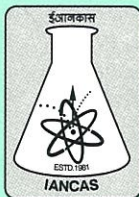


LM-1225
SHRI ARNAB SARKAR
FUEL CHEMISTRY DIV
T.G. BARC
MBAI 40



**INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS**

Fuel Cells

IANCAS
Bulletin

Editorial

A fuel cell is an electrochemical device that combines hydrogen and oxygen to produce electricity, with water and heat as its byproducts. Since the conversion of the fuel to energy takes place via an electrochemical process, not combustion, the process is clean, quiet and highly efficient. Additional benefits are reliability, multi-fuel capability, siting flexibility, durability, scalability and ease of maintenance. No wonder the technology of fuel cells has been improving at a rapid pace, to make use of the above benefits. Fuel cell cars are already on the roads for demonstration trials. Automakers are pledging to commercialize them by 2015. The present thematic bulletin describes the development of various aspects of fuel cells. I am thankful to Dr. Shyamala Bharadwaj for her excellent support as the Guest Editor.

CONTENTS

From Secretary's Desk	186
IANCAS Awards	187
Dr. Tarun Datta Memorial Award	191
Prof. H.J. Arnikaar - Best Thesis Award	193
Focus	197
Guest Editorial	199
Research on Materials for Solid Oxide Fuel Cells Operated at Intermediate Temperatures	201
<i>Shyamala Bharadwaj</i>	
Challenges in PEM Fuel Cell Development	214
<i>K. S. Dhathathreyan and N. Rajalakshmi</i>	
Fabrication of Anode Supported Solid Oxide Fuel Cell	229
<i>R.N. Basu, A. Das Sharma, J. Mukhopadhyay and Atanu Dutta</i>	
Fabrication of Cathode Supported Solid Oxide Fuel Cell	239
<i>Deep Prakash and P.K. Sinha</i>	
Alternate Possibilities for Electrodes and Membranes for Direct Methanol Fuel Cells	245
<i>B. Viswanathan</i>	
Development of Membranes for Polymer Electrolyte Membrane (PEM) Fuel Cells	254
<i>S. Prabhakar, H.S. Sodaye, R.C. Bindal and P.K. Tewari</i>	

Research on Materials for Solid Oxide Fuel Cells Operated at Intermediate Temperatures



Dr. Shyamala Bharadwaj is presently Head, Fuel Cell Materials & Catalysis Section, Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India. She obtained her M.Sc. in Chemistry in 1981 and Ph.D. in Physical Chemistry in 1991 from Mumbai University. Her main area of work during the past 33 years has been determination of thermodynamic properties of nuclear materials using various techniques such as vapour pressure measurements, thermogravimetry, isoperibol calorimeter etc. During 2000–2001, she worked as guest scientist at Juelich Research Centre, Juelich, Germany on Solid Oxide Fuel Cell (SOFC) materials. Her current interests are in the fields of Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC) and Sulphur – Iodine thermochemical cycle for generation of hydrogen from water. She was awarded the NETZSCH –ITAS Award (2006) by the Indian Thermal Analysis Society in the year 2006 for her contributions in the field of thermal analysis. She has more than 95 papers in refereed international journals.

Abstract

Solid oxide fuel cells (SOFCs) are considered promising candidates for production of electricity with high conversion efficiency. In SOFCs the chemical energy of a fuel is directly transformed into electrical energy with a high quality heat stream. But due to high manufacturing costs, fuel cell system price per produced kilowatt hour is still too high in comparison to electricity produced by conventional methods. Secondly the high operating temperature increases the start-up time and reduces the operating life of fuel cell stack. These problems can be solved to a great extent by operating the SOFCs at the intermediate temperature range of 600–800°C. The electrochemical property of the cathode is an important issue in the intermediate temperature operation of SOFCs because the overpotential for oxygen reduction increases at lower temperature range. The catalytic properties and electronic/ionic conductivities of the electrodes have to be increased very much for the intermediate range operation of SOFCs since a reduction in the transport and catalytic properties occurs at lower temperature range. So the optimization of all the components of the SOFCs is necessary to obtain satisfactory power outputs in this range of temperature. Suitable electrolyte materials with high ionic conductivities

at lower temperatures have to be developed. In this article, the materials research aspect for the various components of SOFCs operated at intermediate temperatures is discussed.

Introduction

The main components of any fuel cell stack are the electrolyte, the anode, the cathode and the interconnect. Each component serves several functions in the fuel cell and must meet certain requirements. The common requirements for all these components are stability in working environments, chemical compatibility with other components, suitable electrical conductivity and similar coefficient of thermal expansion. The electrolyte and interconnect must be dense and prevent gas mixing. The anode and cathode must be porous to allow gas transport to the reaction sites. Electrolyte should be strictly an ionic conductor and the interconnect should be an electronic conductor. Anode and cathode can be mixed ionic and electronic conductor.

Solid oxide fuel cells (SOFCs) utilize oxide ion conductors as electrolyte and require operation at elevated temperatures (typically between 973–1273 K). The state of art materials for SOFC are yttria

Dr S.R. Bharadwaj, Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085; E-mail: Shyamala@barc.gov.in

stabilized zirconia (YSZ) as electrolyte, Sr substituted lanthanum manganite (typically $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) as cathode and Ni-YSZ cermet as anode. YSZ is a good oxide ionic conductor only above 800°C and hence SOFCs based on YSZ as electrolyte typically operate at 1000°C . This high temperature operation causes degradation of the cell. Reducing the operating temperature to about $600\text{--}800^\circ\text{C}$ can overcome this problem and also reduce the cost of SOFCs as cheaper materials of construction can be used. SOFCs operating in this temperature range are called Intermediate Temperature Solid Oxide Fuel Cells (ITSOFCs). Advances in chemistry and processing of materials play important role in the development of materials for ITSOFCs. Doped ceria is considered to be a promising electrolyte for ITSOFCs [1]. In general, it is found that the highest oxygen ion conductivity is observed when the aliovalent doping cation in ceria or zirconia is closest to the ionic radius of the host cation. Gadolinium doped ceria $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.9}$ (10CGO) is the most extensively studied ceria based electrolyte. Work by Ishihara et al [2] has shown that Sr and Mg doped LaGaO_3 (LSMG) exhibits high ionic conductivity and low electronic conductivity even at low pO_2 levels. This class of materials potentially offers adequate performance down to about 400°C .

