

The powders obtained from all the routes were examined by X-ray powder diffraction, employing a Siemens D-500 or Siemens/Bruker D5000 powder X-ray diffractometer in the step-scan mode, using $\text{Cu K}\alpha$ radiation. XRD pattern of the resinous powder obtained from the decomposition process and powders heat-treated at various temperatures were recorded at 298 K. The heat-treated fine powders were examined by transmission electron microscope (TEM; JEOL 200 CX 200 kV). Electron diffraction pattern of the thin crystallites were recorded by focusing the electron beam perpendicular to the two-, three- or four-fold crystallographic axis.

The infra-red (IR) spectra of the fluffy mass without heat-treatment or heat-treated at 473 and 1000°K were taken in KBr matrix to identify the presence of organic and hydroxyl groups (Bomem, MB-100 FTIR, resolution 4 cm^{-1}). The powders obtained from the decomposition process were examined by TG/DTA (STA-1500, Rheometric Scientific, UK) in order to find out the weight loss characteristics as well as phase transformation, if any, within the programmed temperature range ($298\text{--}1273^\circ\text{K}$). The compositions of the phase pure, doped compounds were confirmed from chemical analysis of the constituent elements.

Electrical conductivity of the samples was measured by dc as well as ac methods in air. The details of the cell arrangement and sample mounting in the cell

are discussed elsewhere [16,23]. The cylindrical pellets of 5 mm diameter and 8 mm length were used to measure the electrical conductivity at $298\text{--}1273^\circ\text{K}$. The total conductivity of the specimens was measured by the dc method. A Solartron 1255 frequency response analyser backed by a Solartron 1286 electrochemical interface was employed for ac measurements. The frequency range covered in a typical experiment was $100\text{ mHz--}10\text{ MHz}$.

2.5. Deposition of LSGM thin film by centrifugation technique using nano-crystalline powders

Thin films of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ on alumina substrates using centrifugation technique were attempted for the first time. Approximately 2 g of sol-gel precursor (SP1) was added to 50 ml of ethylalcohol in a plastic tube and ultra-sonicated for 30 min. Then the suspension was allowed to settle down for an hour. After an hour a cleaned alumina substrate was placed inside the plastic tube and centrifuged at 3500 rpm for 10 min. After that the alumina substrate was transferred to an empty plastic container and spin-dried at 3500 rpm for 5 min. The alumina substrates with the white coating were dried overnight in vacuum at 60°C . The following day 1 alumina substrate was heated in a microwave at 1200°C for 30 min. The other substrate was conventionally heated at 1400°C for 8 h. In both the cases the coating side of the alumina substrate was brown in colour; subsequently the films were characterized by XRD and SEM.

3. Results and discussion

On adding citric acid ($\text{COOH--CH}_2\text{--COH(COOH)--CH}_2\text{--COOH}$) or tartaric (CHOHCOOH)₂ to the metal nitrate solutions, metal nitrate tartarate or citrate complex is formed. These complexes on heat-treatments at $873\text{--}1073^\circ\text{K}$ range of temperature decomposed to yield nano-materials of LSGM and other perovskite compositions. In this method, the loss of constituents from the precursor was completely ruled out because of low temperature heat-treatment and losses due to co-precipitation, filtration, etc., was avoided. This method has

Fig. 5. Room temperature XRD patterns of $\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ prepared by tartarate route, heated at various temperatures in air and cooled to ambient temperature.

been used for preparation of rare-earth manganites [5,16,23–26], gallates [6,27], Sr- and Mg-doped gallates [6,28]. The formation of complex precursor is evident from the broad hump observed in XRD as shown in Fig. 5. The complexation of the metal cations with tartaric acid/citric acid helps in bringing all the reactants to a single or nearly unique boiling and melting point. Therefore, they boil or melt at a particular temperature. On calcining the powders in furnaces at higher temperatures facilitates the growth of crystallites to bigger size. In contrast to solid-state reactions where several grinding, mixing and pelletizing is required to attend homogeneous mixing of the ions. In wet chemical methods, especially carboxylate gel decomposition methods, the in situ exothermic decomposition process provides enough heat to the crystallization process for the crystallites to grow. The nitrate groups provide oxygen for the effective burning of the organic matter. The chemical reaction taking place during the process is

given below.

The gases evolved on calcinations of the precursor were identified by evolved gas analysis–mass spectrometry (EGA–MS) studies [6]. Based on the EGA–MS and TGA–DTA study of the typical rare-earth gallates [6] Eq. (2) has been formulated. The formation of citrate complexes can also be written like Eq. (2). In case of sol–gel route, the complexation of the metal nitrate with the carboxylate ions forms sols and adding glycerol (trihydric alcohol, $\text{HOCH}_2\text{–CHOH–CH}_2\text{OH}$ form gel). The glycerol helps in esterifying the carboxylic acid and subsequently ends up in forming a resin like product. The resin like product does not stick to the wall of the glass (preparation vessel) beaker; hence, it facilitates handling the precursors for further processing.

The XRD pattern of the product obtained on heat-treatment of the resins are given in Fig. 5. The formation of phase pure $\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_3$ and LaGaO_3 at relatively low temperatures (1273 K) are shown in Fig. 4. The formation of phase pure powders at low temperatures as compared to conventional methods of preparation is attributed to the provision of heat (in situ) by exothermic decomposition of the metal–carboxylate complexes. The formation of La-deficient compositions indicates accommodation of cation vacancy (10% vacancy) in the lattice. This was confirmed from XRD analysis of the powders by showing absence of Ga as Ga_2O_3 phases in the XRD pattern. The TEM examination showed the phase pure powders

(a)

(b)

Fig. 6. (a) TEM micrograph of LaGaO_3 prepared by tartarate route heat-treated at 1073 K/4 h in air. (b) Electron diffraction pattern of $\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_3$ powder prepared by tartarate-gel decomposition, heated at 1023 K/4 h in air.

of $(\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_3)$ are nano-crystalline in nature and the particle size measured is found to be ~ 22 nm (Fig. 6). The crystallite size of the particles were also measured by using Scherrer formula

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (3)$$

where t is the average crystallite size, λ the wavelength of X-rays, θ the position of the reflection in XRD pattern in degrees and B is the integral breadth of a reflection (in radians 2θ) located at 2θ and often calculated by using a solid reference standard, i.e. $B^2 = B_s^2 - B_r^2$. The particle size measured from TEM and XRD confirms the nano-crystalline nature of the particles. The corresponding electron diffraction pattern of the powders shows a cubic square net. Hence, it can be inferred based on XRD (Fig. 5) and TEM studies that the compound prepared is having a cubic crystal structure with a unit cell constant of $3.88(1)$ Å.

The regenerative sol–gel technique is a novel technique which is basically a sol–gel process but it has been adopted to recycle the used rare-earth gallates to overcome the lengthy process of Ga metal dissolution (takes 3 days to dissolve) in concentrated HNO_3 followed by addition of HF. Since Ga is a costly metal, if it can be recycled from the used products or rejected products while fabricating the thick films of LSGM for SOFC devices. The regenerative sol–gel process is being operated at low temperatures; therefore, the loss of Ga due to high temperature sintering can also be avoided. The flow sheet given in Fig. 4 shows the sequence of steps to be followed for the preparation of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3\pm\delta}$ compositions. The XRD pattern (Fig. 7a) of the pellet prepared from solid-state reaction at 1473 K/24 h and further heated at 1673 K/24 h (CP1) shows formation of the product but with presence of un-reacted phases (LaSrGaO_4 , $\text{LaSrGa}_3\text{O}_7$ and MgO). This indicates that even after heating the powders/pellets to such high temperatures does not yield formation of single phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM). The XRD pattern (Fig. 7b) of the pellet prepared by solid-state route and heated for cumulative 32 h produced LSGM with less unreacted phases.

In contrast to ceramic precursor (CP1 and CP2); regenerative sol–gel precursor (SP1, precursor charred at $900^\circ\text{C}/6$ h) whose XRD pattern given in Fig. 8a was heat-treated by microwave with SiC as microwave susceptor yielded the composition with better phase purity within 1 h (Fig. 8b and c). The darkening of the pellet is an indication of phase formation and concomitant densification. The XRD pattern of Fig. 8b shows the evolution of phase on microwave heating of the precursor. Further heating of SP2 improves the phase purity of the product. These observations when compared with the sintering and phase evolution behaviour of ceramic powders (CP1 and CP2) that indicated microwave synthesis have better advantages than conventional/resistive heating methods for these compositions. However, the precursor (SP1, prepared by RSG) on sintering by conventional heating formed the single phase material (Fig. 8d) within 8 h. This can be attributed to the effect of regenerative sol–gel process which produces nano-crystalline particles at relatively low temperature of heat-treatment and yield the product.

Fig. 7. XRD pattern of precursor obtained from solid-state reaction: (a) powders heated at $1200^\circ\text{C}/24$ h called CP1 and (b) CP1 pellets ground repelletized heated at $1400^\circ\text{C}/32$ h called CP2.

The sintering behaviour of the materials prepared from the various routes was examined by scanning electron microscopy (SEM). The SEM micrographs of CP1, CP2 (Fig. 9a and b), SP1, SP2, SP3 and SP4 are given in Figs. 10 and 11. In Fig. 9a, the surface morphology of the pellet CP1 shows no uniform grains with an average grain size of $5\ \mu\text{m}$. In Fig. 9b, the SEM micrograph of pellet CP2 (CP1 pellet ground repelletized and heated at $1400^\circ\text{C}/32$ h) shows better close packing of grains with less pores and a grain size of $8\ \mu\text{m}$. This is attributed to the effect of higher annealing temperature, that makes the small grains to coalesce and form bigger grains and inter grain pores are minimized. The density of the CP2 pellet increases from 88% (at $1200^\circ\text{C}/24$ h) to 93% (at $1400^\circ\text{C}/32$ h) theoretical density.

