*Review Article***High Temperature Fuel Cell**

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In our country, about 60% of the power generated in India is from fossil fuels such as coal, oil and gas, which are eventually responsible for generating large quantities of greenhouse gases. Fuel cell is an electrochemical device and potential technology to generate power in an environmentally benign manner. This chapter of the monogram deals with high temperature ceramic fuel cells, popularly known as solid oxide fuel cell (SOFC). In the beginning, a generalized discussion has been made about fuel cells with particular emphasis on SOFC which is followed by a detailed description of the progress of research related to the development of planar anode-supported SOFC technology that is being pursued at CSIR-Central Glass & Ceramic Research Institute, Kolkata under CSIR-New Millennium Indian Technology Leadership Initiative (NMITLI) programmes over the last few years. Under these technological developmental activities, large numbers of anode-supported single cells of dimension up to $10\text{ cm} \times 10\text{ cm} \times 1.5\text{ mm}$ have been fabricated that show reasonably good power output of $\sim 1.0\text{ W/cm}^2$ at a cell voltage of 0.7 V and at an operating temperature of 800°C . In parallel, this contribution also describes the indigenous development of high temperature glass-based sealant, an essential component for SOFC stacking. Using the developed 10×10 single cells, glass-based sealants, indigenously designed and fabricated metallic interconnect and gas manifolds, several SOFC short stacks (up to 10 cells) have been fabricated and demonstrated for the first time in our country.

Keywords: Solid Oxide Fuel Cell; Anode; Cathode; Electrolyte; Interconnect; Anode-Supported Planar Design; Electrochemical Performances; Stack

Background

Although the invention of fuel cells (FC) as a renewable energy conversion system was initiated in the mid of 19th century, the discovery of the underlying principle was owned by Prof. Christian Friedrich Schonbein (Bossel, 2000) at the University of Basle (1829-1868). However, Sir William Grove has attributed primarily towards the electrical energy conversion system using the science behind the fuel cell. At the beginning of 20th century, the journey of the fuel cell science and the technology has turned out positively because of significant increase in population around the globe and the depletion of natural resources for energies. During the same time, the initiation of distributed power generation plant has been started with an intention of reducing capital cost for the installer and thereby improving the overall

efficiency due to the possibility of co-generation of heat and electricity. Technologically viable fuel cell is expected to facilitate mankind to reduce dependence on conventional energy sources and in addition diminish poisonous emissions into the atmosphere. A simplistic view of fuel cell is that it is a cross between a battery (chemical energy converted directly to electrical energy) and a heat engine (a continuously fuelled air breathing device). Therefore, fuel cell is also referred as “electrochemical engines”. The range of fuel cell applications and the size of potential markets are enormous which includes, battery replacement in small portable electronic devices, prime movers and/or auxiliary power units in vehicles, residential combined heat and power (CHP) and large-scale megawatt (MW) electrical power generation. Fuel cells share the effectivity of its operation with

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high efficiency (>60%), no moving parts, quiet operation and low or zero emissions during application.

The system efficiency of a fuel cell, independent of Carnot's limitation, can be derived from Gibb's free energy (ΔG) and the enthalpy change (ΔH) of the electrochemical reaction in terms of electrical work (W_e) as:

$$(\varepsilon_\gamma)_{FC} = \frac{W_e}{-\Delta H} = \frac{nFV_o}{-\Delta H} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}. \quad (1)$$

Practically, majority of reactions are associated with negative entropy change that causes increase in temperature thereby reducing the thermodynamic efficiency of fuel cell. Regardless of all the polarization factors contributing towards reducing efficiency, the overall system efficiencies of fuel cells are high in comparison to internal combustion engine (ICE) which is discussed in reputed fuel cell handbooks (Blomen and Mugerwa, 1993; Appleby and Foulkes, 1993) and a comparative representation of different systems is shown in Fig. 1. Apart from system output, the fuel cells are superior pertaining to the co-generation of heat and electricity. Efforts are being pursued over the globe to enhance the efficiency of fuel cells and

Fig. 1: Comparative system efficiencies of Carnot-dependent and independent energy conversion systems

coupling with devices to utilize the waste heat for energy conservation. Therefore, owing to the advantages associated with fuel cell technology, security of electricity can be ensured in future which is also expected to induce a new era of 'hydrogen economy'.

High Temperature Fuel Cell

Fuel cell is usually being categorized in terms of electrolyte employed except direct methanol fuel cell (DMFC), in which classification is made with respect to the methanol fuel, fed directly to the anode. An overview of the fuel cell types is provided in Table 1

Table 1: Characteristics of fuel cell systems

Types of fuel cell	Alkaline (AFC)	Polymer electrolyte membrane (PEMFC)	Direct methanol (DMFC)	Phosphoric acid (PAFC)	Molten carbonate (MCFC)	Solid oxide (SOFC)
Operating temperature (°C)	<100	60-120	60-120	160-220	600-800	800-1000 or 500-600
Fuel	H ₂	H ₂	CH ₃ OH	H ₂	H ₂ , CO	H ₂ , CO
Oxidant	O ₂	O ₂ /Air	O ₂	O ₂	O ₂ + C O ₂	O ₂
Anode	Ni, Pt	Pt	Platinized Carbon (Pt/C)	Pt	Ni	Ni-YSZ
Cathode	Ni	Pt	Pt	Pt	Li-doped NiO	Sr-doped LaMnO ₃
Charge carrier in Electrolyte	OH ⁻	H ⁺	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Applications	Transportation, space, Military, Energy storage systems			Combined heat and power for decentralized stationary power systems		Combined heat and power for stationary decentralized systems and for transportation
Realised power	Small plants, 5-150 kW modular	Small plants, 5-250 kW modular	Small plants, 5 kW	Small-medium sized plants 50kW-11 MW	Small power plants, 100 kW to 2 MW	Small power plants, 100-250 kW

(Dufour, 1998; Carrette *et al.*, 2000; Chalk *et al.*, 2000). The available high temperature fuel cell is primarily known as solid oxide fuel cell (SOFC) where all the components are in solid state. High temperature fuel cell employs a solid oxide electrolyte material and is more stable with no leakage problems compared to other classes of fuel cell.

Additionally, being a two-phase gas-solid system, SOFC does not suffer from the problems of water management, slow oxygen reduction reaction rate (ORR), etc. It is considered to be one of the most promising power generation technologies for the future due to its high efficiency, zero or extremely low pollution level and fuel flexibility. The concept of such a ceramic fuel cell started long before in 1911 but the perception of stationary SOFC was presented in 1937 (Baur and Preis, 1937) and significant development started around 1960. A detailed review in this context is presented by Mobius (1997). The power and the voltage of SOFC is increased by connecting individual cells in series to form a 'stack', with each cell connected to its adjacent cell using an electrically conducting interconnect which also serves to distribute the reactant across the surface of the electrodes using the designed flow channels. Working temperature of SOFC is dependent on the activity and application of the associated components. SOFC can be divided into three major categories viz. (a) low temperature SOFC (LT-SOFC) which operates within the working temperature of 500-650°C, (b) intermediate temperature SOFC (IT-SOFC) that operates within 650-800°C and (c) high temperature SOFC (HT-SOFC) which operates in the range of 800-1000°C. If a high temperature fuel cell is integrated with a gas turbine in a hybrid arrangement, then, overall efficiency in excess of the individual efficiencies of the fuel cell and heat engine in isolation can be achieved. The characteristic of high temperature operating SOFC constitutes one of the toughest criteria for the dimensional and chemical stability of anode material in reducing atmosphere (Basu, 2006). Similar to MCFCs, internal reforming in SOFC is possible over anode catalyst and both partial and direct oxidation of fuel has been found to occur (Boder and Dittmeyer, 2006; Ren *et al.*, 1996; Hamakawa *et al.*, 2000; Park *et al.*, 2000; Park *et al.*, 1999). SOFC

offers advantages of using different fuels, e.g., hydrogen, CO, natural gasses, bio gas, any light hydrocarbon, etc. However, the cell functioning is highly prone to the presence of sulphur (<60 ppm).