The electrolytes discussed so far are all oxide ion conductors. Proton conducting ceramics are also being investigated for ITSOFC applications. Since the size of a proton is much smaller than that of an oxide ion, higher conduction at lower temperature is envisaged.

Barium based perovskite structures such as $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ have shown protonic conductivity approaching that of the best oxide ion conductors at the low temperature-end of ITSOFC operation. Ishihara [3] has reviewed proton conducting ceramics for ITSOFCs.

As rare-earth based cobaltites, nicoates and ferrites are known to have higher catalytic activity and higher ionic conductivity than LSM, they have been considered as cathode material for ITSOFC. Using cermets often improves matching in TECs between the electrolyte and the anode. Therefore, cermets are used as structural support in anode supported ITSOFCs. Atkinson et al [4] have

reviewed the recent advances in anode technology for SOFCs which includes development of single phase oxides with mixed ionic and electronic conductivity (MIEC) properties such as ceria and transition metal perovskites. For high temperature solid oxide fuel cells (HTSOFCs), the interconnect must be either a ceramic or a special high Cr or Ni alloy. This can make the interconnect the most expensive component of the stack on a material value basis. ITSOFC operation allows relatively low cost ferritic stainless steel alloys to be used as interconnects as well as for the mechanical support of the ITSOFC.

Synthesis of Ceramic Fuel Cell Components

The SOFC components can be prepared either by solid state or solution route. The solid state route is simple and an extremely versatile process, best suited for bulk production. In their applications, the ceramic oxides are required to have definite shape and microstructure. These characteristics of the sintered body are highly dependent on the starting powder characteristics. It is advantageous to have the material in nano-crystalline form so that its powder characteristics can be precisely tuned. This can be achieved by reducing the reaction temperature and having the reactants as a homogeneous mixture. In the solution route, mixing of constituents will be at molecular level in the liquid state. Several solution routes such as combustion, co precipitation, sol-gel and cation complexation have been routinely employed in the preparation of ceramic fuel cell components. Experimental details about the solid state and solution methods for ceramic materials are described in the following paragraphs.

Solid State Route

The solid state synthesis route involves mechanical mixing of the solid constituents (oxides/carbonates), repeated grindings and annealing at elevated temperatures, generally over a long duration. For preparation of large quantities of the material, the constituents are usually ground in a ball mill.

The solid state reactions are diffusion controlled and follow a parabolic law given as $dx/dt = kx^{-1}$, where x is the degree of reaction (thickness of

the product layer) t is the time and k is a constant. Since the reactants are high melting refractory solids, it is only at high temperatures that the ions have sufficient thermal energy to enable them to jump off their normal sites to diffuse through the crystals. Initially the reaction is faster and then the rate becomes slow as now the reactants have to diffuse through the product layer that is formed in order to come in contact with one another. The reactants are ground and mixed thoroughly as the subsequent reaction rate depends to a large extent on the particle size of the reactants, the degree of homogenization achieved on mixing, the intimacy of contact between the grains and the temperature. The area of contact between the reacting solids (their surface area) is an important factor for enhancing the reaction of solids. The surface area of the solids increases with decreasing particle size. In order to increase the surface area, the reactants are crushed into fine powder and the area of contact is increased by pressing the reacting powder into a pellet. It is necessary to repeat the procedure of grinding and pelletization after heat treatment and often the same procedure is repeated several times. This brings fresh surfaces in contact and also reduces the particle sizes of the reaction powders.

Wet Chemical Routes

As we have seen earlier, there are several variations of the wet chemical routes and they can be adopted to tailor make materials, with preset properties and structure.

Sol-Gel method

In sol-gel method the starting precursors like metal alkoxides, oxalates, nitrates etc are converted into gel form using gelating agents like 2-ethyl-1-hexanol, urea etc. The various processes in this synthesis method are hydrolysis, polymerization, gelation, drying, dehydration, calcination and densification.

The materials used along with the procedures and heating protocols adopted are described by giving an example of cathode material preparation for ITSOFC.

The cathode material, Sr and Co substituted lanthanum manganite, viz., $\text{La}_{0.76}\text{Sr}_{0.19}$

$\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_{3\pm\sigma}$ (LSM $\text{Co}_{0.2}$) was synthesized by sol-gel route [5].

In this method, urea was used as the gelating agent. La, Sr, Mn and Co nitrates were used as starting materials. From the stoichiometry of the compound, a solution with appropriate concentrations of the starting materials was prepared. Urea concentration was fixed at $\phi = 10$ where $\Phi = [\text{urea}]/\Sigma [\text{metal ions}]$

The solvent (water) was evaporated directly on a hot plate with continuously stirring at temperature ranging between 348 and 410 K, which corresponds to melting temperature of urea. On cooling, a gel was formed, which was decomposed in an oven at 523 K in air for 3 h, yielding a fairly porous precursor. After milling in an agate mortar, the precursor, in powder form was calcined at 873 K for 24h. The second heat treatment was for 48 h at 1173 K. The final sintering was carried out at 1673 K for 10 h. XRD patterns of $\text{LSMCo}_{0.2}$ synthesized by sol gel method and heat treated at 1173 K and 1673 K are given in Fig. 1. It can be seen that $\text{LSMCo}_{0.2}$ synthesized by sol gel route showed a change in symmetry from orthorhombic at 1173 K to rhombohedral at 1673 K. $\text{LSMCo}_{0.2}$ synthesized by solid state route and heat treated similarly at 1173 K and 1673 K indicated rhombohedral symmetry at both these temperature [5]. Thus it can be seen that the crystal structure of the material depends on the method of synthesis.