In Fig. 10a, sol–gel precursor heated at $900^\circ\text{C}/6$ h (SP1) shows an average grain size of $100\ \mu\text{m}$ with uneven grain-size distribution. In Fig. 10b, the sample pellet SP2 which is obtained on heating SP1 at 1200°C for 30 min by microwave

Fig. 8. XRD of: (a) SP1 obtained by calcining regenerative sol–gel (RSG) precursor in air at 900 °C/6 h; (b) SP1 obtained by microwave heating of RSG precursor (SP1) at 1200 °C/30 min; (c) SP3 obtained by microwave heating of RSG precursors (SP2) at 1200 °C/1 h; (d) SP4, obtained by conventional heating of RSG precursor (SP1) at 1400 °C/8 h.

shows merger of grains and closing of space between the grains. Fig. 10c shows the microstructure of SP3 pellet (SP2 heated at 1200 °C/1 h by microwave) indicating the closeness of the grains, however some inclusion like porous spots are observed on

the surface. These porous spots may be $\text{LaSrGa}_3\text{O}_7$ as detected by XRD. The exact composition of these impurity phases need to be quantized by EDAX. Fig. 11a and b shows the pore free smooth microstructure of the pellet (SP4) with an average grain

Fig. 9. SEM micrograph of: (a) CP1 (2000 magnification) and (b) CP2 (3000 magnification).

Fig. 10. SEM micrograph of: (a) SP1 (RSG precursor heated 900 °C/6 h; 200 magnification), (b) SP2 (microwave heated at 1200 °C/30 min; 5000 magnification) and (c) SP3 (microwave heated at 1200 °C/1 h; 2000 magnification).

Fig. 11. SEM micrograph of SP4 (conventionally sintered at 1400 °C/8 h): (a) 2000 magnification and (b) 550 magnification.

Fig. 12. LSGM thin film conventionally sintered LSGM film on alumina substrate: (a) 2000 magnification and (b) showing a pit on the film. (c) SEM microwave sintered LSGM film on alumina substrate (2000 magnification).

size of 10 μm . This indicates the effect of sintering on the precursor SP1 at 1400 $^{\circ}\text{C}/8\text{ h}$ by conventional heating. The sintering behaviour of the pellets was also confirmed from the density measurement. The pellets obtained from RSG achieved 98% theoretical density whereas the pellets obtained from conventional route attained 93% theoretical density. The lower density of the pellets may be attributed to the loss of oxygen because of prolonged heat-treatment at higher temperatures and presence of minor phases.

The thin film prepared by centrifugation technique with microwave sintering achieved better microstructure with minimum pores. The grain size measured from SEM studies is found to be 10 μm (Fig. 12a and b). Fig. 12b shows there are several pits on the resistively/conventionally sintered LSGM film surface on the alumina substrate. Fig. 12c is the SEM pictures of microwave sintered LSGM films on alumina substrates. The preliminary experiments have shown that the quality and the thickness of the film depend on several parameters: (a) the nature of solvent, (b) the strength of the suspension, (c) centrifugation rate and (d) duration of centrifugation.

Fig. 13 shows the $\log(\sigma T)$ versus $1/T$ plots of several compositions prepared by wet chemical methods. The conductivities fall in the 0.01–0.21 S cm^{-1} at 600–1000 $^{\circ}\text{C}$. The activation energy of electrical conduction estimated from the Arrhenius plot of these compositions were $\sim 1.00\text{ eV}$. The activation energy of conduction shows that these materials are oxide ion conductors. The variation of electrical conductivities among the various compositions attributed to the variation of chemical compositions and preparation routes. The lowest conductivity observed in case of LaGaO_3 is attributed to lower concentration of anion vacancies in the lattice. The highest ionic conductivity observed in case of LSGM, which are known to have higher concentration of anion vacancies. The substitution of Mn at Ga-sublattice introduces electronic conduction in the lattice and makes the material a mixed conducting one. Further work is on the way to study the electrical conductivity of the films prepared by microwave sintering and bulk pellets which will be treated separately.

4. Conclusions

The wet chemical methods of synthesis play an important role in the synthesis of nano-perovskites. The desired properties of the materials can be engineered with multi-valent substitution with phase pure material at relatively low temperature of heat-treatment. The regenerative sol–gel technique can be effectively used to recycle the rare-earth gallates in nano-form. Nano-crystalline perovskites can yield high dense thin film with microwave sintering. The nano-crystalline perovskites with mixed conducting properties for SOFC cathode and perovskites oxides compatible with LSGM cathode can be suitably synthesized in bulk as well as thick/thin membranes by using wet chemical methods.

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Fig. 13. $\log(\sigma T)$ vs. $1/T$ of LaGaO_3 and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ in air.

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**EFFECT OF SONOCHEMICAL, REGENERATIVE SOL GEL, AND MICROWAVE ASSISTED
SYNTHESIS TECHNIQUES ON THE FORMATION OF DENSE ELECTROLYTES AND POROUS
ELECTRODES FOR ALL PEROVSKITE IT-SOFCs.**

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Abstract

The influence of preparation techniques on the microstructure, grain-size and consequently on the electrical transport properties of the ABO_3 structured materials used as electrode and electrolytes in all perovskite IT-SOFC were investigated. Nano-crystalline powders of $La_{1-x}M_xGa_{1-y}N_yO_{3\pm\delta}$ ($M = Sr, \square$; $x = 0.10$ to 0.15 ; $N = Mg$; $y = 0.10$ to 0.15) (LSGM) as electrolyte, porous $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3\pm\delta}$ (LSCF) or $LaNi_{1-x}Fe_xO_{3\pm\delta}$ ($x=0-0.5$) (LNF) as cathode, $La_{0.8}Sr_{0.2}Cr_{0.7}Mn_{0.3}O_{3\pm\delta}$ (LSCM) as anode and $LaCrO_3$ or substituted $LaCrO_3$ as interconnect were synthesized by various wet chemical methods. The wet chemical methods like metal-carboxylate gel decomposition, hydroxide co-precipitation, sonochemical and regenerative sol-gel process followed by microwave sintering of the powders have been used. Microwave sintering parameters were optimized by varying sintering time, and temperature to achieve higher density of LSGM pellets. The phase pure systems were obtained at sintering duration of 30 min at 1200°C . The XRD, HR-TEM, and SEM measurements revealed the average grain size of these perovskites was ~ 22 nm range. The electrical conductivities of the compositions were measured by ac (5Hz-13MHz) and dc techniques. The conductivity of the sintered pellets was found to be ~ 0.01 - 0.21 S/cm at 550 - 1000°C range for electrolyte and 1.5 - 100 S/cm at 25 - 1000°C for electrodes respectively. The effect of sonochemical, and regenerative sol-gel methods in processing large quantities of nano-crystalline perovskites with multi-element substitutions at A- and B-sites to achieve physico-chemical compatibility for fabricating zero emission all perovskite IT-SOFCs are reported in this paper.

Keywords: Regenerative sol-gel synthesis, Nano-perovskite oxides, IT-SOFC, Ionic conductivity

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1. INTRODUCTION

An overall trend in the anode supported planar SOFC technology is to reduce the module temperature, to alleviate material and modular design constraints, to reduce materials and systems cost, and to increase materials life time and thermodynamic efficiency. The all perovskite stack will be comparable or cheaper based on the materials selected for the SOFC components and the process chosen to fabricate the components. The advantage with all perovskite stacks is that it will be free from corrosion even after several cycles of operations at higher temperature. However, perovskite oxide-interconnects in all perovskite-SOFC will not have good thermal and mechanical properties in comparison to metal bipolar plates. Metal bipolar plates can also be an option as interconnect material in SOFCs to be used with intermediate temperature oxide ion or proton conducting perovskite as an electrolyte. This combination can bring down the over all operating temperature of SOFC, thereby making it intermediate temperature –SOFC (IT-SOFC). The schematic of all perovskite IT-SOFC is shown in Figure 1. One of the main advantages of this design is the ability to use conventional fuels, such as natural gas (usually $H_2 + CO$, or CH_4). Hydrogen would be preferred fuel cell feed. The fuel enters the anode chamber and gets oxidized. Oxygen enters the cathode chamber, reduced by the cathode material to oxide ion and gets transported through the electrolyte to the anode. The porous anode serves to provide electrochemical reaction sites for oxidation of the fuel (H_2 or natural gas) and byproducts to be delivered and removed from the surface sites, and to provide a path for electrons to be transported from the reaction sites to the interconnect in SOFC stacks. The electrolyte prevents the two electrodes from coming into electronic contact by blocking the electrons and allows the flow of oxygen ions to maintain the overall electrical charge balance.