SOFC is therefore a class of electrochemical cell through which free energy of a chemical reaction is converted to electrical energy. Correlation between change in Gibbs free energy (ΔG) and cell voltage is given as (Carrette *et al.*, 2000):

$$\Delta G = -nF\Delta U_0 \quad (2)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant and ΔU_0 is the voltage of the cell at thermodynamic equilibrium in the absence of a current flow. The schematic of SOFC is given in Fig. 2, where an oxygen ion conducting solid electrolyte is sandwiched between anode and cathode.

Even under no load condition, the open circuit voltage (OCV) can be lower than the thermodynamic Nernst value due to mixed potential formation or other parasitic processes. Under load condition, a deviation from OCV occurs corresponding to the electrical work performed by the cell termed as 'overpotential or polarization (η)'. The several losses that are being encountered during the operation of high temperature fuel cell are given in Fig. 3.

Fig. 2: Schematic of solid oxide fuel cell

Fig. 3: Several polarization factors towards cell performance and trend of cell voltage vs current density (top) and power output vs. current density (bottom)

Cell Components

Solid oxide fuel cell essentially consists of two porous electrodes; cathode and anode, separated by a dense ion conducting electrolyte material. Ceramic fuel cell is fabricated in several designs (discussed in subsequent sections), but the basis of the material selection is based on the following criteria:

- Sufficient electrical conductivity values
- Matching thermal expansion among the cell components
- Minimal reactivity and interdiffusion among the components to avoid degradation
- Adequate chemical and structural stability at high temperature

The components for SOFC are discussed in brief as follows:

Cathode

The state-of-the-art cathode material satisfying the SOFC operating criteria is the electronically conductive ceramic oxide based perovskite e.g. lanthanum manganite (Basu, 2006; Song *et al.*, 2009).

In general, substituted lanthanum manganite is used in which 'La' is partially substituted by strontium (i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, commonly termed as LSM). These perovskite are electronic p-type conductors for which the electrical properties are determined by the La/Sr ratio. Formation of $\text{La}_2\text{Zr}_2\text{O}_7$ and SrO upon interaction with adjacent 8 mol% yttria stabilized zirconia (YSZ) electrolyte is inhibited by incorporating an excess of Mn (1-10 %) in the composition and keeping the sintering temperature below 1300°C (Stochniol, 1995). The side products as mentioned above impair the cathode performance. The function of cathode in SOFC is based on the capability to reduce oxidant viz. air and oxygen, etc. It is generally assumed that oxygen reduction is a multistep reaction involving adsorption and surface diffusion in a region around the triple phase boundary (TPB) as shown in Figure 4. Mixed ionic and electronic conductor (MIEC)-based perovskite cathodes such as $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ (LSF), $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ (LSCF), and $\text{Ba}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ (BSCF) are also being used as SOFC cathode materials for some specific advantages over prior ones e.g., the conventional LSM cathode. Significant reduction in the cost of air electrode is possible by utilizing composition that has low rare earth content.

Electrolyte

The solid electrolyte for SOFC application needs to be a fast ion conductor and should simultaneously confront both reducing and oxidizing environment. Among innumerable oxygen ion conductors viz. ceria, La-gallate (Ishihara *et al.*, 1998); zirconia stabilized in conductive phase with up to 10 mol% of either yttria or scandia, can be used either as tetragonal zirconia polycrystals (TZP) (3YSZ: ZrO_2 doped with ~3 mol% Y_2O_3) or cubic stabilized zirconia viz. CSZ (8YSZ: ZrO_2 doped with ~8 mol% Y_2O_3) (Manner and Ivers-Tiffée, 1991) are the promising candidates. Fully stabilized zirconia offers the best choice of electrolyte having satisfied criteria of conductivity, chemical stability, durability, etc. Although the oxide ion conductivity of TZP is relatively lower than the fully stabilized zirconia, this material is advantageous because of its outstanding mechanical stability. Significant efforts are also put in to study the traditional zirconia material in terms of appropriate co-dopants

(Hirano *et al.*, 1999; Batista and Muccillo, 2011) for improved bulk and grain boundary conductivity. Activities for alternative electrolyte compositions are generally concentrated on doped CeO_2 or doped LaGaO_3 materials (Steele, 2000). In the absence of suitable materials, minimizing the thickness of YSZ layer effectively reduces the polarization losses and thus reduces the cell operating temperature to 800°C .

Anode

Under reducing atmospheres at anode, metals are stable over a wide range of operating conditions. Among various experimental metals, 'Ni' has been selected due to its high electrochemical activity for hydrogen oxidation reaction, low cost and acceptable compatibility with other cell components (Singhal and Kendall, 2003; Daniel *et al.*, 2008). However, the usual practice is to unify Ni with ceramic component, viz. YSZ (yttria stabilized zirconia), ScSZ (scandia stabilized zirconia), etc. The prime function of the ceramic phase is to prevent Ni from agglomeration, and thereby retain the porous and highly disperse microstructure of the anode. However, the ratio of Ni:YSZ needs to be optimized on basis of the requirement of conductivity and minimization of ambipolar resistance. Although Ni-YSZ has advantages as mentioned above, the high susceptibility of Ni to coking, re-oxidation in case of fuel loss and sensitivity to poisoning of the electrode by sulphur are the main concerns regarding the durability and degradation of Ni-YSZ anodes (Singhal and Kendall, 2003). Experiments have shown that performance of SOFC starts degrading upon increasing the sulphur content beyond ~ 5 ppm (Zhang *et al.*, 2010). As alternative anodes, focus is on the development of fluorites, pyrochlore, perovskite, tungsten and bronze-based materials (Tao and Irvine, 2004). With regard to the competitive performance of Ni-YSZ, only ceria-based, $\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{1.8}$, (Mogenson, 2005) Ni-CGO and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{0.3}$ (LSCM) (Tao and Irvine, 2004; Mogenson, 2005) have been developed. With respect to compatibility with YSZ electrolyte, yttria-titania-modified zirconia (Y2T) is also found to be a promising mixed conducting fluorite-based anode material (Verbreken *et al.*, 2005). From the aforementioned research, it can be mentioned that

SOFC has the potential of using variable fuels viz. H_2 , CO, CH_4 , etc. based on the possible cell component materials.