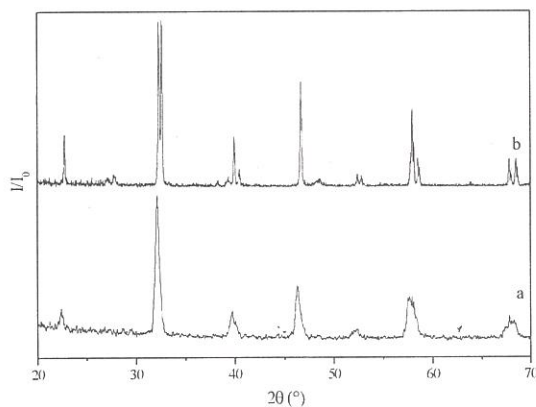


Fig. 1 XRD patterns of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ prepared by sol gel route, calcined at (a) 1173 K (orthorhombic) and (b) 1673 K (rhombohedral).

Combustion Method

This is a non-conventional method for material synthesis, which makes use of an exothermic chemical reaction. This method relies on a balance between the heat generated and dissipated in chemical reactions. It involves mixing of different reactant powders, such as metals, metal oxides, non-metals etc., which on initiation produce exothermic chemical reaction that is self sustaining due to a positive energy balance. The reactants produce rapid heating and cooling which aids propagation by a combustion wave that moves from the source of initiation. Two relatively new synthetic variants have been developed which negate the need for external heating. These are based on self propagating reactions, which provide energy to overcome the solid state diffusion barrier internally, within the starting materials by promoting exothermic chemical reactions. These processes are termed as self propagating high temperature synthesis (SHS).

Combustion method is a very fast synthesis technique involving release of gases to give high purity solid product. The process consists of initiation, propagation and termination. Initiation is a low caloric reaction taking place at the surface of the reactants. The reaction may be initiated by heating on a hot plate or in a furnace. Propagation is the second stage in combustion synthesis in which all the wave points initiated move at the constant speed to the thermal release zone to transform the reacting materials into the final products after termination of the synthesis reaction.

The procedure for combustion synthesis is as follows: The nitrate salts of the metals of interest are mixed together in the required stoichiometry in an aqueous media to produce the transparent mixed metal nitrate solution. Since the combustion involves reaction between fuel and oxidant, nitrates fulfill the requirement of oxidant by providing the oxygen for combustion of the fuel. A suitable fuel (e.g. glycine, citric acid etc.) is then added in an appropriate amount to this mixed metal nitrate solution. This fuel serves the dual purpose of not only providing the heat of reaction during the redox combustion process, but also binding the reacting metal ions so as to bring them in close proximity to one another. The transparent aqueous solution

containing metal nitrates and a suitable fuel is then converted to a viscous liquid (called gel) by thermal dehydration (on a hot plate to remove excess of solvent) at about 353K. The gel thus formed maintains an intimate blending between fuel and an oxidant which is necessary for a combustion process. The thermal dehydration process is an important step, because any excess water left behind would lead to sluggish combustion, deteriorating the phase purity and powder quality. The gel thus obtained is then subjected to an external temperature, depending on the nature of the fuel (~423 K for glycine), initiating the combustion reaction which is then self propagating. At this stage, the exothermic decomposition of fuel-oxidant precursor occurs resulting in a voluminous powder with a simultaneous evolution of gaseous products. The voluminous product thus obtained may be the desired phase, or a semi decomposed precursor having a considerable carbonaceous residue, depending on the nature and amount of fuel used in the process. The very high exothermicity generated during combustion reflects in the form of flame or a fire and the process is termed as auto-ignition. Since the time for which the auto-ignition exists is rather short (< 10 seconds), the powder is further calcined at temperatures around 873K. This is to remove the traces of any undecomposed fuel, nitrates or their decomposition products, so as to have chemically pure and crystalline product. The oxidant to fuel ratio has a significant bearing on the product phase as well as the product properties, because the extent of exothermicity associated with the combustion process is determined by this ratio. According to the concept of propellant chemistry [6,7] the ratio of oxidizing and reducing valencies should be unity to achieve maximum exothermicity.

The calculation of these valences and ratio satisfying this concept is illustrated by the following example:

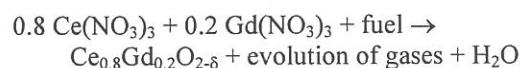
For synthesis of gadolinium doped ceria (GDC), a promising electrolyte for ITSOFC, glycine was used as fuel and Ce and Gd nitrate were used as starting materials (oxidants) [8]. Based on the stoichiometry of the compound considered, a solution with appropriate concentration of the starting materials was prepared. The oxidant to fuel ratio was based on the concept of propellant

chemistry. The solution of metal nitrates and fuel was evaporated directly on a hot plate. After thermal dehydration, gel was formed which auto-ignited resulting in formation of amorphous compound. However, this compound is likely to contain impurity such as carbon. Hence, it was subjected to calcinations at 873 K for 15 mins. The final sintering was carried out at 1673 K for 10 hrs.

As we had seen earlier, according to the concept of propellant chemistry the ratio of oxidizing and reducing valencies should be unity to achieve maximum exothermicity. The calculation of these valencies and the ratio satisfying this concept for the synthesis of $Ce_{0.8}Gd_{0.2}O_{2.8}$ can be explained as follows:

- (i) $Ce(NO_3)_3$: (Oxidising valency of Ce= 3+, N= 0, reducing valency of O = 2-)
The oxidizing valency is 15-
- (ii) $Gd(NO_3)_3$: (Oxidising valency of Gd= 3+, N= 0, reducing valency of O = 2-)
The oxidizing valency is 15-
- (iii) NH_2CH_2COOH (glycine): (Oxidising valency of N= 0, H= 1+, C= 4+, reducing valency of O = 2-)
The reducing valency is 9+

The valencies of C and N are taken as 4+ and 0, as these species are lost as CO_2 and N_2 respectively, during the combustion process. The equation for the reaction can be written as:



The net oxidizing valency = $0.8 (15-) + 0.2 (15-) = 15-$

The oxidizing valency is 1.67 times the reducing valency. Therefore, the oxidant to fuel ratio was kept as 1:1.67, which is the propellant chemistry ratio.