Therefore, to address the challenge of reducing high temperature operation to below or within 700-800 °C, significant efforts have been directed towards the development of undoped and doped perovskite based systems (ABO_3) to be used as anode, electrolyte, cathode, and interconnect in SOFCs. The $LaGaO_3$ -based perovskite, in particular Sr- and Mg doped $LaGaO_3$ (LSGM), exhibit high oxide ion conductivity [1-3], supposed to be a popular candidate as an electrolyte in IT-SOFCs. It has exceptional structural and chemical compatibility with mixed conducting perovskites (materials which carry both oxygen ions and electrons) such as lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium ferrite (LSF), lanthanum nickel ferrite ($LaNi_{0.7}Fe_{0.3}O_{3\pm\delta}$) and $La_{1-x}Sr_xFe_{1-y}Co_yO_{3\pm\delta}$, $LnCoO_3$ $Ln=La, Gd, Sm, Nd$,

$\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$) are considered as candidate cathodes and anodes for IT-SOFC applications respectively[1-14]. For interconnects, chromia-forming ferritic stainless steels are the most promising candidates due to their good thermal expansion match with other SOFC components. Metal bipolar plates have higher electronic conductivity and can be a preferred material as interconnect at intermediate temperatures of operation of SOFC. But at higher temperature of operation metal bipolar plate will be prone to corrosion. However, it is possible to lower the operating temperature and enhance life of the device with the use of perovskite type oxide materials which can be tailored to exhibit high electronic conductivity (comparable to metals) as interconnect and high ionic conductivity for the electrolyte and mixed conductivity for the electrodes at temperatures $<700^\circ\text{C}$. This may be possible to fabricate a cell by selecting materials having the similar crystal structure, compatible thermo-physical and chemical properties.

The crystal structure of ideal perovskite is cubic, but most of the known perovskites stabilize in orthorhombic, rhombohedral or tetragonal systems. The ABO_3 crystal structure in which, the A-cations are surrounded by 12 anions in cubo-octahedral coordination and the B cations are surrounded by 6 anions in octahedral coordination. The O anions are coordinated by two B site cations and 4 A-site cations [15-18]. The stability of the structure arises mainly from the electrostatic (Madelung) energy, so that the relative sizes of the “A” and “B” cations are important. In order to have contact between the ions, (R_A+R_O) should be equal to $\sqrt{2} (R_B+R_O)$, where R_A , R_B and R_O are the respective ionic radii. Goldschmidt [19] defined a tolerance factor, t , to define the limits of stability of the structure.

$$t = (R_A+R_O) / \sqrt{2}(R_B+R_O) \quad (1)$$

The perovskite structure is stable within the range $0.7 < t < 1.00$ with t lying between 0.8 and 0.9 in most cases.

Tailoring of properties of perovskites is possible because of its versatile structure to substitution. The microstructure, grain size and nature of point defects are influenced by the preparation (sintering) conditions and the starting ingredients used to synthesize the material. Solution assisted synthetic methods will also have influence on the selectivity of substitution of a particular element and influence on the microstructure, sinter density and hence on electrical transport properties of the materials. The solid state reaction and wet chemical methods used for the synthesis of perovskite powders have profound influence on the physico-chemical properties of these materials. The solid state reaction routes are

believed to be primitive and produce microcrystalline materials often with heterogeneous phases on heat-treatment at elevated temperatures. The solid state route results in hard agglomerates and coarser grains which inhibit sintering to obtain dense electrolyte materials. The ball milling of hard agglomerates may cause contamination from the milling and grinding medium. Whereas the solution technique, providing homogeneity at molecular level, is maintained at all levels of processing, will enable synthesis of these oxides at lower temperature and consequent higher densification. Since solution techniques result in soft agglomerates, ball milling if employed will cause no contamination. Water is a benign solvent and preferable for large scale synthesis. Therefore development of aqueous solution techniques which make use of cheaper precursors will be of great advantage.

To overcome heterogeneity and to achieve nano-crystalline phase pure powder solution based precursor techniques is a pre-requisite. The well-known solution based techniques [6,16] are (i) hydroxide/carbonate/oxalate co-precipitation (ii) metal carboxylate gel decomposition such as, urea, tartarate, citrate gel combustion (iii) hydrothermal etc. to name a few. The solution-based techniques provide homogeneous mixing in atomic scale and allow the reactants to form product at relatively low temperatures. The metal nitrate-carboxylic acid complexes help in bringing all the reactant ions into a single complex, which decomposes at a specific temperature facilitating the formation of the product. The hydrothermal or gel to crystallite techniques can be used to prepare proton conducting perovskites.

Recently, regenerative sol-gel (RSG) synthesis has been reported for the synthesis of germanium based apatites where the products obtained from the solid state route were recycled to regenerate the same product by solution technique at a much lower temperature with improved properties compared to that obtained from the solid state method [6]. The RSG technique is a novel technique which basically a sol-gel process but it has been adopted to recycle the used rare-earth gallates to overcome the lengthy process of Ga-metal dissolution (takes 3 days to dissolve) in concentrated HNO_3 followed by addition of HF. Since Ga is a costly metal, if it can be recycled from the used or damaged products or rejected products while fabricating the pellets/thick films of LSGM for SOFC devices. The regenerative sol-gel process is being operated at low temperatures; therefore the loss of Ga due to high temperature sintering can also be avoided. Amongst the synthetic techniques, the use of microwaves as energy source for synthesis and sintering has aroused substantial amount of interest due to shorter processing time for those materials which effectively couple with microwaves either at room temperature or elevated

temperature. The sol-gel synthesis and microwave sintering of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.825}$ ($x+y>0.35$) has been reported using costly gallium metal as a precursor [7]. Highly sintered mixed phase sample was obtained by microwave processing at 1500°C for 10 mins. The RSG technique has been used for preparation of $\text{Ln}_4[\text{Ga}_{2(1-x)}\text{Ge}_{2x}\text{O}_{7+x}\square_{1-x}\text{O}_2]$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}; x \leq 0.4$) by Chesnaud et al. [20]. To the best of our knowledge there are no reports on recycling of old LSGM samples to obtain new samples of same composition but with different properties. In view of increasing importance to produce dense LSGM ceramics on a large scale with better phase purity at lower temperatures in a cost effective manner for use as electrolytes, an investigation was carried out to study the effect of conventional and microwave assisted sintering of the recycled LSGM samples obtained from RSG route which is a combination of solidstate reaction and Pechini-type method.

The ultra-sonication assisted reaction for the preparation of perovskite oxides is carried out in case of precursors chosen as hydroxide gels or mixture of hydroxide gels followed by hydrothermal treatment of the reaction mixture. The co-precipitated hydroxides of the constituent reactants taken in stoichiometric concentrations were sonicated in an ultra sonic source (40kHz, 60W) for 30-60 minutes or else can be irradiated with high power ultrasonic source (i.e $>40\text{-}750\text{ W}$). During the sonication process, ultrasound sources produce pressure waves with a frequency of 20,000 to 1,00,000 Hz. Ultrasonic irradiation of liquids produce acoustic cavitation (the formation, growth and implosive collapse of bubbles) and provide the primary mechanism for sonochemical effects. During cavitation, bubble- collapse produces intense local heating; high pressures followed by extremely rapid cooling [21-23] can produce temperatures as high as 5000°C (locally). These waves exert pressure on the suspended sol-gel particles in the solution to undergo numerous collisions with each other and mix homogeneously to avoid agglomeration of the same type of reactants. The collision of the reactants and the solvent molecules generate temperature, which facilitate the diffusion of ions (cations and anions) facilitating the formation of the product. The perovskite compositions were synthesized by various methods to tailor required properties of the component materials of all IT-SOFC and their microstructural and electrical transport properties were studied. The results of the experimental observations are discussed in this paper.

2. EXPERIMENTAL

2-1 Metal-Carboxylates gel decomposition method.

Metal nitrate solutions were prepared by dissolving pre-calcined La_2O_3 (at 1000 K for 4 h), Ga- and Mn- metal powders in 1:1 HNO_3 . The nitrate solution of reactants (i.e $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) were mixed and boiled for 10 minutes. The concentration of tartaric acid added was three times the mole ratio of $\text{La}(\text{NO}_3)_3$ and $\text{Ga}(\text{NO}_3)_3$. (i.e $\text{La}(\text{NO}_3)_3 : \text{Ga}(\text{NO}_3)_3 : (\text{CHOHCOOH})_2 = 1:1:3$ proportion). The mixed solution was heated on a hot plate (373 K) for 1 h. A cream coloured fluffy mass was obtained with the evolution of brown fumes from the solution mixture. Similar procedure was employed to prepare LaGaO_3 and doped compositions by adding sucrose solution, keeping the above mole ratio.

2-2 Co-precipitation of hydroxides

Stoichiometric amounts of La_2O_3 and Ga-metal were dissolved in 1:1 HNO_3 . The nitrate solutions of La and Ga were mixed and boiled for 5 minutes. The solution was diluted and the pH of the solution was brought to 7 by adding NaOH solution. Ultrasonic sources (power 60 Watt) were used to mix the precipitate thoroughly. The white precipitate formed was allowed to settle down; then the precipitate was filtered and washed with boiled distilled water till the precipitate was free from sodium. The washed white precipitate was heated at 973, 1273 or 1623 K for 4 h in air. The powders were examined by XRD.