Other Components

Selection and fabrication of interconnect material is another important concern for fuel cell development. The interconnect should fulfill the prime requirements of being electrically conductive and act as a separating component for restricting fuel/oxidant gasses to intermix at either electrodes. Additionally they should be dense, chemically and dimensionally stable in dual oxidizing and reducing atmosphere. Bipolar plates based on ceramic materials viz. LaCrO_3 offer better thermal compatibility with other cell components. However, sufficient conductivity is observed upon formation of Cr_2O_3 layer on the surface of LaCrO_3 -based interconnect. (Casteel *et al.*, 2009; Ghosh *et al.*, 2006). A new metallic-ceramic alloy is developed by Plansee (Austria) which shows high corrosion resistance, good thermal conductivity, high mechanical strength and low expansion coefficient. The alloy is based on a CrFe stainless steel metallic component mixed with an yttrium oxide ceramic (Carrette *et al.*, 2001). In addition; Fe-Cr ferritic steel alloys are also used as effective materials applicable for IT-SOFC (Yasuda *et al.*, 2009). Commercialization of SOFC is limited by the development of suitable sealant material capable of working at high operating temperatures. Sealants are required for preventing the intermixing of fuel and oxidant gases in the electrode compartments. (Steele, 2001; Mogenson *et al.*, 1992) Promising candidates for sealing purpose could be 'glass (SiO_2)' or 'ceramic-foams'. Normal glasses are proved to be ineffective sealants, as they often evaporate and soften with a likelihood of leakages. Pyrex seals are used and proved to have sufficient stability at high temperature and pressure so that leakages can be avoided (Momma *et al.*, 1997). Ceramic foams consisting of Co-doped LSM materials have been found to have high electronic conductivity and a reasonable compressive strength, but these do not exhibit creep behaviour (Will and Gauckler, 1997). SOFC seals can be broadly classified into two major categories, for e.g., composition specific sealants that include compressive and rigid seals and

bond-specific seals (ceramic-ceramic, ceramic-metal and metal-metal). Additionally, rigid seals consist of: (a) glass ceramic, (b) self-healing type, (c) composite and (d) brazing seals (Furgus, 2005; Reis and Brow, 2006). The application of sealant type is entirely dependent on the nature of its application.

Fuel Cell Research in India

In India, fuel cell research has primarily been catered by the academic institutions and government R&D organizations. However, there is growing interest among many private and PSU organizations which are initiating their own R&D programmes on fuel cell (Reis and Brow, 2006; Confederation of Indian Industry, 2010). The R&D activities have been primarily focused on PAFC, PEMFC and SOFC. India's policy on fuel cells and financial support is driven largely by three agencies, viz. Ministry of New and Renewable Energy (MNRE), Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR). So far as ceramic fuel cell is concerned, CSIR-Central Glass & Ceramic Research Institute, Kolkata has the strongest R&D group for technology development where the related research activities were initiated in the mid-90s. Besides CGCRI, some other R&D laboratories and academic institutes are also carrying out R&D on SOFC. Fuel Cell Lab at IIT Delhi is trying to develop SOFC that operates directly on hydrocarbon feedstock. Similarly, efforts are being made at the CSIR-Institute of Minerals & Materials Technology, Bhubaneswar, to develop high-performance intermediate-temperature SOFC by low-cost ceramic processing technique. IIT Bombay and IIT Kanpur have also recently initiated activities on new materials development for SOFC along with simulation and modelling for planar SOFC. Bhabha Atomic Research Centre (BARC), Mumbai is mainly engaged in tubular SOFC technology development. International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad has started working on SOFC that is based on a typical design of honeycomb structures for specific application. In addition to R&D establishments, multinational companies such as GE (India), Bangalore and Bloom Energy (India) Pvt. Ltd., Mumbai have

ventured into this area, primarily to assemble imported parts supplied by their principals. Bharat Heavy Electricals Limited, CTI, Bangalore has initiated the research with SOFC single cell testing using their own developed glass-based seals. Gas Authority India Ltd (GAIL) and National Thermal Power Corporation (NTPC) have also planned to initiate activities on SOFC. With respect to gasification of Indian coal, Thermax Limited, Pune is involved in building a gasifier for coal and biomass for quite some time and is now looking for application of biogas in SOFC in collaboration with IIT Bombay.

Development of anode-supported SOFC technology: Activities in CSIR-CGCRI, Kolkata

Among the various designs, the planar anode-supported thin film electrolyte design, introduced by Forschungszentrum Jülich, Germany as one of the pioneering organizations of the design, is followed by many of the SOFC developers because of several advantages associated with this design (Ishihara, 2003). Generally, electrolyte-supported cells and electrode-supported cells are the two possible configurations of planar design that are available in the market. In case of electrolyte-supported design, it is practically possible to achieve a mechanically stable structure only when the electrolyte thickness is greater than 200 μm . However, for such a high thickness of the electrolyte, the ohmic loss across the same is appreciably high and the cells have to be operated at a very high temperature of around 1000°C in order to have sufficient conductivity through the electrolyte to be useful for practical device application (Steele, 2000). This hinders the commercialization of SOFC due to the necessity of using costly construction materials to withstand such a high temperature. These problems can be overcome if a thin electrolyte layer is fabricated over a thick and porous electrode-support which is the basis of anode-supported design. In this design, while the porous anode provides the mechanical support, the thinness of the electrolyte helps in lowering the ohmic losses across it. The thinness of the electrolyte helps in reducing the internal resistance of the electrolyte, thereby making it possible to lower the temperature of operation and consequently, to use metallic interconnects which are

much easier to fabricate than their ceramic counterpart. As the resistance of the electrolyte is proportional to its specific resistance and thickness, the total resistance of the electrolyte layer can be reduced by reducing its thickness to such a level that it more than compensates the increase in specific resistance caused due to a lowering in operating temperature. Thus, for an anode-supported SOFC, the operating temperature can be lowered down to about 800°C or even less (depending on the thickness of the electrolyte film) without compromising with the power output. This allows the device to be made of less expensive materials. However, in such a configuration, the major technical challenge involves fabricating a pinhole and crack-free dense layer of YSZ electrolyte of thickness 50µm or less on NiO-YSZ (anode) substrates of high porosity. The YSZ film must be well-bonded to the NiO-YSZ substrate without excessive infiltration into the electrode porosity and there must be minimal interface polarization. However, for such a configuration, the major technical challenge involves fabricating a dense and gas-tight YSZ electrolyte layer of thickness 50 µm or less supported on a porous NiO-YSZ (anode) substrate. Several studies describe the performance of such anode-supported SOFC (Basu *et al.*, 2005; Kim *et al.*, 1999; Yoon *et al.*, 2007). Under the CSIR-New Millennium Indian Technology Leadership Initiative (NMITLI) projects in two different phases (initiated in 2004), CSIR-CGCRI Kolkata is engaged in the development of anode-supported SOFC technology using inexpensive, simple and up-scalable processing techniques, such as tape casting and screen printing. All the processing parameters have been optimized to fabricate single cells of dimension up to 10 cm × 10 cm × 1.5 mm. The fabricated cells have been characterized through microstructural, electrical and electrochemical performance studies using LSM-based conventional cathode. While, in the technology mode, CSIR-CGCRI is engaged in the development of kW-level SOFC power pack based on such single cell using their own novel patentable design and CGCRI developed high temperature glass sealants, CSIR-CGCRI is also engaged in the research and development of several material component developments, viz. new class of doped lanthanum

Fig. 4: Possible reaction steps at air electrode in SOFC

ferrite based mixed ionic and electronic (MIEC) cathodes, spinel-based protective coating, new cathode-electrolyte interface interlayer materials, new anode materials by electroless technique, etc.