$Ce_{0.8}Gd_{0.2}O_{2.8}$ prepared by combustion synthesis had a crystallite size of 12 nm and its ionic conductivity was higher than that prepared by solid state route [8].

Cation Complexation Method

This method proposed by Courty et al [9] is a variant of the sol gel technique. Synthesis of GDC2 ($Ce_{0.8}Gd_{0.2}O_{2.8}$) by this method is described below as an example to illustrate the procedure and heating protocols [8].

Ce and Gd nitrates were used as starting materials. Based on the stoichiometry of the compound considered, a solution with appropriate concentration of the starting material was prepared. Citric acid was used as the complexing agent, which was added to the solution of nitrates. The molar ratio of the metal : citric acid was set to 1:2. After homogenization of this solution, the temperature was raised to 353 K and maintained under stirring to remove excess of water and convert it to a transparent gel. While raising the temperature, the solution becomes more viscous with evolution of foam and finally it gelled without any visible formation of precipitate or turbidity. There was increase in viscosity with elimination of water and NO_2 as the temperature was maintained at 353 K. The initial thermal decomposition of the precursor was carried out at 523 K for 1 hr. The resulting ash-like material was pyrolysed at 873K for 1 hr. The final sintering was carried out at 1673K for 10 hrs.

The SEM images of GDC2 synthesized by solid state route and cation complexation route are given in Figs 2 and 3. It can be seen that the sample prepared by cation complexation method indicates smaller size particle and better compaction. GDC2 synthesized by this technique was obtained at lower temperature with particle size of about 17 nm. Sintering this powder at higher temperature of 1673 K led to better densification which resulted in higher grain and grain boundary conduction [8].

Processing of Materials for Ceramic Fuel Cells

Basically there are two types of geometries for ceramic fuel cells (e.g. SOFC) viz. planar and tubular. The processing methods depend on the geometry of the cell. Typical processing technologies used for SOFC are tape casting, screen printing, calendaring, electrochemical vapour deposition, spray pyrolysis etc.

Typically for planar cells, the electrolyte is tape-cast or calendered. Flat and dense plates of YSZ

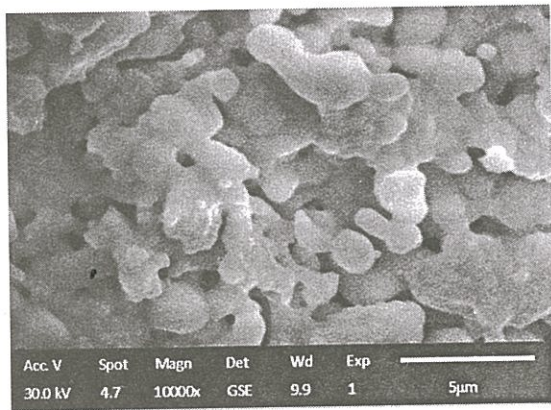


Fig. 2 SEM image of GDC2 sample synthesized by solid state route, calcined at 1400°C for 10 h.

having thickness down to 150 µm can be readily fabricated. The anode and cathode materials are then applied (as a slurry) on to the faces of the electrolyte and heated to high temperatures. Alternatively cathode, electrolyte and anode may be formed together by tape casting and the stack can be cofired. Similarly, the interconnect ceramic can be tape-cast or hot pressed. In all these processing techniques, it is absolutely essential that the assembled stack must make good electrical contact with one another.

The most challenging process for the planner geometry is to obtain gas tight seals at the edges of the stack, with the help of metals, glasses or glass-ceramics. Serious problems arise in this process because of the inevitable thermal expansion mismatches and the resulting mechanical stress.

The Forschungszentrum Julich (FZJ), Germany has been active in designing anode substrate based SOFCs since 1990 [10]. The cell fabrication involves several processing steps followed by intermediate firing steps [11]. Porous NiO/YSZ cermet substrates are prepared by warm pressing and sintering. The porosity of the substrate is usually within the range of 35-40%. Thin films of anode functional layer (AFL) (Ni/YSZ cermet ~ 5 µm), electrolyte (YSZ, ~ 5 µm), cathode functional layer (CFL) (LSM+YSZ ~15 µm) and cathode (LSM ~ 40 µm) and deposited sequentially on these substrates with intermediate firing steps and thus a single SOFC is formed [Fig. 4]. Basu et al [12] have

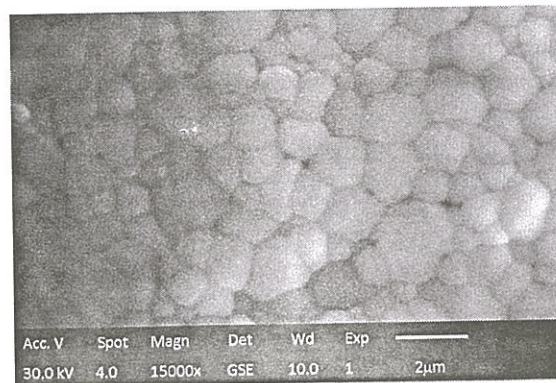


Fig. 3 SEM image of GDC2 sample synthesized by cation complexation method, calcined at 1400°C for 10 h.

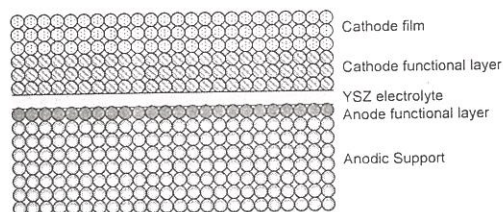


Fig. 4 Schematic of an anode-supported thin film structure.

described the fabrication of anode supported planner single cells of dimensions 5 cm X 5 cm X 1.5 mm and 10 cm X 10 cm X 1.5 mm. Their process involves room temperature lamination of several porous layers of tape cast NiO-YSZ together with one dense layer of YSZ electrolyte followed by cofiring. LSM+YSZ cathode functional layer and LSM cathode layer are screen printed on to the half cell consisting of anode and electrolyte prepared as described above.