2-3 Regenerative Sol-Gel synthesis

The regenerative sol-gel (RSG) method of synthesis uses re-dissolution of the used materials as starting ingredients instead of individual reactants obtained from their respective elements or compounds. Stoichiometric amounts of La_2O_3 , SrCO_3 , Ga_2O_3 MgO were taken ground and mixed, pelletized and heat-treated at 1473 K for 24 hs. A portion of the product was ground repelletized and again heated at 1673 K for 24 hs (this is taken as precursor for regenerative sol-gel synthesis henceforth named as CP1). A known quantity (4.0 gm) of ceramic precursor (CP1) was dissolved in hot doubly distilled water whose pH was adjusted to 0.5-1.0 range. Citric acid ($\text{COOH}-\text{CH}_2-\text{COH}(\text{COOH})-\text{CH}_2-\text{COOH}$) and glycerol ($\text{HOCH}_2-\text{OHCH}-\text{CH}_2\text{OH}$) in 2:1 molar ratio were added to the nitrate solution of CP1. The resulting solution was introduced into a domestic microwave oven equipped with a platinum-sheathed thermocouple and a temperature controller at maximum power (2.45GHz; 700W) for 10min. No turbidity or precipitate was observed at any stage of processing. Microwave treatment transformed the solution first into a gel and then into a dark brown crisp resin. The resin was pulverized, transferred to a porcelain container and introduced into a muffle furnace (Thermolyne, Furnace 6000) for charring and calcination. The

temperature of the furnace was raised at 10°C/min from room temperature to 900°C where it was held for 6h and allowed to cool down to room temperature at 10°C/min. The product obtained is referred to as sol-gel precursor, SP1. The sol-gel precursor (SP1) was ground, milled with PVA as a binder and uniaxially pressed into 11mm dia pellets under a load of 3 tons. Some of the pellets were heated in a microwave and others were conventionally heated. One of the pellets was rapidly heated in a microwave at 1200°C for 30 minutes is referred as SP2. The pellet referred as SP2 is further heated for 30 minutes in microwave and designated as SP3. The sol-gel precursor (SP1) was ground pelletized and heated conventionally in air at 1400°C for 8h; the final product is designated as SP4. The pellet CP1 was ground repelletized and conventionally heated in air at 1400°C for 8h is designated as CP2. The details of the regenerative sol-gel process for the preparation of $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$ compositions are given as a flow sheet (Fig.2).

2- 4 Glycine nitrate combustion method

Stoichiometric concentrations of metal nitrates all from M/s. Aldrich were taken and dissolved in deionized water. Ultrasonication was done to achieve complete homogenization of the reaction mixture. To the mixed reactant solution glycine ($\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$) powder was added and the entire content was heated on a hot plate (~100°C). The solution froth and fumed then burned into flame yielding fine powders of LNF, LSCF. The same technique is used for all the substituted compositions of cathode and anode materials.

2-5 Characterization of the powders

The powders obtained from all the routes were examined by X-ray powder diffraction, employing a Siemens D-500 or Siemens/Bruker D5000 powder X-ray diffractometer in the step- scan mode, using CuK_α radiation. XRD pattern of the resinous powder obtained from the decomposition process and powders heat-treated at various temperatures were recorded at 298 K. The heat-treated fine powders were examined by transmission electron microscope (TEM; JEOL 200 CX 200 kV). Electron diffraction pattern of the thin crystallites were recorded by focusing the electron beam perpendicular to the 2, 3 or 4-fold crystallographic axis.

Electrical conductivity of the samples was measured by DC as well as AC methods in air. The details of the cell arrangement and sample mounting in the cell are discussed elsewhere [16, 24]. The cylindrical pellets of 5 mm diameter and 8 mm length were used to measure the electrical conductivity at

298-1273 K. The total conductivity of the specimens was measured by the DC method. A Solartron 1255 frequency response analyser backed by a Solartron 1286 electrochemical interface was employed for AC measurements. The frequency range covered in a typical experiment was 100 mHz to 10 MHz.

2-6 Deposition of LSGM thin film by centrifugation technique using nano-crystalline powders.

Thin films of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ on alumina substrates using centrifugation technique were attempted for the first time. Approximately 2g of sol-gel precursor (SP1) was added to 50ml of ethylalcohol in a plastic tube and ultra-sonicated for 30 mins. Then the suspension was allowed to settle down for an hour. After an hour a cleaned alumina substrate was placed inside the plastic tube and centrifuged at 3500 RPM for 10 minutes. After that the alumina substrate was transferred to an empty plastic container and spin-dried at 3500RPM for 5 minutes. The alumina substrates with the white coating were dried overnight in vacuum at 60°C. The following day one alumina substrate was heated in a microwave at 1200°C for 30 mins. The other substrate was conventionally heated at 1400°C for 8h. In both the cases the coating side of the alumina substrate was brown in color; subsequently the films were characterized by XRD and SEM.

3. RESULTS AND DISCUSSIONS

There are various carboxylate complexing agents that are used for the preparation of perovskite powders from the constituent reactants. The citric and tartaric acids are some of them. On adding citric acid ($\text{COOH-CH}_2\text{-COH(COOH)-CH}_2\text{-COOH}$) or tartaric (CHOHCOOH)₂ to the metal nitrate solutions, metal nitrate tartarate or citrate complex is formed. These complexes on heat-treatments at 873–1073 K range of decomposed to yield nano-materials of LSGM and other perovskite compositions. In this method, the loss of constituents from the precursor was completely ruled out because of low temperature heat-treatment and losses due to co-precipitation, filtration etc. was avoided. This method has been used for preparation of rare-earth manganites [5, 16, 24-26] gallates [6] Sr and Mg doped gallates [6,27]. The formation of complex precursor is evident from the broad hump observed in XRD pattern as shown in Fig. 3. The complexation of the metal cations with tartaric acid/citric acid helps in bringing all the reactants to a single or nearly unique boiling and melting point. Therefore the reactant complexes decompose or boil or melt at a particular temperature. On calcining the precursor powders in furnaces at higher temperatures facilitates the growth of crystallites to bigger size. In contrast to solid state reactions where several grinding, mixing and palletizing is required to attend homogeneous mixing of the ions. In wet chemical

methods, especially carboxylate gel decomposition methods, the insitu exothermic decomposition process provide enough heat for the crystallites to grow. The problem associated with the combustion synthesis is the control over the crystallization process. However, the combustion process can be controlled by using lower or calculated amounts of fuel that avoids the sudden ignition of the reactant mixtures to higher temperatures. In this combustion process nitrate groups provide oxygen for the effective burning of the organic matter. The chemical reaction taking place during the process is given below.

The gases evolved on calcinations of the precursor were identified by evolved gas analysis – mass spectrometry (EGA-MS) studies [6]. Based on the EGA-MS and TGA-DTA study of the typical rare-earth gallates [6] the equation 2 has been formulated. The formation of citrate complexes can also be written like equation 2. In case of sol-gel route, the complexation of the metal nitrate with the carboxylate ions forms sols and adding glycerol (trihydric alcohol, HOCH₂-CHOH-CH₂OH form gel). The glycerol helps in esterifying the carboxylic acid and subsequently ends up in forming a resin like product. The resin like product does not stick to the wall of the glass (preparation vessel) beaker; hence it facilitates handling the precursors for further processing.

The XRD pattern of the product obtained on heat-treatment of the resins are given in Fig. 3. The formation of phase pure and LaGaO₃ at relatively low temperatures (1273 K) are shown in Fig.3. The formation of phase pure powders at low temperatures as compared to conventional methods of preparation is attributed to the provision of heat insitu by exothermic decomposition of the metal carboxylate complex. The formation of La-deficient compositions indicates accommodation of cation vacancy (10 % vacancy) in the lattice. This was confirmed from XRD analysis of the powders by showing absence of Ga as Ga₂O₃ phases in the XRD pattern. The TEM examination showed the phase pure powders of (La_{0.9}Ga_{0.9}Mn_{0.1}O₃) are nano-crystalline in nature and the particle size measured is found to be ~22 nm (Fig. 4). The crystallite size of the particles were also measured by using Scherrer formula

$$t = 0.9\lambda / B \cos\theta \quad (2)$$

Where, t = Average crystallite size, λ = wavelength of X-rays, θ = the position of the reflection in XRD pattern in degrees, B = integral breadth of a reflection (in radians 2θ) located at 2θ and often calculated by using a solid reference standard, i.e $B^2 = B_s^2 - B_r^2$. The particle size measured from TEM and XRD confirms the nano-crystalline nature of the particles. The corresponding electron diffraction pattern of the powders shows a cubic square net. Hence it can be inferred based on XRD (Fig.3) and TEM studies that the compound prepared is having a cubic crystal structure with a unit cell constant of 3.88 (1) Å.

The glycine ($H_2NCH_2CO_2H$) –nitrate gel decomposition is another method which has been used to prepare $LaNi_{0.7}Fe_{0.3}O_3$ (LNF). The glycine molecules form complexes with the metal nitrates to form metal nitrate-glycine complexes. The complex on heating at $100^\circ C$ (on a hot plate) undergoes exothermic decomposition yielding the precursor. The precursor on further calcinations at $750-800^\circ C$ forms the product. The effects of calcinations on the evolution of phases are characterized by XRD and are given Fig. 5(a) for $LaNi_{0.7}Fe_{0.3}O_3$. The XRD patterns (Fig.5 (a)) shows the formation of the phase pure material at $800^\circ C$ from the precursor phase (shown as broad humps in the XRD pattern). The nano-crystalline nature of the powder was examined by TEM as shown in Fig. 5(b). The particle size measured is ~ 20 nm.