Component material synthesis

a) Cathode

Strontium-doped lanthanum manganite and lanthanum ferrite cathodes by soft chemical route:

CSIR-CGCRI is engaged in the synthesis of nanocrystalline lanthanum strontium manganite (LSM) and various lanthanum ferrites (LSF)-based cathode materials by combustion technique using L-alanine as novel fuel. The nanocrystalline nature of these cathode materials can play significant role on the ORR kinetics. Details for choosing L-alanine as a novel fuel are provided in studies by Pal *et al.* (2007) and Dutta *et al.* (2009a). Several compositions that were synthesized by this soft chemical route and studied are provided in Table 2. The synthesis procedure adopted for all the compositions is schematically shown in Fig. 5 (Dutta *et al.*, 2009a). Owing to the presence of the oxidant and reductant group in a definite ratio in the solution, an instantaneous burning

Table 2: Cathode compositions and their corresponding sample IDs (Dutta *et al.*, 2009a)

Cathode Composition	Sample ID
$\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$	LS1
$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	LS2
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	LS3
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	LS4

Fig. 5: Schematic for synthesis of cathode powders by soft chemical route (Dutta *et al.*, 2009a)

of the precursor gels leads to the autocombustion synthesis producing finer precalcined ash. The as-synthesized powders (ash) are then calcined at 700° and 825°C for 4 h in air.

Strontium-doped lanthanum manganite cathode by spray pyrolysis technique

CSIR-CGCRI has successfully synthesized Sr-doped lanthanum manganite ($\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$) cathode composition using an indigenously designed spray pyrolysis technique. The main motivation behind the synthesis is not only to prepare powders in larger quantity but also to control the particulate size and morphology which was not feasible by the soft chemical auto-combustion technique. For this purpose, metal nitrate salt solutions with definite ratio of citric acid are prepared with variation in molarity with respect to the metal salt. The precursor solution is sprayed into the reaction zone of an indigenously made pyrolyser using a peristaltic pump and the two-fluid nozzle assembly. The inlet temperature of the spray unit is maintained at 400°C. The ashes generated as a result of the auto-combustion reaction is collected in cyclonic separators. A schematic of the spray pyrolysing process is provided in Fig. 6. For sufficient particulate growth during the pyrolysis reaction, batches are also formulated with a definite amount of addition of precalcined ashes derived from the previous pyrolysis into the precursor solution as the seeding agent. Details of the synthesis procedure, mathematical modelling related to the nucleation and growth process during *in situ* pyrolysis and the effectivity of such materials for the use as cathode functional layers (CFL) and cathode current collection

Fig. 6: Schematic for synthesis of cathode powder by spray pyrolysis route (Mukhopadhyay *et al.*, 2013a)

layer (CCCL) are reported in literature (Mukhopadhyay *et al.*, 2013a; Mukhopadhyay *et al.*, 2013b).

b) Anode

NiO-YSZ anode by liquid dispersion technique

In order to have a homogeneous distribution of the Ni particles in the YSZ matrix of the Ni-8YSZ cermet, a liquid dispersion technique is adopted by CSIR-CGCRI to synthesize the precursor NiO-YSZ powder (Pratihari *et al.*, 1999). In this technique, 8YSZ powder was dispersed in a solution of nickel nitrate hexahydrate dissolved in methanol. The slurry was then heated under stirring and evaporated to dryness. The dried mass was calcined in air at 900°C for 2 h. The calcined powder thus obtained, was ground to fine powder which was used for further characterization and processing. The volume fraction of metallic nickel in the cermet powder varied from 0.1 to 0.6.

Ni-YSZ functional anode materials by electroless technique

Preparation of in-house Ni-YSZ anode powder using a novel electroless technique by CSIR-CGCRI involves two important steps:

- a) Initial sensitization of YSZ particulates by surface adsorption of metallic palladium (Pd^0)
- b) *In situ* reduction of Ni^{2+} from its salt solution to metallic nickel (Ni^0) and its subsequent deposition onto sensitized YSZ powders.

For the sensitization process, the required amount of YSZ powder is added into a redox bath containing palladium chloride solution and stannous chloride solution where metallic palladium (Pd^0) is produced *in situ* by the equation as mentioned below:

Pd^0 formed due to such redox reaction, gets adsorbed on YSZ surface upon placing the redox bath in a high energy ultrasonifier. The sensitized bath was then kept to attain equilibrium for effective adsorption of Pd^0 and complete precipitation of sensitized YSZ powder. An electroless bath containing aqueous solution of nickel nitrate hexahydrate is prepared for the deposition of Ni particulates onto sensitized YSZ particulates. The reduction is carried out using hydrazine hydrate in an ammoniacal pH of ~ 10 . A process flow chart for the synthesis of Ni-YSZ cermet by electroless technique with YSZ sensitized by ball milling is reported in literature (Mukhopadhyay *et al.*, 2008) and shown in Fig. 7.

Fig. 7: Process flow chart for ball mill assisted electroless technique (Mukhopadhyay *et al.*, 2008)

c) Ceramic interconnect and protective coating:

Doped lanthanum chromite-based powders by soft chemical route

Efforts have been made by the group for the cost-effective synthesis of perovskite-based lanthanum chromites by doping alkaline earth metal ions or transition metal ions at 'A' site (La) and 'B' site (Cr), respectively. From the viewpoint of thermal expansion compatibility with other cell components, strontium is the most preferred element as a substituent in the La-site of LaCrO_3 -based perovskite, whereas calcium is responsible for enhancing the electrical conductivity when substituted in the same position. Both pure and doped lanthanum chromites have been developed using combustion synthesis technique wherein ammonium dichromate has been used as the source of chromium that has several advantages over the conventionally used chromium nitrate (Ghosh *et al.*, 2006; Ghosh *et al.*, 2007). Several compositions having the general formula $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{M}_y\text{O}_{3-\delta}$, where M is Al/Mg/Co, $0 \leq x \leq 0.3$ and $0 \leq y \leq 0.1$, have been prepared.

MnCo₂O₄ Based Spinel Powders by Soft Chemical Route

Nanocrystalline powders of $\text{MnCo}_2\text{O}_{4-\delta}$ spinel have been synthesized in-house by the group through combustion synthesis technique (Das Sharma *et al.*, 2011). In order to optimize the fuel to oxidant ratio the combustion reaction was carried out under varying fuel to nitrate ratio using different fuels viz., citric acid and glycine. While a single fuel (either glycine or citric acid) is used for maintaining stoichiometric fuel to nitrate ratio, a mixture of glycine and citric acid has been used for the fuel lean and fuel rich batches. Aqueous solutions of the metal nitrates, taken in a glass beaker in stoichiometric amounts, were mixed with the fuel (dissolved in water). The clear solution was then heated under stirring. The liquid turned viscous and began to set into a deep black gel which finally auto ignited to produce a light and fragile ash. The ash, thus obtained, was calcined between 600° and 750°C for 4 h in air to obtain the powder.

Electrolyte/Interlayer Materials

In the research on low temperature SOFC (LT-SOFC), CSIR-CGCRI, Kolkata has successfully synthesized gadolinium-doped ceria (CGO) using fuel-assisted combustion technique: 20 mole% gadolinium has been successfully doped into the ceria matrix. In order to reduce the sintering temperature for normal CGO, doped transition metal ion (Co^{2+}) has been co-doped with gadolinium during the synthesis (Dutta *et al.*, 2009b). This attempt is in conjunction with the development of co-fired CGO-based interlayer compatible with new class of lanthanum ferrite based mixed ionic and electronic conductor (MIEC) cathode.