Having optimized the design of a single cell, the next challenge is that of interconnecting many such cells in series to form a stack to increase the total voltage. This is done by making use of bipolar plates (or interconnect) which links the anode of one cell to the cathode of next. Fig. 5 illustrates how the interconnection is achieved in the planner configuration.

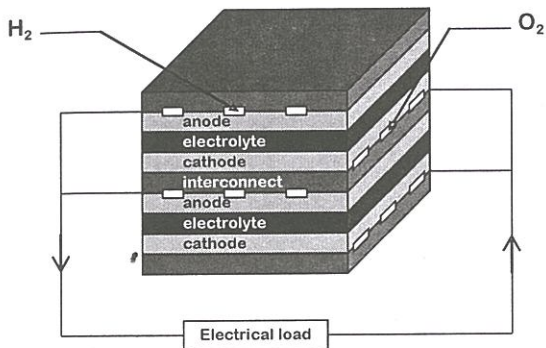


Fig. 5 Illustrating the connecting of two fuel cells via bipolar interconnects.

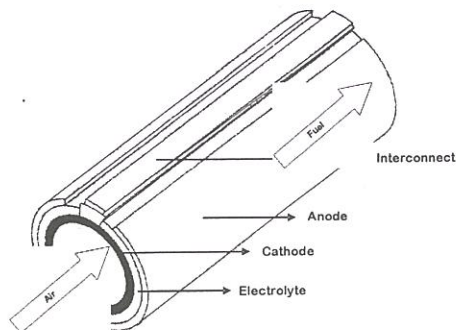


Fig. 6 Electrode arrangement in a tubular SOFC configuration.

The arrangement of cell component for the tubular geometry as adopted by Siemens-Westinghouse [13] is shown in Fig. 6. The long tubular cathode (~1.5 m) is obtained by extrusion of a mixture of Sr-doped lanthanum manganite (LSM) powder with other organic compounds such as starch to develop the necessary porosity. The tube is sintered in air at ~ 1500EC. The electrolyte (YSZ) layer (~40 μm) is applied to the cathode by Electrochemical Vapour Deposition (EVD) process. This being an expensive route, other cost effective methods such as plasma spraying and electrophoretic deposition are being explored. The anode consists of an approximately 120 μm thick Ni/YSZ cermet layer. This is achieved by applying a slurry of nickel and YSZ powders to the electrolyte and sintering. The advantage of this design is the absence of critical gas tight seals that are required for planar cells.

The lanthanum chromite interconnect strip is applied along the length of the tube by plasma spraying. The connections between the cells are made through soft Ni-felt so as to avoid mechanical stress between the tubes. The mode of connection of individual cells, along their lengths, in a series/parallel array is shown schematically in Fig. 7.

Electrochemical Characterization of Materials for SOFCs

The mode of electrical conduction for the various components of ceramic fuel cells (i.e. SOFCs) depends upon their function as electrolyte,

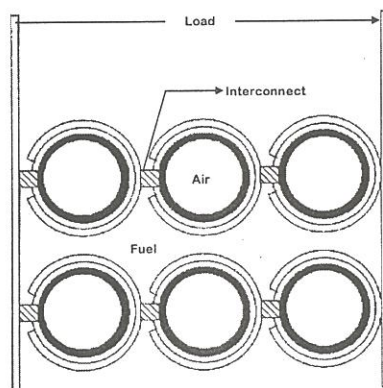


Fig. 7 Schematic of a parallel fuel cell stack.

electrode material or interconnects. Electrolytes for ceramic fuel cells are characterized by their ionic conduction. The interconnect materials have to be electronic conductors, while the anode and cathode materials can be mixed conductors with higher transference number for electronic conduction. The simple four probe technique can be used for measuring the electronic conduction of electrodes and interconnects. Impedance spectroscopy is a powerful technique used for electrical characterization of electrolytes. There are several methods for measuring the partial ionic and electronic conductivities in mixed ionic-electronic conductors (MIEC). The widely used methods are the Hebb-Wagner polarization method, determining the electronic and ionic conductivities from the

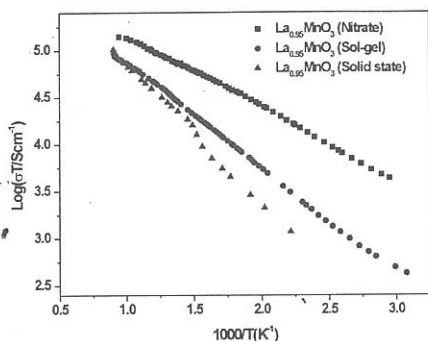


Fig. 8 *Log σT versus $1000/T$ plots for $\text{La}_{0.95}\text{MnO}_3$ prepared by different routes*

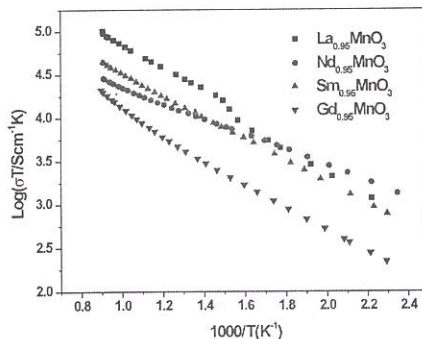


Fig. 9 *Log σT versus $1000/T$ plots for $\text{Ln}_{0.95}\text{MnO}_3$ prepared by solid state route*

activity dependence on the total conductivity dependence of average ionic transference number by EMF measurements etc [14].

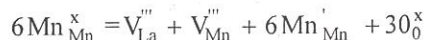
Electrical Conductivity of Cathode Materials

Improvement in the performance of solid oxide fuel cells can be brought about by solving the problems of ohmic and polarization losses at the cathode side of the cell. There are several requirements for the cathode materials that are useful for their performance at high temperatures in SOFCs. The most important requirements are their high electronic conductivity, non-negligible ionic conductivity, high catalytic activity for oxygen reduction, chemical stability and matching thermal expansion coefficient with other cell components.