The regenerative sol-gel technique is a novel technique which basically a sol-gel process but it has been adopted to recycle the used rare-earth gallates to overcome the lengthy process of Ga-metal dissolution (takes 3days to dissolve) in concentrated HNO_3 followed by addition of HF. Since Ga is a costly metal, if it can be recycled from the used products or rejected products (defective or damaged pellets/films) while fabricating the thick films of LSGM for SOFC devices before assembling the components. However, the used and assembled components of SOFC can be used as raw materials, but it may need to be reprocessed to remove unwanted contaminants, thereby making the process more complicated and time consuming. In the other hand it has its own advantages like, the RSG process is being operated at low temperatures; therefore the loss of Ga due to high temperature sintering can also be avoided. The flow sheet given in Fig.2 shows the sequence of steps to be followed for the preparation of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3\pm\delta}$ compositions. The XRD pattern (Fig. 6a) of the pellet prepared from solid state reaction at 1673 K/ 24h (CP1) shows formation of the product but with presence of un-reacted phases. This indicates that even after attaining such high temperatures does not yield formation of single phase $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM). The XRD pattern (Fig.6b) of the pellet prepared by solid state but heated for a cumulative 32 h produced LSGM with less unreacted phases. In contrast to ceramic

precursor (CP1, CP2); regenerative sol-gel precursor (SP1, precursor charred at 900°C/6h) was heat-treated by microwave with SiC as microwave susceptor yielded the composition with better phase purity within 1 hour. The darkening of the pellet is an indication that phases formation and densification has occurred concomitantly. The further heating of SP2 improves the phase purity of the product. These observations when compared with the sintering and phase evolution behavior of ceramic powders (CP1, CP2) it indicates that microwave synthesis have better advantages than conventional/resistive heating methods for these compositions. However, the precursor (SP1, prepared by RSG) on sintering by conventional heating formed the single phase material within 8h. This can be attributed to the effect of regenerative sol-gel process which produces nano-crystalline particles at relatively low temperature of heat-treatment and yielding the product.

The sintering behaviour of the materials prepared from the various routes was examined by Scanning electron microscopy (SEM). The SEM micrographs of CP1, CP2, SP1, SP2, SP3, SP4 are given in Fig.7. The pellets prepared from conventional route with resistive heating does not yield phase pure LSGM or its doped composition with a heating duration of 24 h. The pellets prepared by regenerative sol-gel technique produce nano-crystalline powders which has better sintering properties. This may be attributes to the uniform and nano-crystalline particles obtained in the precursor stage by regenerative sol-gel technique. This is further evident from the surface morphology of the pellets in the SEM shown in Fig. 7 (a-d). The SEM picture of LSGM-2015 pellet obtained from the powders by solid state reaction route and re-sintered at 1400°C/8h (Fig. 7a) shows the sample has grains of 5~10 μm . The smaller grains coalesce together on sintering with thin grain boundaries and plenty of cavities inside the material. On the contrary, the SEM micrograph of the pellet (LSGM-2015) obtained from RSG precursor as shown in Fig. 7b has a highly compact microstructure. The crystal grains closely contact to each other with distinct grain boundaries. Ninety percent of the grains are in the range of 1~5 μm . Similarly, the LaGaO₃ pellet obtained from the solid-state route powders has plenty of cavities occupying high percentage of the material volume (Fig. 7c), However, LaGaO₃ pellet made from RSG route has compact microstructure (Fig. 7d). The similar grain sizes for the LaGaO₃ and the LSGM-2015 shown in Fig. 7a and 7c, as well as in Fig. 7b and 7d, indicate the two materials have similar diffusion coefficients even though they have different compositions.

The thin film prepared by centrifugation technique with microwave sintering achieved better microstructure with minimum pores. The grain size measured from SEM studies is found to be 10 μm (Fig.8) SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ film on alumina substrate (a) first cycle of sintering at 1200°C/8 h (b) 1200°C/16h (c) 1400°C/8h (d) 1500°C/8h. Fig.8(a) shows the surface of the film sintered at 1200°C/8 h and subsequently the film was sintered for 16h at 1200°C (Fig. 8(b)) and 1400°C/8h. From the Fig 8(a-d) it is clear that sintering temperature has effect on the compactness of the film. The preliminary experiments have shown that the quality and the thickness of the film depend on several parameters: (a) the nature of solvent, (b) the strength of the suspension, (c) centrifugation rate, (d) duration of centrifugation.

Fig.9 shows the $\log(\sigma T)$ vs. $1/T$ plots of several compositions prepared by wet chemical methods. The conductivities fall in the 0.01S/cm to 0.21 S/cm at 600 to 1000°C. The activation energy of electrical conduction estimated from the Arrhenius plot of these compositions were ~ 1.00 eV. The activation energy of conduction shows that these materials are oxide ion conductors. The data obtained in this study are comparable with that of literature [1-5]. The electrical conductivity of the films prepared by microwave sintering and bulk pellets will be communicated in a separate manuscript.

4. CONCLUSIONS

The wet chemical methods of synthesis play an important role in the synthesis of nano-perovskites. The desired properties of the materials can be engineered with multi-valent substitution with phase pure material at relatively low temperature of heat-treatment. The regenerative sol-gel technique can be effectively used to recycle the expensive rare-earth gallates in nano-form. The RSG technique described in the paper can be extended to manufacture perovskites in large quantities needed in the SOFC technology. The ultrasonic assisted reaction by sonochemical technique was implemented to prepare homogenous single phase perovskites. Nano-crystalline perovskites can yield high dense thin film with microwave sintering. The nano-crystalline perovskites with mixed conducting properties for SOFC cathode and perovskites oxides compatible with LSGM cathode can be suitably synthesized in bulk as well as thick/thin membranes by using wet chemical methods. The scope of developing zero emission natural gas fuelled all perovskite SOFC believed to be challenging and has a potential for commercialization. Natural gas will become a popular fuel in the century, in particular in parallel with raising electricity production, where 10 fold capacity increases between 1990 and 2020 is predicted.

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FIGURE CAPTIONS

Figure 1. Schematic of Solid Oxide Fuel Cell

Figure 2. Showing the steps followed for the regenerative sol-gel synthesis for the preparation of $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$.

Figure 3. Room temperature XRD patterns of $\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ prepared by tartarate route, heated at various temperatures in air and cooled to ambient temperature.

Figure 4. TEM micrograph of LaGaO_3 prepared by tartarate route heat-treated at 1073 K 4h in air.

Figure 5 (a). XRD patterns of $\text{LaNi}_{0.7}\text{Fe}_{0.3}\text{O}_3$ prepared by glycine nitrate gel decomposition method

Figure 5 (b) TEM micrograph of LNF single phase powder prepared by glycine nitrate method showing nano-crystalline nature.

Figure 6 XRD patterns of LSGM prepared by regenerative sol-gel method.

Figure 7. SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015) and LaGaO_3 : heated at $1400^\circ\text{C}/8\text{h}$ (a) solid-state route(SSR) pellet of LSGM-2015; (b) RSG pellet of LSGM-2015; (c) solid-state route pellet of LaGaO_3 ; and (d) RSG pellet of LaGaO_3

Figure 8, SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ film on alumina substrate (a) first cycle of sintering at $1200^\circ\text{C}/8\text{ h}$ (b) $1200^\circ\text{C}/16\text{h}$ (c) $1400^\circ\text{C}/8\text{h}$ (d) $1500^\circ\text{C}/8\text{h}$

Figure 9. Log σT vs. $1/T$ of LaGaO_3 and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$ in air.

Fig. 1 SOFC with oxide ion conducting electrolyte.

Figure 2. Flow sheet for the preparation of $\text{La}_{1-x}\text{M}_x\text{Ga}_{1-y}\text{N}_y\text{O}_{3\pm\delta}$ compositions by regenerative sol-gel method.

Figure 3. Room temperature XRD patterns of $\text{La}_{0.9}\text{Ga}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ prepared by tartarate route, heated at various temperatures in air and cooled to ambient temperature.

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Figure 6. XRD spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$: (a) solid-state route precursor; (b) solid-state route pellet starting from the ground powders of (a); (c) regenerative sol-gel route precursor; and (d) regenerative sol-gel pellet.

Figure 7. SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015) and LaGaO_3 : heated at $1400^\circ\text{C}/8\text{h}$ (a) solid-state route(SSR) pellet of LSGM-2015; (b) RSG pellet of LSGM-2015; (c) solid-state route pellet of LaGaO_3 ; and (d) RSG pellet of LaGaO_3

Fig. 8 SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$ film on alumina substrate (a) first cycle of sintering at $1200^{\circ}\text{C}/8\text{ h}$ (b) $1200^{\circ}\text{C}/16\text{ h}$ (c) $1400^{\circ}\text{C}/8\text{ h}$ (d) $1500^{\circ}\text{C}/8\text{ h}$

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PROTON TRANSPORT IN NANOCRYSTALLINE BIOCERAMIC MATERIALS: AN INVESTIGATIVE STUDY OF SYNTHETIC BONE WITH THAT OF NATURAL BONE

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Abstract

Hydroxy apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a ceramic material. This has been used for biological applications such as bone and teeth enamel. In this paper various preparation methods including sonochemical followed by microwave sintering technique has been used to prepare the material. The material was characterized by XRD, TEM, SEM and its electrical transport (proton) is measured by impedance spectroscopy. The conductivity measured is 0.091×10^{-6} to $19.20 \times 10^{-6} \text{ Scm}^{-1}$ at 25 - 850°C range of temperature at 100 kHz applied frequency. Conductivity found to increase with increasing applied frequency at a given temperature of measurement. The prevalence of protons in the lattice has been confirmed by proton NMR studies. The results of the experimental observations on proton migration in the apatite lattice for electrical conduction are discussed.