Characterizations of Component Materials

a) Structural, Thermal and Microstructural Characterization

Cathode: Fig. 8a and b shows a typical X-ray diffractogram of the as-synthesized and calcined LSM powder, respectively. No significant differences in the diffractograms are observed for the powders prepared either by soft chemical route and spray pyrolysis (SP) techniques. Rietveld analysis of the same shows a phase purity of about 50% and 70% without any significant amount of LaMnO_3 and Mn_3O_4 as secondary phases for cathode synthesized either by soft chemical route (Pal *et al.*, 2007) or spray pyrolysis (Mukhopadhyay *et al.*, 2013b) respectively. After calcinations at 950°C , irrespective of precursor

Fig. 8: X-ray diffractograms for LSM cathode prepared by soft chemical and SP routes (Dutta *et al.*, 2009a)

Fig. 9: X-ray diffractograms for LSCF cathode prepared by soft chemical and SP routes (Dutta *et al.*, 2009a)

solution concentration phase purity improves to more than 99% with the formation of a single-phase rhombohedral $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ (LS1). The calculated lattice parameters are found to be $a = b = 5.467\text{\AA}$ and $c = 13.494\text{\AA}$. The average crystallite size of the calcined LSM prepared by SP is found to be ~ 30 nm. Fig. 9 shows X-ray diffractograms of the various doped lanthanum ferrite based cathode powders (LS2, LS3 and LS4) calcined at 825°C . Phase analysis of the diffractograms reveals that LS2 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$) consists of a predominantly rhombohedral phase together with an orthorhombic phase. For LS3 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$), on substitution of Fe with Co, the structure becomes completely rhombohedral with no other secondary phase. However, for LS4 ($\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$), along with the rhombohedral phase, presence of a small amount of La_2O_3 is observed. The average crystallite sizes are found to be 23, 24 and 19 nm for LS2, LS3 and LS4, respectively (Dutta *et al.*, 2009a).

Coefficients of thermal expansion (CTE) of these cathodes measured at 800°C are given in Table 3. It is observed that CTE increases with

Table 3: Coefficients of thermal expansion (CTE) (Dutta *et al.*, 2009a)

Cathodes	LS1	LS2	LS3	LS4
CTE ($\times 10^{-6}$) K^{-1} (sintered at 900°C)	12.99	10.11	19.26	18.31
CTE ($\times 10^{-6}$) K^{-1} (sintered at 1100°C)	13.05	12.11	19.32	19.23

increase in sintering temperature for all the cathode materials. However, CTE values are quite high enough for 'Co' doped samples (LS3 and LS4) even in the lowest sintering temperature (900°C) which is not at all compatible with other SOFC cell components.. However, electrochemical performances of single cells with doped ceria as an interlayer in between these cathodes and YSZ electrolyte do not show any microcracks which seems that this interlayer compensates some mismatch of CTE for these cathodes with YSZ electrolyte. A typical FESEM micrograph for LSM and LSCF powders prepared by soft chemical route calcined at 700°C is shown in Fig. 10. All the micrographs reveal agglomerated nature of the particles with an estimated size of ~50

nm (Dutta *et al.*, 2009a). FESEM micrograph for LSM cathode powders prepared by spray pyrolysis technique synthesized by *in situ* particulate growth is given in Fig. 11A and B (Mukhopadhyay *et al.*, 2013b).

Anode: Detailed XRD peak profile analysis suggests that on sintering at high temperature in air atmosphere, NiO starts diffusing into the zirconia grains in the samples prepared by solid state and liquid dispersion techniques (Pratihari *et al.*, 1999). This is reflected by the lattice parameter change of the Ni/YSZ cermets. The lattice parameters of YSZ and Ni/YSZ system have been determined from the profile fitting of the (400) reflection. The change in lattice parameters caused by dissolution of Ni^{2+} into cubic

Fig.10: FESEM micrograph for LSM and LSCF prepared by soft chemical route (Dutta *et al.*, 2009a)

Fig. 11: FESEM micrograph SP-synthesized LSM prepared for (A) cathode functional layer and (B) current collection layer (Mukhopadhyay *et al.*, 2013b)

Table 4: Measured lattice parameters of YSZ and Ni/YSZ

Specimen	Lattice Parameter	Reliability Indices	
	a_c (Å)	R_p %	R_{WP} %
YSZ	5.4103 (3)	2.767	3.478
Ni/YSZ	5.0525 (3)	4.042	5.144

YSZ is shown in Table 4. The X-ray diffraction pattern of as-synthesized Ni-YSZ cermet prepared by electroless technique is shown along with the XRD pattern of precursor YSZ powder in Fig. 12.

Fig. 12: X-ray diffraction pattern of: (A) precursor YSZ powder and (B) Ni-YSZ cermet prepared by electroless technique (Mukhopadhyay *et al.*, 2009)

Fig. 13: Comparative plots for coefficients of thermal expansion (CTE) for electroless and conventional anode in conjunction with YSZ electrolyte

Comparison of Fig. 12A and B clearly indicates the formation of phase pure biphasic matrix of Ni-YSZ cermet prepared by electroless technique (Mukhopadhyay *et al.*, 2009). For application in high temperature ceramic fuel cell, the prepared anode happen should enable similar expansion behaviour with the adjacent YSZ electrolyte. Fig. 13 describes comparative expansion plots among electroless and conventional anode in conjugation with the YSZ electrolyte. It can be observed that, electroless anode having only 28 vol% is found to be thermally compatible with adjacent YSZ electrolyte ($10.85 \times 10^{-6} \text{ K}^{-1}$). Completely distinct microstructures are observed in the functional anodes prepared by electroless technique that forms core-shell microstructures with Ni in grain boundary region and YSZ in the core. In comparison, conventional anode prepared by solid state technique comprises uniform dispersion of Ni and YSZ phases. Fig. 14A and B show optical micrographs of the anode synthesized by electroless and solid state techniques (Mukhopadhyay *et al.*, 2008).

Ceramic Interconnect and Protective Coating

The developed LCR materials have been thoroughly analyzed using different techniques such as XRD, SEM-EDX, TEM and particle size analysis for their bulk characterization. Owing to very fine crystallite size (ranging from 10 to 50 nm) as observed from XRD and the high reactivity of the powders (surface area as high as $25 \text{ m}^2/\text{g}$), the sintering temperature reduces drastically (1300°C). TEM micrograph of LCR materials reveals particles as fine as 50-70 nm synthesized by soft chemical route (Ghosh *et al.*, 2006; Das Sharma *et al.*, 2011). Fig. 15 shows the X-ray diffractograms of phase pure MnCo_2O_4 spinel-based protective coating materials that are obtained upon calcination of the ash at a temperature as low as 650°C . It is observed that phase purity of $>99\%$ is achieved upon calcination of the powder at 650°C . Spinel phase of Mn_2CoO_4 is identified with crystallite size of $\sim 38 \text{ nm}$. Transmission electron microscopic (TEM) images of such calcined powders confirm the nanocrystallinity within the synthesized particulates. The size range of such synthesized powders is found to be within 40-50 nm (Fig. 16), (Das Sharma *et al.*, 2011) Upon consolidation, it is possible to sinter the

Fig. 14: Optical micrographs for anode synthesized by (A) electroless and (B) solid state techniques (Mukhopadhyay *et al.*, 2008)

Fig.15: X-ray diffraction pattern of (A) as-synthesized and (B) calcined powder (700°C/4 h) of $\text{MnCo}_2\text{O}_{4-\delta}$ Spinel (Das Sharma *et al.*, 2011)

Fig. 16: TEM image of $\text{MnCo}_2\text{O}_{4-\delta}$ calcined powder (Das Sharma *et al.*, 2011)

bulk samples at a temperature of only 1100°C with a density more than 95% of theoretical value. Linear thermal expansion behaviour with an average coefficient of thermal expansion (CTE) of $13.1 \times 10^{-6} \text{ K}^{-1}$ (from 30-1100°C) is obtained. Thus, the CTE is found to be quite close to that of commonly used metallic interconnects such as Crofer22APU (CTE: $\sim 12 \times 10^{-6} \text{ K}^{-1}$).