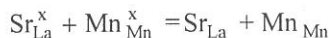
ABO_3 oxide systems with perovskite structure, where A is a rare earth element and B a transition metal (Fe, Ni, Co, Mn) fulfil these requirements and have been extensively studied for their application as cathode materials [15-17]. Sr doped LaMnO_3 (LSM) is the most widely studied system. LaMnO_3 is the only compound in the LaMO_3 (M= first row transition metal) series which shows oxygen excess. This excess oxygen cannot be accommodated as an interstitial ion in the closed packed structure of ABO_3 because of its large radius. Therefore, it can only be considered in terms of Schottky-type disorder, cation vacancies,

$$\text{NiI} = V_{\text{La}}''' + V_{\text{Mn}}''' + 3V_{\text{O}}''$$

The defect reaction causing oxygen non-stoichiometry in the oxygen excess regime can be written as,



In $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$, the conduction process is analogous to that of LaMnO_3 with charge transfer occurring from a Mn_{Mn}^x site to neighboring Mn_{Mn}^x site, i.e., as jumps of p-type carriers respectively over available sites. However, in this case p-type carriers are a result of a partial replacement of La by Sr.



Thus in LSM, the substitution of La^{3+} ions by Sr^{2+} leads to the existence of Mn^{4+} along with Mn^{3+} in the B-positions which removes the lattice distortion and significantly modifies the structure and electrical properties [18]. The charge carriers are transported by the $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ network. It is well known that Mn^{4+} removes John-Teller distortion and correspondingly reduces hopping activation energy, E_a for LSM (0.143 eV) as compared to LaMnO_3 (0.285 eV). Electrical conductivity measurements carried out on LaMnO_3 synthesized by solid state, sol-gel and coprecipitation route showed higher conductivity for LaMnO_3 synthesized by coprecipitation method [19]. [Fig. 8].

The electrical conductivity studies of $\text{Ln}_{0.95}\text{MnO}_{3+\delta}$ (Ln= La, Nd, Gd) showed a clear

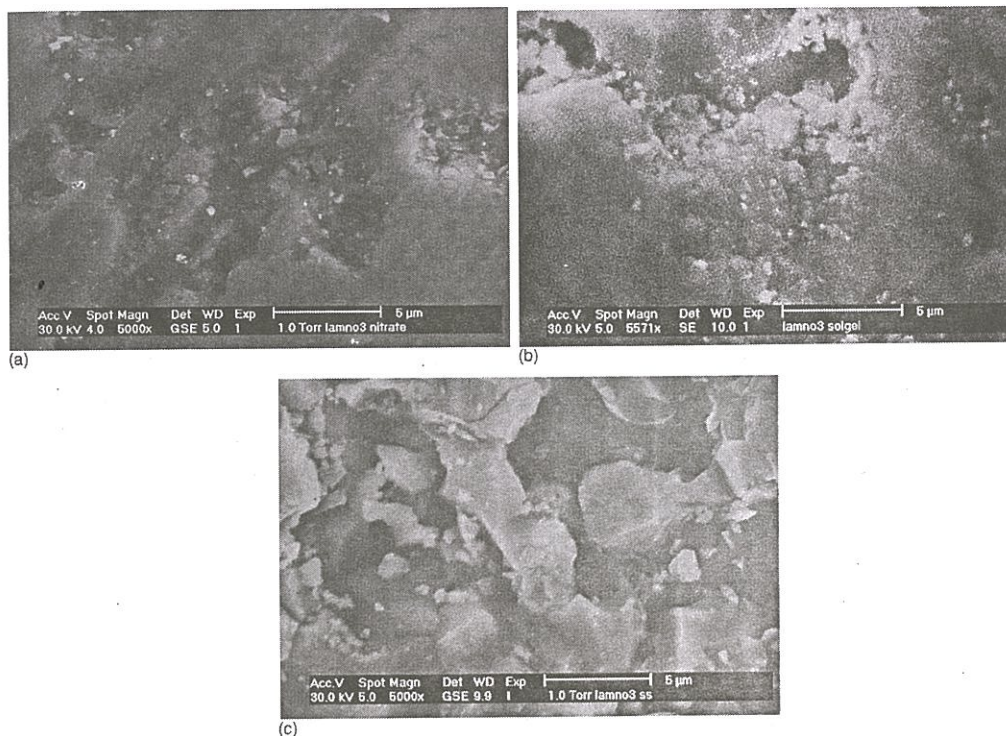


Fig. 10 SEM pictures of LaMnO_3 prepared by different routes and heated at 1673 K. (a) nitrate route (b) sol-gel route and (c) solid state route.

phase transformation in case of $\text{La}_{0.95}\text{MnO}_{3+\delta}$ synthesized by solid state route which was missing in all other rare earth manganites prepared by solid state route and wet chemical methods [Fig.8] and [Fig. 9].

SEM images of $\text{La}_{0.95}\text{MnO}_{3+\delta}$ synthesized by different routes [Fig.10] indicates that ceramic route resulted in much larger particle size of about 3-5 μm . On the contrary $\text{La}_{0.95}\text{MnO}_{3+\delta}$ prepared by sol gel and nitrate route leads to smaller particle in the range of 500 nm.

This effect is possibly related to the data of electrical conductivity in which sample synthesized by solid state shows lowest conductivity [Fig 8]. The SEM photographs [Fig.13] indicate that compounds synthesized by different routes have different microstructural characteristics. Among the perovskites LSCo (Sr substituted lanthanum cobaltite), LSM (Sr substituted lanthanum manganite) and LSF (Sr- substituted lanthanum ferrite), LSCo shows the highest conductivity [Fig.

11]. Cobaltites also have high electrocatalytic activity for oxygen reduction [20]. But, the thermal expansion coefficient of LSCo is very high [Fig. 12] and hence cathodes made of LSCo are not compatible with other cell components. Optimum composition of cobaltite mixed with manganite or ferrite might lead to a better cathode material [5, 20].