1. Introduction

Hydroxy apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Ca-HAp) is a bio-ceramic and is an alternative candidate for hard tissue replacements such as stainless steel and titanium based solids [1-4]. The existing materials such as stainless steel etc. are prone to corrosion, wear, fibrous tissue encapsulation, inflammation, implant loosening due to poor adhesion, and stress shielding which leads to bone resorption. Ceramic based hydroxyapatite (HAp) are better suited as these are bioactive providing an interfacial bond between the implant and the surrounding tissue forms, leading to good fixation, and generally no fibrous tissue encapsulation. The

PROTON CONDUCTING (PC) PEROVSKITE MEMBRANES FOR HYDROGEN SEPARATION AND PC-SOFC ELECTRODES AND ELECTROLYTES

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Abstract

SrCeO_3 , $\text{SrCe}_{1-x}\text{M}_x\text{O}_3$ compositions were synthesized by sonochemical treatment followed hydrothermal method and sintering is done by microwave heating. CeO_2 hydrated gel was obtained from Ce(IV) ammonium nitrate and mixed with $\text{Sr}(\text{OH})_2$ and sonicated for 30 min., then the reactants were subjected to hydrothermal treatment at 150°C for 4 h. SrCeO_3 was found to form orthorhombic perovskite above 1200°C of heat-treatment. The powders were characterized by XRD, TEM, and EIS techniques. The effect of ball milling was also studied on sintering of the pellets. The 10% substitution of dysprosium at Ce site does not form single phase. Instead Sr_2CeO_4 is formed along with SrCeO_3 . Similarly, Eu, Er (10 % and 90 %Ce) were also attempted to substitute at Ce site; however, $\text{SrCe}_{1-x}\text{M}_x\text{O}_3$ ($x=0.10$) does not take up 10 % substitution. The electrical conductivity measurements were carried out on the single phase pellets by ac impedance techniques. The results of the experimental results obtained in this study are discussed in this paper.

1. Introduction

Proton conducting perovskite solids have been investigated by many research groups across the globe to arrive at optimized compositions to achieve enhanced proton conductivity at relatively lower temperatures. The property of selective hydrogen permeation through the solid in a wide a range of temperatures makes it attractive to be considered as hydrogen separation membrane [1-6]. Proton conducting solids can be used as electrolyte in solid oxide fuel cells in place of traditionally known oxide ion conducting yttria stabilized zirconia (YSZ) electrolyte (Fig.1). YSZ or Sr- and Mg-doped LaGaO_3 (LSGM) are good oxide ion conducting solid electrolytes, however, these materials need to be operated at $700\text{-}1000^\circ\text{C}$ temperatures to work as an effective electrolyte. The higher operating temperature of the electrolyte affects the material life, problems in operating the cell at higher temperature, selecting the compatible electrode and interconnects components. The higher operating temperature of solid oxide fuel cell can be avoided by replacing intermediate temperature proton conducting perovskite solid electrolytes in place of oxide ion conducting electrolytes. Perovskites can be suitably tailored to exhibit proton

ELECTROCERAMIC MATERIALS FOR THE DEVELOPMENT OF NATURAL GAS FUELLED SOFC/GT PLANT IN DEVELOPING COUNTRY (TRINIDAD & TOBAGO (T&T))

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Abstract

Various compositions of ceria, Gd-doped ceria and perovskite such as Sr-, Mg- doped LaGaO₃, Sr-doped LaMnO₃, Sr-doped lanthanum ferrate, cobaltate, LaCrO₃ and doped compositions were prepared by adopting several preparation methods. The materials were tailored to be used as anode, cathode, and electrolyte and interconnect in solid oxide fuel cells (SOFCs). The materials were characterized by XRD, TEM and other spectrochemical methods. Electrical conductivity of the compositions was measured by electrochemical impedance spectroscopy (EIS). These experiments were carried out to optimize the composition and various properties of the materials to be used in natural gas fuelled SOFCs. The study is aimed at developing materials to fabricate natural gas fueled SOFC hybridized to a gas turbine (SOFC-GT) to enhance power production and maximum utilization of resources in Trinidad.

1. Introduction

It has been said over and over again by many experts that the T&T in the Caribbean region is ideally located to promote the advanced power source technologies based on natural gas (NG). At present the NG reserves are estimated at approximately 27 trillion cubic feet with a current production rate of about one billion cubic feet per day. Crude oil and condensate reserves are about 550 million barrels with production levels for 122,627 barrels per day. Almost 75 % of the country's energy consumption come from NG and use it for electricity, petrochemical, and other industries. In the last four years, the natural gas industry has been growing at an average annual rate of 10%. The World Bank has ranked T&T as "an upper middle-income oil producing country" which has lead to an intensive industrialization thrust, and believed to be most prosperous among the Caribbean countries. The vision of T&T is moving towards shifting from oil-based economies to knowledge-based economies in which innovation and implementation in energy sector is key to long-term competitiveness. Power generation by fuel cells and gas conversion in Fischer-Tropsch synthesis are creating possibilities for making T&T a strong industrialized nation.

To utilize the NG assertively for sustainable development and growth of the region, there is an urgent need to explore distributed energy

sources fuelled by NG that can provide customers with reliable, local energy supplies while lowering the emissions of air pollutants. In this scenario, the renewable energy technology for power generation that is in the verge of commercialization is the fuel cell technology for both stationary, and transportation applications. Very recently, Dr. Ramsey Saunders of University of West Indies, Trinidad, and Dr. Bobba of Southern University, Baton Rouge, USA proposed to establish a national center for research excellence for promoting hydrogen economy entitled "Center for Hydrogen Energy and Advanced Power [CHEAP]" for conducting study, research, consultancy, organizing seminars and conferences in areas of fuel cells and hydrogen, and establishing a model decentralized 10-50 kW NG fuelled solid oxide fuel cell (SOFC) power plant in T&T jointly with the T&T NG Company. All activities of the centre will move from materials research for component and cell development, production, and formulating strategies for developing decentralized power generation source that can be highly efficient, clean, quiet, scalable, reliable, and potentially cheap. Such power packs will become popular for energizing the medium, and business complexes (malls), hospitals, centralized office complexes, airports, educational institutions, residential complexes, and remote villages in T&T. Global market analysts expect that the overall market for fuel cell technology could reach \$95 billion by the year 2010. The vision of this industrial/academic R & D CHEAP is to prepare T&T for grabbing the market share that belong to decentralized power based on NG.

Solid oxide fuel cell (SOFC) is a high temperature device that permits the electrochemical conversion of chemical energy to electricity. The tubular SOFC of Siemens-Westinghouse (SW) Power Corporation operates at around 900-1000°C, while Delphi planar SOFC operates at around 750-800°C. It has ceramic-based membrane and electrodes. The standard materials for the tubular cell components are: Yttria-stabilized zirconia (YSZ) for the dense electrolyte, a porous mixture of Sr-doped LaMnO_3 (LSM) + YSZ for the cathode, a porous mixture of Ni + YSZ for the anode and doped LaCrO_3 and high temperature alloys for the interconnect. The tubular SOFC system has been developed by Siemens-Westinghouse and other European and Japanese companies; units as large as 200 kW have been successfully demonstrated. The uniqueness and attractiveness of the tubular design is that it is a seal-less design, because sealing is an extremely challenging problem at high operating temperatures. However, the tubular SOFC has quite low volumetric and area power density. For example, the maximum power density of the tubular SW cells is only 2.5 kW/m² (0.25 W/cm²) at 1000°C. The high temperatures have resulted in very high cost of the components of the balance of power plant. Hence recently, the interest has shifted to the planar SOFC concepts, operating at 700-800°C, with research focusing on even lower temperatures, 650°C or lower. The planar SOFC system being developed by Delphi Corporation has 5 kW capacity and 106 cm² cell area. The SOFC based on the concept of planar, anode-supported design has led to power densities approaching 20 kW/m²

at 800°C in small cells, and as high as 10 kW/m² in short stacks (up to 10 × 10 cm 10 cell stacks). At 700°C operating temperature, the cost of the metallic interconnect, manifolds and end plates reduce significantly. Lower temperature operation makes available numerous materials for the seals, and reduces the insulation size and the associated cost. However, with the lower temperatures, the internal resistance of the cell rises sharply leading to a significant drop in the power density.

NG fueled SOFC system, in general consists of three converter units shown in Figure 1: They are: 1) a high temperature chemical conversion in a fuel processor, where methane based fuel is transformed to syn gas, 2) the electrochemical combustion of syn gas within the SOFC stack to generate heat and d.c electricity, and 3) electrical unit that converts and maintains the SOFC module to a useful application.

Natural Gas Fueled SOFC

Figure.1 Schematic of natural gas fueled SOFC.

In the first (chemical converter shown in Fig. 1) mixed ionic-electronic conducting ceramics (MIEC), can be employed to process the feed fuel into syngas by means of partial oxidation. In the second (electrochemical converter), the ceramic cells determine the system electrical efficiency by means of their internal resistance. Due to the high operating temperature, an important factor in the design of a solid oxide fuel cell stack is the matching of thermal expansion coefficient of the cell components and interconnects, to prevent cracking of the intrinsically brittle ceramic cells, gas leakage and loss of electrical contact.