Electrolyte/Interlayer materials

Due to the nanocrystallinity of the synthesized Co-doped CGO, it has been possible to reduce the sintering temperature of these electrolytes to 1100°C. The sintered microstructure of the Co-doped CGO along with the synthesized powder is given in Fig. 17.

Fig. 17: FESEM of sintered Co-doped CGO with nanocrystalline powders of calcined powder (inset) (Dutta *et al.*, 2009b)

b) DC Electrical Conductivity Characterization

Cathode: The electrical conductivity of LSM (LS1), and doped lanthanum ferrites (LS2, LS3 and LS4) materials synthesized by soft chemical route are measured in the sintered conditions (Fig. 18). For all the materials except LS1, the increase of conductivity is significant. In case of LS1 and LS3, conductivity decreases with the increase of temperature from 500°C to 900°C in all the samples sintered at 900–1100°C showing a metallic behaviour (Dutta *et al.*, 2009a). For spray pyrolysed LSM cathode, similar trend of linear semiconducting type behaviour within the measurement temperature range of 500–800°C is observed. Smaller particulates having average particulate size of ~0.24 μm for cathode functional layer promote sintering at a lower temperature and results in higher electrical conduction of 195 S cm^{-1} at 800°C having open porosity <2% when sintered at 1100°C (Mukhopadhyay *et al.*, 2013b).

Fig. 18: Electrical conductivities for perovskite cathodes (Dutta *et al.*, 2009a)

Anode: Fig. 19 shows the comparative electrical conductivity values at 800°C of SOFC functional anodes (prepared at transient and non-transient equilibrated sensitized bath) with conventionally prepared anode. The conductivity percolation threshold is brought down to ~28 vol% of Ni in

Fig. 19: Electrical conductivity percolation plot for anodes prepared by various techniques (Mukhopadhyay *et al.*, 2008)

functional anode prepared with transient equilibrated sensitized bath in comparison to ~40 vol% Ni for conventionally prepared samples. Reduction in metallic phase in the cermet not only helps in matching the thermal coefficient of the cell components but also reduces the changes of Ni coarsening due to long-term operation of cells (Mukhopadhyay *et al.*, 2008; Mukhopadhyay *et al.*, 2007).

Ceramic Interconnect and Protective Coating

For LCR materials prepared by combustion synthesis, a dramatic improvement in densification (nearly theoretical density) is observed for aluminum substitution, when sintered at as low a temperature as 1300°C. Depending on the substituent, the electrical conductivities of the sintered samples in air, at 1000°C, were found to be in the range of 10–45 S cm^{-1} , and are more than that of the values required for SOFC application (Ghosh *et al.*, 2006). Four probe electrical conductivity measurements for the developed spinel-based materials show a high enough conductivity (>100 S cm^{-1} at 800°C) to be suitable for protective coating application. Semiconducting behaviour with average activation energies of 0.25 and 0.33 eV, respectively is obtained for the various redox systems (i.e. fuel lean and fuel rich) (Das Sharma *et al.*, 2011).

Electrolyte/interlayer Materials

Doping of metallic cobalt in CGO helps in reducing the sintering temperature to $\sim 1100^\circ\text{C}$ which results in co-sintering of Co-CGO and lanthanum ferrite or cobaltite based cathodes. A reasonably high ionic conductivity of $\sim 0.01 \text{ S}\cdot\text{cm}^{-1}$ is achieved at a temperature $\sim 750^\circ\text{C}$. Arrhenius plot of the electrical conductivity for Co-doped CGO as a function of temperature is shown in Fig. 20. Reasonably low activation energies of 0.47 and 0.79 eV are found for the material when sintered at 900°C . The same is found to be 0.43 and 0.75 eV for the materials sintered at 1100°C .

Fig. 20: Temperature dependent electrical conductivity for Co-doped CGO (Dutta *et al.*, 2009b)

c) Electrochemical Impedance Spectroscopic Studies

Cathode: Spray pyrolysed LSM cathode is characterized by impedance spectroscopic studies using symmetric cell configuration onto YSZ electrolyte substrate. Associated polarizations of symmetric cell fabricated by combining the cathode current collection layer (CCCL) and cathode functional layer (CFL) having variable micro to nano porous particulates is found to be the lowest. Fig. 21 shows the impedance spectra of such symmetric cell in the temperature range of $700\text{--}800^\circ\text{C}$. It is also vivid from the impedance spectra that the incorporation of CCCL reduces the diffusion polarization occurring at the lower frequency, thereby enhancing the formation and dissociation of peroxide ion observed at the middle frequency range of the applied AC field (Mukhopadhyay *et al.*, 2013b). In addition, the mutual union of CFL and CCCL tends to reduce the charge transfer polarization through proper inter-connectivity between YSZ and YSZ ionic phases, diffusion

Fig. 21: Impedance spectroscopy of SP-synthesized cathode (Mukhopadhyay *et al.*, 2013b)

polarization of molecular oxygen and polarization related to formation of oxide ion. Such a composite cathode is found effective having a total cathode thickness of $\sim 50 \text{ nm}$ with minimum polarization resistance of $\sim 0.18 \text{ W}\cdot\text{cm}^2$ at 800°C (Mukhopadhyay *et al.*, 2013b).

Anode: Electroless anode in the form of the thin anode active layer (AAL) having dense microstructure and higher charge conduction possesses better electrocatalytic activity at the anode/electrolyte interface and thereby causes lesser charge transfer polarization (Mukhopadhyay *et al.*, 2013c). Additionally, thinner electroless AAL in conjugation

Fig. 22: Impedance spectroscopy of cell with electroless Ni as AAL (Mukhopadhyay *et al.*, 2013c)

with conventional anode support helps in gas diffusion in the porous conventional anode layer, which enumerates lower concentration polarization. Anode of such configuration also helps in lowering the resistance of electronic flow path by minimizing the intra anodic stratum (Mukhopadhyay *et al.*, 2011). Consequently, the single cell with 32 vol% Ni in AAL and conventional anode cermet exhibits least polarizations ($\sim 0.3 \text{ W-cm}^2$) as observed from the impedance spectra (Fig. 22).

Single Cell Fabrication

a) Fabrication of Anode-supported Half-cell by Tape Casting and Lamination Technique

For the development of anode-supported single cells, the major technical challenge involves fabricating a dense and gas-tight 8 mol% YSZ electrolyte layer of thickness $50 \mu\text{m}$ or less that should be well-adhered to the porous NiO-YSZ (anode) substrate so as to minimize the interfacial polarization. Under the NMITLI programme, simple and up-scalable techniques such as tape casting and screen printing have been used to fabricate anode-supported single cells of dimensions up to $10 \text{ cm} \times 10 \text{ cm} \times 1.5 \text{ mm}$ (Basu *et al.*, 2008; Basu *et al.*, 2010). The whole fabrication process is shown schematically in Fig. 23.