Electrochemical Characterization of Electrolytes

Solid electrolytes should be highly dense for practical applications in SOFC, due to requirements of gas tightness between cathode and anode compartments. For the development of electrolytes for SOFC applications, studies of their sintering behavior and microstructures are important for obtaining dense material with high ionic conductivity. In recent years a growing interest in properties of nanostructured ion conductors has been observed [21-22]. The sintering rates are considerably enhanced even at lower temperatures with nano crystalline powders as starting materials,

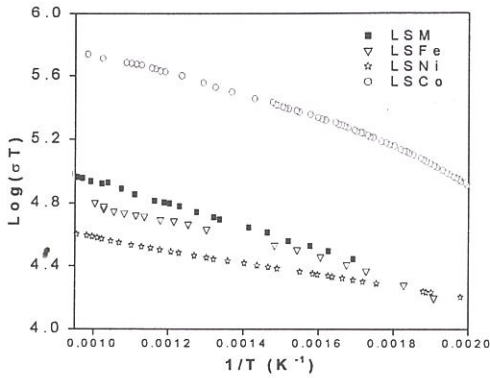


Fig. 11 Electrical conductivity ($\log(\sigma T)$) versus $1/T$ of Sr-substituted LaMnO_3 (LSM), Sr-substituted LaFeO_3 (LSFe), Sr-substituted LaCoO_3 (LSCo) and Sr-substituted LaNiO_3 (LSNi) as a function of temperature.

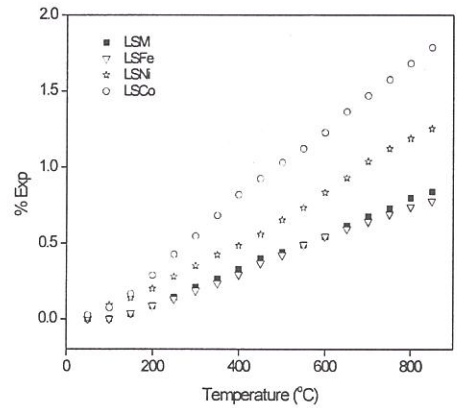


Fig. 12 Thermal expansion behaviour of Sr-substituted LaMnO_3 (LSM), Sr-substituted LaFeO_3 (LSFe), Sr-substituted LaCoO_3 (LSCo) and Sr-substituted LaNiO_3 (LSNi) as a function of temperature

which results in higher bulk densities and enhancement in conductivity.

The plot for grain and grain boundary conduction as a function of temperature for gadolinium doped ceria (GDC2) with a composition of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, (synthesized by solid state route and sol-gel route) is shown in Fig. 13.

The sample synthesized by solid state route required prolonged heat treatments, thus increasing the particle size and consequently leading to lower densification, resulting in higher resistance due to grain boundary. For the sample synthesized by sol-gel method, the grain boundary resistance is distinctly lower than that observed for the sample synthesized by solid state method. The activation energies for the above mentioned conduction processes are listed in Table 1 [8].

Besides microstructures, impurities at the grain boundaries also influence the conduction behavior in electroceramics. Our studies on 20 mole% Eu-doped ceria [23] (EDC2) has shown that Si-impurity at the grain boundaries of combustion synthesized samples resulted in its lower conductivity. Cation complexation synthesized product lead to formation of agglomerates and hence the sintered sample showed higher porosity compared to combustion

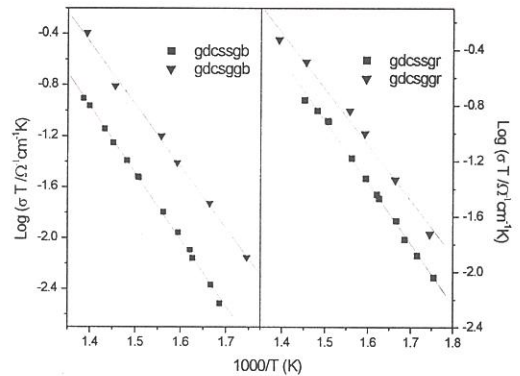


Fig. 13 Plot of $\log(\sigma T)$ vs. $1/T$ for grain (gr) and grain boundary (gb) of GDC prepared by sol-gel (sg) and solid state (ss).

synthesized sample. However, despite high packing density, the combustion synthesized sample showed lower grain boundary and total conductivity than cation complexation synthesized product due to the formation of silicious film at the grain boundary. Micrograph showing the fracture of sintered (1673K) EDC2 samples synthesized by (i) solid state route (ii) cation complexation method and (iii) combustion synthesized methods are shown in Fig. 14 (a,b,c).

TABLE 1. Activation energies for total conduction, grain and grain boundary conduction for GDC2 synthesized by Different routes.

Method of synthesis	Activation Energies		
	E_a (eV)(total)	E_g (eV) (grain)	E_{gb} (eV) (grain boundary)
Solid state route	2.186	0.873	1.034
Sol-gel route	1.941	0.791	0.958

TABLE 2. Conductivity values for EDC2 synthesized by different routes

Synthesis route	Conductivity at 667K (10^{-5} Scm $^{-1}$)		
	Bulk	Grain boundary	Total
Solid state	6.697	1.451	1.462
Cation complexation	96.181	49.437	32.86
Gel Combustion	109.251	9.121	8.716

The presence of agglomeration can be distinctly observed in the case of sample synthesized by cation complexation method (Fig. 14 b). Dense uniform structure with negligible porosity is observed for sample synthesized by combustion method (Fig. 14 c).

The temperature dependence of the conductivity (grain, grain boundary and total) can be seen in Fig. 15 for EDC2 synthesized by different routes. Table 2 gives conductivity values at 667 K.

Solid state synthesized EDC2 shows least conductivity which is quite expected as a result of poor morphology of the sample as seen in SEM micrograph (Fig. 14 a). This poor microstructure with large porosity is a result of prolonged heating at higher temperature. However, SEM microphotographs (Fig. 14 b and c) indicate better packing density for EDC2 synthesized by combustion in comparison to cation complexation method. Despite this, the grain boundary and total conductivity is lower in case of EDC2 synthesized by combustion method. Only bulk conductivity is superior in case of EDC2 synthesized by combustion method. To understand this result, EDAX analysis were carried out which showed presence of Si impurities along the grain boundaries of the combustion synthesized EDC2 (Fig.14 c). This Si

impurity could be a result of the glass container in which high temperature combustion was carried out. Si impurity decreases the grain boundary conduction and eventually the total conduction despite better densification. Thus, Si-impurities play a dominating role in comparison to density in determining the conductivity of the sample.