A SOFC is mainly composed of two electrodes (the anode and the cathode), and a solid electrolyte. The fuel is also important as the principal parameter but independent of the other as it is most of the time converted into hydrogen. The SOFC, which relies on O₂ oxygen ion transport, also works with high purity hydrogen, but it does not rely upon this fuel, which is expensive to produce and difficult to handle. The main function of the electrode is to bring about reaction between the reactant (fuel or oxygen) and the electrolyte, without itself being consumed or corroded. It must also bring into contact the three phases, i.e., the gaseous fuel, the solid electrolyte and the electrode itself. The anode, used as the negative post of

the fuel cell, disperses the hydrogen gas equally over its whole surface and conducts the electrons, which are freed from hydrogen molecule, to be used as a useful power in the external circuit. The cathode, the positive post of the fuel cell, distributes the oxygen fed to it onto its surface and conducts the electrons back from the external circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water. The electrolyte determines the operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the electrons. It also allows the flow of charged ions from one electrode to the other to maintain the overall electrical charge balance. It can either be an oxygen ion conductor or a hydrogen ion (proton) conductor. Each component of the SOFC serves several functions and must therefore meet certain requirements such as: 1) proper stability (chemical, phase, morphological, and dimensional), proper conductivity, chemical compatibility with other components, similar thermal expansion to avoid cracking during the cell operation, dense electrolyte to prevent gas mixing, porous anode and cathode to allow gas transport to the reaction sites, High strength and toughness properties, fabricability, amenable to particular fabrication conditions, compatibility at higher temperatures at which the ceramic structures are fabricated, and low cost.

Figure 2 shows the schematic of all perovskite anode supported planar SOFC system, under progress at the Solid State Ionics Laboratory in the Southern University lead by Dr. Bobba.

Figure 2 Schematic of all perovskite SOFC

In this paper, we report the progress of the proposed hybrid SOFC/GT system shown in Figure 3 with an emphasis on utilizing the nanocrystalline electroceramic materials synthesized at low temperatures. To date, the following electroceramic materials: 1) nanocrystalline (La,Sr)(Ga,Mg)O₃

(LSGM) electrolyte, 2) $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.9}\text{M}_{0.1}\text{O}_3$ ($\text{M}=\text{Fe}, \text{Ni}, \text{Mn}$) cathode, 3) Ni-based perovskite cermet or $(\text{La}, \text{Sr})(\text{Ga}, \text{Mn})\text{O}_3$ (LSGMn) anode, 4) LaCrO_3 interconnect, and 5) ceria based anodic catalysts materials, were prepared in the form of bulk and thin films using innovative wet chemical processing methods, and pulsed laser deposition (PLD) techniques [1-3]. The interfacial reactions between electrolytes and anodes or cathodes were studied. The exceptional structural and chemical compatibility of LSGM with $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.9}\text{M}_{0.1}\text{O}_3$ ($\text{M}=\text{Fe}, \text{Ni}, \text{Mn}$) as perovskite based cathode, as anode, makes it a unique electrolyte for all perovskite based IT-SOFC.

Figure 3 Schematic of natural gas fuelled SOFC-GT hybrid.

1.1 Conversion of natural gas (NG) to Syngas

There are three reactions which produce hydrogen from methane: partial oxidation, steam reforming, and cracking. Cracking should of course be avoided as it produces a carbon deposit in the anode and gradually poisons it. At temperatures of 800 to 1000°C, the partial oxidation of methane is difficult to control, especially since complete oxidation must be avoided as it does not produce any hydrogen. Steam reforming is therefore the most commonly used reaction in industry, either in external reformers or in internal reforming within high temperature cells.

In general two types of SOFCs will be used for the catalytic and electrocatalytic experiments: (i) The conventional type where CH_4 is fed to the anode compartment of the SOFC and (ii) the simplified SOFC type where the mixture of $\text{CH}_4 + \text{H}_2\text{O}$ and O_2 is supplied to the reactor so that

both anode and cathode are exposed to $\text{CH}_4 + \text{H}_2\text{O}$ and O_2 mixture respectively. In the case of the conventional type the anode should exhibit high resistance to carbon deposition, resulting mainly from the methane decomposition reaction producing C and H_2 . Therefore the catalytic properties of these electrocatalysts should adsorb C originating from methane dissociation with high thermodynamic activity, thus preventing C-nucleation to graphite at low C coverages on the catalytic surface.

In decreasing order of efficiency the steam reforming catalysts used are: $\text{Ru} > \text{W} > \text{Rh} > \text{Ir} > \text{Ni} > \text{Co} > \text{Os} > \text{Pt} > \text{Fe} > \text{Mo} > \text{Pd} > \text{Ag}$. Nickel (Ni) is the most widely used today because of its excellent cost/efficiency ratio. Moreover, it is contained in today's most commonly used SOFC anode material: a zirconia-nickel compound belonging to the cermet family. We are developing alternate materials such as ceria (doped and undoped) and transition metal containing perovskites and fluorite-related structures [2]. The target for electronic conductivity for anode materials is often set to be 100 S cm^{-1} , but the actual requirement depends on the cell design and particularly the length of the current path to the current collection locations. A suitable benchmark material is the perovskite $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, which has been thoroughly investigated as an interconnect material for SOFCs and is also a potential anode material for SOFCs due to the relatively good stability in both reducing and oxidizing atmospheres at high temperatures. The acceptor doping gives high p-type conductivity in air but, as with all p-type materials, this decreases under reducing conditions. The introduction of other transition elements into the B-site of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{MyO}_3$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) has been shown to improve the catalytic properties for methane reforming.

2 Experimental

Various wet chemical preparation methods have been used to prepare the (1) anode (2) cathode (3) electrolyte (4) interconnect materials. The techniques used were (i) combustion synthesis (ii) co-precipitation methods (iii) sonochemical methods. Stoichiometric concentrations of reactants were taken for preparing specific compositions and dissolved to make solutions then ligating agents were added to form complexes and the complex was heated on hot plate to decompose and finally on calcinations yielded the product. The details are available in our earlier publications [1-3].

3. Results and Discussions

3.1 Anode

The materials selection for an SOFC anode is determined by a number of factors. First, the function required of it as the site for the electrochemical oxidation of the fuel associated with charge transfer to a conducting contact. Second, the environment in which it operates, at high temperature in contact not only with the fuel, including possible impurities and increasing concentrations of oxidation products, but also with the other materials, the electrolyte and contact components of the cell, and all this with stability over

an adequate commercial lifetime at high efficiency. With regards to stability, whilst in normal operation the ambient oxygen partial pressure is low, it can vary over several orders of magnitude, and to accommodate fault conditions or even just to provide flexibility of operating parameters, the ability to recover even after brief exposure to air at high temperature would be advantageous. A further aspect of this stability is the maintenance of structural integrity over the whole temperature range to which the component is exposed, from the sintering temperature during fabrication through normal operating conditions and then, repeatedly, cycling down to ambient temperature. Compatibility with other cell component materials implies an absence of solid state contact reactions, with interdiffusion of constituent elements of those materials or formation of reaction product layers which would interfere with anode functionality. It also requires a match of properties, such as shrinkage during sintering and thermal expansivity to minimise stresses during temperature variations due to operating procedures, start-up and shut-down. By definition of its role, it is a requirement that the anode material should be an adequate electronic conductor, and also be electrocatalytically sufficiently active to sustain a high current density with low overpotential loss. Ceramic anodes, made of perovskite-type rare-earth and strontium cobaltites substituted in both sublattices, exhibit a high electrocatalytic activity for the oxygen evolution reaction in alkaline media. We have analyzed the relationship between cation composition, defect structure, electronic conductivity and electrochemical performance for a wide group of perovskite-like cobaltites, including $\text{Ln}_{1-y}\text{A}_y\text{CoO}_{3-\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$; $\text{A} = \text{Sr}, \text{Ca}$; $y = 0-0.4$), $\text{La}_{1-x-y}\text{Sr}_x\text{Bi}_y\text{CoO}_{3-\delta}$ ($x = 0-0.6$, $y = 0-0.1$), $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$, $\text{Sr}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ ($x = 0.1-0.2$) and $\text{SrCo}_{1-y}\text{M}_y\text{O}_{3-\delta}$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Ti}, \text{Cu}$; $y = 0.10.6$). SOFC anodes are fabricated from composite powder mixtures of electrolyte material (YSZ, GDC, or SDC) and nickel oxide NiO (the nickel oxide subsequently being reduced to nickel metal prior to operation, which serves to inhibit sintering of the metal particles and to provide a thermal expansion coefficient comparable to those of the other cell materials).

3.2 Cathode

Perovskite-type lanthanum strontium manganite, LaSrMnO_3 (LSM) and lanthanum calcium manganite, LaCaMnO_3 (LCM) offer excellent thermal expansion match with zirconia electrolytes and provide good performance at operating temperatures above 800°C . For applications requiring lower temperature operation ($600-800^\circ\text{C}$), a range of alternative perovskite-structured ceramic electrode materials are available. These include: Lanthanum strontium ferrite (LSF), $(\text{LaSr})(\text{Fe})\text{O}_3$, Lanthanum strontium cobaltite (LSC), $(\text{LaSr})\text{CoO}_3$, Lanthanum strontium cobaltite ferrite (LSCF), $(\text{LaSr})(\text{CoFe})\text{O}_3$, Lanthanum strontium manganite ferrite (LSMF), $(\text{LaSr})(\text{MnFe})\text{O}_3$, Samarium strontium cobaltite (SSC), $(\text{SmSr})\text{CoO}_3$, Lanthanum calcium cobaltite ferrite (LCCF), $(\text{LaCa})(\text{CoFe})\text{O}_3$, Praseodymium strontium manganite (PSM), $(\text{PrSr})\text{MnO}_3$, and

Praseodymium strontium manganite ferrite (PSMF), $(\text{PrSr})(\text{MnFe})\text{O}_3$. For even better electrode performance, some companies offer a line of composite electrode powders, with electrolyte materials (YSZ, SDC or GDC) admixed with the perovskite electrode materials (LSM, LSF, or PSMF). As in the other fuel cell types, the oxygen reduction largely determines the efficiency of the SOFC. Cathodes using LaSrMnO_3 , $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) have the advantages of lower losses at lower temperatures (600–700 °C) and are reported to be less sensitive to Cr-poisoning. LSM thin film was prepared by pulsed laser deposition by our team, the TEM micrograph of the film with columnar microstructure are shown in Fig. 4

Figure 4. Columnar growth in PLD of LaSrMnO_3 (LSM).