Fig. 23: Flow chart of the single cell fabrication (Basu *et al.*, 2008)

A cost-effective and up-scalable processing technique viz., tape casting has been used to fabricate a dense YSZ electrolyte layer on porous anode support (40 vol% Ni + 60 vol% YSZ). The production of ceramic tapes by this process requires the use of significant amounts of organic compounds (e.g., solvents, binders, plasticizers, dispersing agents, etc.). The mechanical and physical characteristics of the green tapes are very important for further processing and the final properties of the material.

b) Screen Printing of Cathode Layers for Single Cell Fabrication

Processing parameters have also been optimized for screen printing of LSM-based cathode functional layer (CFL) and cathode current collector layer (CL) onto the co-sintered flat dense electrolyte surface of the half-cell to produce SOFC single cell. Utilizing the optimized parameters, large numbers of single cells of dimensions $5 \text{ cm} \times 5 \text{ cm} \times 1.5 \text{ mm}$ and $10 \text{ cm} \times 10 \text{ cm} \times 1.5 \text{ mm}$ were fabricated, photographs of some of which are shown in Fig. 24. The right kind of microstructure is obtained in the developed cells (Fig. 25) with $\sim 10 \text{ mm}$ thin, gas-tight YSZ electrolyte sandwiched between a porous anode (Ni-YSZ) support on one side and a LSM-based layer

Fig. 24: Fabricated single cells: (a) $5 \text{ cm} \times 5 \text{ cm}$ and (b) $10 \text{ cm} \times 10 \text{ cm}$ (Basu *et al.*, 2008)

Fig. 25: SEM micrograph of a cross-section of the developed single cell (Basu *et al.*, 2008)

(comprising ~10 mm CFL and a ~50 mm porous CL layer) on the other side.

Electrochemical Performance Evaluation of Single Cells

a) Electrolyte Thickness Dependent Cell Performance

Table 5 shows the comparative electrochemical performance of 5 cm × 5 cm single cells having different YSZ thicknesses (20–40 μm) at 800°C at 0.7 V. As expected, the performance of the cells improves with a decreasing electrolyte thickness and for the optimized thickness of 20 μm, a high current density of 1.35 A/cm² is achieved. The electrochemical performance curves for the coupon cells as well as the 5 cm × 5 cm cells (having optimized YSZ thickness of 20 μm) are shown in Fig. 26. It can be seen from Fig. 26 that for both the coupon cell (dia ~15 mm) and square cells (5 cm × 5 cm), current-voltage (I-V) and current-power density (I-P) are similar in nature. For a cell voltage of 0.7 V, the current density and power density for 5 cm × 5 cm cell is found to be 1.35 A/cm² and 0.94 W/cm² respectively;

Table 5: Electrochemical performance of SOFC single cells (at 800°C, 0.7 V) with variable YSZ thickness (measured at Forschungszentrum, Jülich)

Electrolyte thickness (μm)	Current density (A/cm ²)	Power density (W/cm ²)
20	1.35	0.95
30	1.2	0.84
40	1.0	0.70

Fig. 26: Electrochemical performance of single cells at different operating temperatures: (A) coupon cell (dia ~15 mm) (B) 5 cm × 5 cm square cell (thickness for each cell: 1.5 mm) (Basu *et al.*, 2008)

while for the coupon cell the values are 1.42 A/cm² and 1.0 W/cm², respectively. Thus, the cell performances are size-independent, establishing the fact that the processing technology followed is up-scalable (Basu *et al.*, 2007; Basu *et al.*, 2008).

b) Performance Evaluation with Doped Lanthanum Manganite Synthesized by Soft Chemical Route and by Spray Pyrolysis Techniques

Fig. 27A shows a typical performance of SOFC consisting of cathode functional and current collection layer (CFL and CCCL) synthesized by conventional SP route [cell configuration: Ni-YSZ/YSZ/CFL (conventional SP-synthesized LSM + YSZ)/CCCL (conventional SP-synthesized LSM)]. Fig. 27B exhibits the performance of SOFC fabricated using optimized spray pyrolysed LSM both for CFL and CCCL. Significant enhancement in single cell performance is observed for the single cells with cathode synthesized by spray pyrolysis technique. Thus, at 0.7 V and 800°C, much higher current density of 3.2 A.cm⁻² is observed for single cells with cathodes synthesized by spray pyrolysis technique compared to single cells having cathode synthesized by soft chemical route (2.0 A.cm⁻²) (Mukhopadhyay *et al.*, 2013b). Furthermore, the induced functionality within SP-synthesized cathode layers (CFL and CCCL) is well-justified from the reduced area specific resistance (ASR) of ~109 mW.cm² at 800°C for cells with SP-synthesized cathode compared to that of 184.8 mW.cm² at 800°C for cells having cathodes prepared by soft chemical route.

c) Single Cell Performance with Lanthanum Ferrite Based Cathodes Synthesized by Soft Chemical Route

The electrochemical cell performance using optimized lanthanum ferrite as cathode La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (LS4) is conducted in the temperature range of 700–800°C. The approximate thickness of CGO coating was 10 μm and that of LS4 cathode was 50 μm after the heat treatment. The CGO coating was sintered at 1200°C for 6 h while LS4 cathode coating was finally fired at 1100°C for 4 h. The cell performance increases with the increase of operating temperature and at

Fig. 27: Electrochemical performance of single cells at with cathode prepared by: (A) soft chemical route and (B) spray pyrolysis techniques (Mukhopadhyay *et al.*, 2013b)

800°C the current density is ~ 1.7 A/cm² at 0.7 cell voltage (Dutta *et al.*, 2009a). The I-V characteristics at different temperatures clearly indicate that the activation polarization exists (below 100 mA/cm² cell current) i.e., at lower temperature oxygen reduction reaction at the cathode/electrolyte interface is kinetically limited. Further systematic research on the optimization of cell fabrication, especially the cathode firing temperature and interlayer composition has been in progress.

High-temperature Glass-based Sealant

For planar SOFC stacks, gas-tight seals must be applied along the edges of each cell and metallic interconnect plates in order to avoid intermixing of fuel gas (on anode side) and air (on cathode side). For such a design, two types of sealing viz., metal-metal and ceramic-metal, are of particular importance. The seals must be stable in a wide range of oxygen partial pressure (in air and fuel) and be chemically compatible with adjoining cell components, while minimizing thermal stresses during high-temperature operation. They must also have high electrical resistivity to avoid short circuiting between different layers of the stack. Generally, glass and glass-ceramic-based sealants meet most of these requirements and therefore, have found widespread application as high temperature sealants. However, these sealants are required to be developed indigenously as they are not

easily available in the market. Hence, major emphasis was given to development of glass-based sealants for planar anode-supported SOFC stack application. At CSIR-CGCRI, efforts have been made towards the development of several glass-based sealing materials based on BaO-Al₂O₃-SiO₂ (BAS), BaO-CaO-Al₂O₃-SiO₂ (BCAS), MgO-Al₂O₃-SiO₂ (MAS) and MgO-BaO-Al₂O₃-SiO₂ (BMAS) systems and their extensive characterization for ultimate use as sealant for SOFC (Ghosh *et al.*, 2008a; Ghosh *et al.*, 2008b; Ghosh *et al.*, 2010). To estimate the applicability of these glasses as sealants, their thermal properties (e.g., glass transition temperature T_g , coefficient of thermal expansion, CTE and softening temperature T_s), crystallization behaviour, electrical resistivities, microstructure upon different heat-treatment schedule and the overall bonding characteristics with ceramic electrolyte (YSZ) and high chromium ferritic steel (e.g., Crofer 22APU) have been investigated. Fig. 28 shows a complete process flow chart of the detailed sample preparation of the glass-based sealants and the different characterizations as performed using such samples.

The prime requirement of matching the CTE both with the electrolyte and interconnect have been achieved by tailoring the compositions in the BCAS and BAS systems. The compositions have been tailor made in such a way that even after prolonged heat-

treatment at the SOFC operating temperature (800°C), the resultant glass-ceramics have compatible CTE with YSZ and the interconnects. Table 6 shows the list of different systems and compositional ranges extensively studied along with their physical properties in order to find out the best possible system and compositions.