In our laboratory various compositions have been attempted to optimize conductivity of the electrode for ions and electrons and the accessibility for oxidant, improvement in microstructure and phase composition at load conditions.

3.3 Electrolyte

The properties of electrolytes used in SOFC are mainly, but not only, dictated by the high operating temperature, high ionic conductivity ($\geq 0.1 \text{ S cm}^{-1}$); low electronic transference number ($< 10^{-3}$); large electrolytic domain; chemical stability with respect to electrode materials, oxygen, and fuel gas; thermodynamic phase stability; a good match of thermal expansion coefficient (TEC) with other cell components; gas tightness; fracture toughness. Current technology employs several ceramic materials for the active SOFC components. Although a variety of oxide combinations has been used for solid non-porous electrolytes, the most common to date has been the stabilised zirconia with conductivity based on oxygen ions (O_2), especially yttria-stabilized zirconia (Y_2O_3 —stabilized ZrO_2 or YSZ, $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ for example) in which a tiny amounts of the element yttrium, a silvery-grey metal, is added to the zirconia during manufacture. This choice is mainly due to availability and cost. YSZ exhibits purely oxygen ionic conduction (with no electronic conduction). The crystalline array of ZrO_2 has two oxide ions to every zirconium ion. But in Y_2O_3 there are only 1.5 oxide ions to every yttrium ion. The result is vacancies in the

crystal structure where oxide ions are missing. So, oxide ions from the cathode leap from hole to hole until they reach the anode.

The most commonly used stabilizing dopants are CaO, MgO, Y₂O₃, Sc₂O₃ and certain rare earth oxides such as Nd₂O₃, Sm₂O₃, Yb₂O₃. Other oxide based ceramic electrolyte that can be used in SOFCs include: Cerium oxide doped with samarium (SDC), (Ce_{0.85}Sm_{0.15})O_{1.925} Cerium oxide doped with gadolinium (GDC), (Ce_{0.90}Gd_{0.10})O_{1.95}. Recently, the synthesis and electrical property measurements on nano-crystalline ceria and Gd-doped ceria has been done in our lab. The XRD and TEM results are given in Fig.5 and Fig.6 (a-b) respectively.

Figure 5. XRD pattern of nano-crystalline ceria powders

Figure 6 TEM and SAED of a) CeO₂ cerium nitrate and DMU (b) Ce_{0.8}Gd_{0.2}O_{1.9}

For operation at 600 °C or even lower, La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85} electrolytes offer superior conductivity, but exhibit stability problems caused by evaporation of Ga, and low mechanical stability and high gallium costs. Scandium doped ZrO₂ offers improved oxygen ion conductivity and relatively high mechanical strength, at the expense of using high cost scandium. Lanthanum gallate ceramic that include lanthanum strontium gallium magnesium (LSGM), (La_{0.80}Sr_{0.20})(Ga_{0.90}Mg_{0.10})O_{2.85} or (La_{0.80}Sr_{0.20})(Ga_{0.80}Mg_{0.20})O_{2.80}, Bismuth yttrium oxide (BYO), (Bi_{0.75}Y_{0.25})₂O₃, Barium Cerate (BCN), (Bi_{0.75}Y_{0.25})₂O₃, and Strontium Cerate (SYC), Sr(Ce_{0.95}Yb_{0.05})O₃

To produce submicron LSGM powders for high-quality membrane fabrication, the combustion technique via aqueous solutions is usually preferred to the conventional solid-state mixed-oxide method. The solution route provides many advantages, for example, molecular homogeneous precursors, reduced sintering temperature for obtaining dense ceramics, and controllability of uniform superfine grain size. One major disadvantage of LSGM is the high cost of the gallium containing precursors. Once LSGM materials are used as electrolyte in commercial stage, regeneration of LSGM will be a cost-effective effort. Based on this concern, we have explored the possibility of regenerating the LSGM ceramics to be aqueous solution precursor. Although the solid Ga_2O_3 remains insoluble, our experiments have shown the LSGM ceramics are completely soluble in the acidic solution. In addition, the regenerative route is also cost-effective and time-saving for in-lab researches which usually prepare large amount of LSGM samples, for example, to tailor effects of composition or synthesis condition on the properties of LSGM.

The sintering behaviour of the materials prepared from the various routes was examined by Scanning electron microscopy (SEM) shown in Figure 7. The pellets prepared by regenerative sol-gel technique produce nano-crystalline powders which has better sintering properties as indicated in Fig. 7 a-b and Fig. 7c-d.

Fig.7.SEM micrographs of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.8}$ (LSGM-2015) and LaGaO_3 : heated at $1400^\circ\text{C}/8\text{h}$

(a) solid-state route(SSR) pellet of LSGM-2015;
 (b) RSG pellet of LSGM-2015;
 (c) solid-state route pellet of LaGaO_3 ; and
 (d) RSG pellet of LaGaO_3

The Fig. 8 illustrates the impedance spectroscopy measurement of the LSGM-2015 pellets synthesized through both the regenerative sol-gel route and solid-state route. The resistances in all bulk and in all grain-boundary (R_b and R_{gb}) of the pellets were estimated from the real axis intercepts of the depressed semicircles based upon the equivalent series circuit of two R-C parallel circuits. The first depressed semicircle near the origin corresponds to the bulk resistance and the second corresponds to the grain-boundary resistance. The first real axis intercept offers the R_b and the second offers the sum of R_b and R_{gb} . The resistances were unified by

multiplying the ratio of area to thickness of the measured pellets. Although we got the resistances, because volume fractions of the bulk and grain-boundary are unknown, it is impossible to calculate the bulk and grain-boundary conductivities. The Arrhenius relations of the bulk and the grain-boundary resistances in [3] indicate the grain boundary resistance is almost equal to the bulk resistance. Based on the Arrhenius relation of $T/R \propto \exp(-E/kBT)$, we estimated the activation energies for the oxide-ion conduction across the whole pellet ($E_t=1.01$ eV), the bulk part ($E_b= 0.97$ eV), and the grain-boundary part ($E_{gb}= 1.03$ eV). The Arrhenius relation of the total conductivities [3] indicates the regenerative sol-gel LSGM-2015 has a higher temperature-dependent conductivity than that of the solid-state route LSGM-2015. At 800°C and 700°C, the solid-state route LSGM-2015 has a conductivity $\sigma_t \approx 0.056$ and 0.025 S/cm respectively, and the regenerative sol-gel LSGM-2015 has a conductivity $\sigma_t \approx 0.066$ and 0.029 S/cm respectively, which is 16-18 % more than the solid-state LSGM-2015 conductivity and is comparable to the conductivity of conventional sol-gel route LSGM starting from liquid-mixing of salt solutions (refer to [3], $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$, $\sigma_t \approx 0.065$ S/cm and 0.034 S/cm at 800°C and 700°C respectively).

Figure 8. Cole-Cole plots recorded on LSGM pellets.

3.4 Interconnects

Separator plates are in SOFC mostly called interconnects. At high temperatures, one option is to use ceramic interconnects. The ceramic plates are based on LaCrO_3 . Doping with Ca, Sr or Mg leads to higher electrical conductivity. Pure ceramic plates have the tendency to be partially reduced at the anode side, leading to warping and breakage of the sealing besides, more cost effective materials and fabrication methods are needed for bringing this technology to the commercial stage. Metallic interconnects would lead to lower fabrication costs, are less brittle and have a higher electrical and thermal conductivity.

3.5 SOFC-GT hybrid system

The Hybrid system comprises of a natural gas fueled SOFC with a gas turbine as shown in the Fig. 3. Natural gas with necessary purification is sent to the anode chamber and excess gas is recycled. Similarly, air is sent (pumped) to the cathode compartment and recycled. Since the fuel cell operates at high temperatures $\sim 8000\text{C}$ and produces DC current, the used hot gases can be sent to the gas turbine (GT) to produce AC current by the gas turbine turbine and generator. Thereby, increasing the efficiency of the process. By doing so maximum utilization of gas and heat can be achieved. A prototype set up will be fabricated and the fuel cells will be tested in our site.

4. Conclusion

Exploitation of fossil fuels to produce energy is reaching its limits. Future alternatives must therefore be developed for long-term and environmental-friendly energy supply needed by a constantly growing world population. SOFCs provide highly efficient, pollution free power generation. Their performance has been confirmed by successful operation of power generation systems throughout the world. Electrical-generation efficiencies of 70% are possible nowadays, along with a heat recovery possibility. SOFCs appear to be an important technology for the future as they operate at high efficiencies and can run on a NG produced in Trinidad.

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