A distinctly new approach of “*bi-layered sealing*” was introduced for the first time during this investigation which has been successfully applied to make crack-free joints between the metal-glass-YSZ interfaces (Ghosh *et al.*, 2008b, Ghosh *et al.*, 2008c) (Fig. 29). In addition, the extent of chemical interaction during long-term heat-treatment of the developed sealants with the metal (Crofer 22APU) and the ceramic interconnects, particularly under the oxidizing environment, has been investigated in detail. Electrical conductivity of the sealants has also been investigated under sandwiched condition between two metal plates, especially under the oxidizing environment. Gas tightness of the sealants has been assessed by performing leak/permeability test in presence of helium using an indigenously fabricated helium leak test set-up. In order to lower the extent of chemical interaction between the sealant and adjoining SOFC components, the Crofer22APU interconnect in particular, a novel glass sealant within the BaO-La₂O₃-SiO₂ (BLS) system with relatively low content of BaO has been developed (Ghosh *et al.*, 2008c). These sealants were found to be significantly effective in reducing the chemical interaction while joining with the metallic and ceramic interconnects. Using the developed sealants, near theoretical open circuit voltages (OCV)

of ~1.15 V per cell have been observed during stack testing at 800°C without any appreciable degradation of the OCV, which confirmed the perfect hermetic sealing during such experiments.

Fabrication and Demonstration of Short SOFC Stack

The overall voltage output from a single cell is very low which is neither sufficient to use in any practical device nor is the same significant for use as stationary power. Therefore, several numbers of such single cells need to be stacked thorough interconnects for voltage build up. For intermediate temperature SOFC (IT-SOFC) operating in the range of 700-850°C, ferritic steel based metallic interconnects (Crofer 22 APU) are widely used. CGCRI's SOFC stack is based on counter flow design of the fuel and the air/oxidant. Based on this design, different stack components viz. cell holders, bi-polar and current collector plates have been fabricated with ferritic steel (Crofer 22 APU). Using the indigenously developed 10 cm × 10 cm × 1.5 mm single cells, glass-based high temperature sealants and metallic stack components, several numbers of short SOFC stacks (up to 10-cell level) have been fabricated and tested for their performance evaluation using hydrogen as fuel and air/oxygen as oxidant. At 800°C, the open circuit voltage (OCV) per cell is ~1.1 V which is quite close to the theoretical value (1.15 V). A characteristic 3-cells stack result under different constant current loads of 2.5 Amp, 5 Amp and 7 Amp is shown in Fig. 30A. Demonstration of 10-cell stack resulted in a total power output of ~100 W. Thus, CSIR-CGCRI has successfully

Table 6: Different systems and compositions range for high-temperature glass-based sealants

System	Compositions in mol%	Minor additives (<5 mole %)	Thermal properties			
			T _g (°C)	T _s (°C)	T _c (°C)	CTE (x 10 ⁻⁶ /K)
MAS	MgO:18-20, Al ₂ O ₃ :10-15, La ₂ O ₃ :10-15, SiO ₂ :10-30	B ₂ O ₃ ZnO Co ₃ O ₄ La ₂ O ₃ TiO ₂ ZrO ₂	635-725	670-780	765-825	8-9
BMS	BaO:5-30, MgO:16-20, SiO ₂ :5-50		560-680	625-710	680-750	9.5-11
BAS	BaO:35-40, Al ₂ O ₃ :8-10, SiO ₂ :30-40		610-630	660-680	735-760	10-11
BCAS	BaO:28-35, CaO:5-15, Al ₂ O ₃ :0-6, SiO ₂ :8-30		600-665	665-700	730-780	9.5-12.5

Fig. 28: Schematic of sample preparations and characterizations (Ghosh *et al.*, 2008b)

Fig. 29: SEM of polished cross-section of Crofer22APU-YSZ samples sealed at 850°C/1 h, using bilayer glass; closure view of the YSZ-glass interface (top side) and glass-Crofer22APU interface (bottom side) (Ghosh *et al.*, 2008b)

demonstrated working of SOFC stacks for the first time in India. Fig. 30B shows a close view of the CSIR-CGCRI-developed 10-cell SOFC stack.

Material and Design Challenges and Commercialization of SOFC Technology

The fuel cell component materials face significant challenges for redox cyclability with respect to conventional anode materials such as Ni-YSZ, cathode degradation, especially for doped lanthanum cobalt ferrite or barium cobalt ferrite based MIEC compositions under high current during long-term operation. Apart from the cathode and anode, owing

Fig. 30: (A) Stack testing under constant current load (3-cell stack) and (B) CSIR-CGCRI developed 10-cell SOFC stack

to processing defects, formation of hot spots in the impervious YSZ-based electrolyte layers may create internal crossover of fuel and oxidant during long-term operation under electrical load. These cause cell and stack degradation after a reasonable period of time and percentage of degradation are found to be higher based on the materials composition and microstructural aspects. Evaporation of Cr_2O_3 vapour from either LaCrO_3 -based or commercial SS 430 grade ferritic steel also causes significant deterioration in the cathode by blocking active sites for the electrochemical reaction (Casteel *et al.*, 2009; Ghosh *et al.*, 2006). High-temperature glass-based sealant also faces significant challenges with respect to its thermal cyclability and long-term endurances under the SOFC operating conditions. The application of these high-temperature glass-based sealants also imposes significant problems while developing SOFCs in planar design in the level of several kW. While power density of the planar SOFC design overpowers the same for the other famous tubular design, the latter faces challenges for fabrication of longer tubular support with stricter process optimization for depositing thin impervious electrolyte film onto a large dimension substrate.

In the global scenario, the research on SOFC has reached a reasonably mature stage, particularly in advanced countries such as USA, Canada, Germany, UK, Denmark, Australia, Japan, etc., where commercialization of the technology seems to be viable through prototype demonstration as well as installation of systems, particularly for residential and transport applications. However, high costs, issues

related to reliability and degradation during continuous operation are some of the major bottlenecks that are preventing commercialization of SOFC technology and need to be resolved. The technology development so far has been realized through major programmes such as SECA (USA), Framework programme on SOFC (Europe), NEDO (Japan), etc. One of the key features of all such programmes has been the strong industry-institute participation with clear-cut objectives and deliverables. As an outcome of these programmes, several industries have enhanced their capabilities to develop the technology. An excellent review on the present status of these developments is available in a recent report on this subject (McPhail *et al.*, 2013).

Conclusions and Future Direction

Ceramic fuel cell commonly known as solid oxide fuel cell (SOFC) is one of the most promising technologies emerging out as an alternative source for generating power in an environmentally benign manner. The technology is in an advanced stage of development in many of the developed nations of the world such as USA, Germany, Australia, Canada, Japan, UK, etc. and is on the verge of commercialization after successful demonstration of prototype stacks and systems of different capacity (1-10 kW level). However, in India, research on high temperature ceramic fuel cells was initiated in the early 90s with pioneering contribution from CSIR-Central Glass & Ceramic Research Institute (CSIR-CGCRI), Kolkata.

Till date, most of the other research organizations/academic institutions engaged in SOFC research in India have focused on material development. At CSIR-CGCRI, an attempt is being made to develop an indigenous technology that is based on the planar anode-supported design for a national project under CSIR-NMITLI programmes. The research in this area so far has led to the successful development of planar anode-supported single cells of dimension 10 cm x 10 cm x 1.5 mm, suitable high-temperature glass-based sealants along with design and fabrication of ferritic steel (Crofer 22APU) interconnects with various flow fields for reactant gases. Using the indigenously developed cells, high temperature sealants and fabricated metallic interconnects; demonstration of working SOFC stacks has successfully been made for the first time in our country.

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