Electrical Conductivity and Microstructures of Anodes

Anode for ceramic fuel cells are porous cermets (a composite of ceramic and metal), the micro structure of which is optimized to have high electronic conduction and active triphal phase boundary for electro-oxidation of the fuel.

Use of cermets improves matching in TECs (thermal expansion coefficients) between the electrolyte and electrode (anode). In anode supported IT-SOFCs, cermets are used as structural support. Ni in the cermet is an excellent electrocatalyst for the oxidation of hydrogen, but it also promotes the formation of carbon from hydrocarbon fuel [24]. In order to avoid this problem, copper is being explored as a replacement, since it does not catalyze the carbon formation reaction. In cermets such as Cu-GDC etc., copper

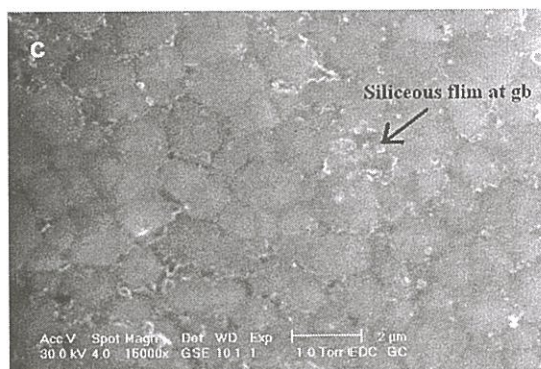
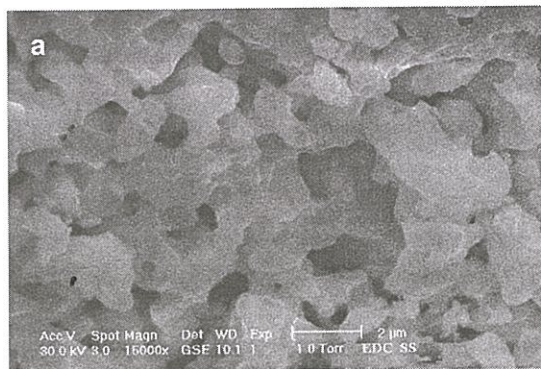


Fig. 14 Micrographs of sintered (1673 K) EDC2 samples synthesized by (a) solid state route (b) cation complexation method and (c) combustion method.

acts as an electron conducting matrix while ceria performs the electro oxidation catalyst role [25, 26].

Applications

Solid oxide fuel cells, in which various electroceramics are used as cathodes, electrolytes and anodes, can have broad applications ranging

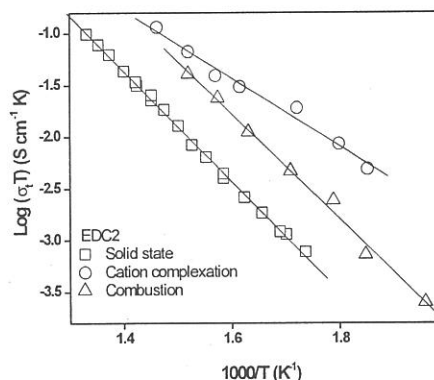
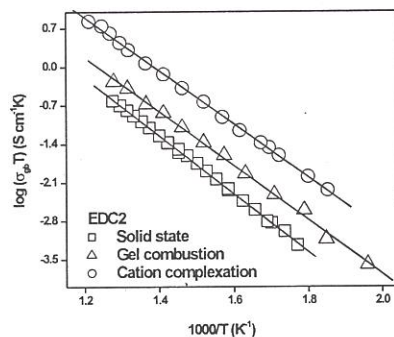
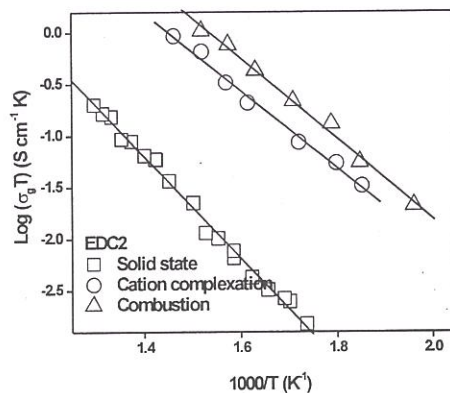


Fig. 15 Plot of $\log(\sigma T)$ vs. $1/T$ for grain (σ_{gb}), grain boundary (σ_{gb}) and total (σ) of EDC2 prepared by solid state, cation complexation and gel combustion routes.

from large scale power plants to smaller home-scale power plants and portable or emergency power generators. When biological waste gases are available from waste treatment plants, SOFC can convert waste gases (methanol from biomers) to electricity and heat with minimal environmental damages [27].

Researchers around the world are making a concerted effort in the development of suitable materials and ceramic structures which are presently the key technical challenges facing SOFCs. Simple ceramic processes have to be developed so that thin film electrolytes that decrease the cell resistance can be utilized. This improvement doubles the power output and significantly reduces the cost of SOFCs. Global SOFC making companies continue to realize very significant improvement in basic fuel cell design. Higher power densities contribute to lower weight, size and cost of fuel cell systems. SOFCs could be soon suitable for small scale residential market applications, if ultimate cost goals of \$1000/kw are reached.

Acknowledgements

I thank Ms Rohini Wandekar for the experimental work reported in this article.

References

1. B.C.H. Steele, *Solid State Ionics*, 134 (2000) 3.
2. T. Ishihara, H. Matsuda, and Y. Takata, *J. Am. Chem. Soc.* 116 (1994) 3801.
3. T. Ishihara, in *Handbook of fuel cells – Fundamentals, Technologies and Applications*. Ed. Vielstich W., Gasteiger and H.A., Lamm A., John Wiley & Sons, New Jersey, USA vol.4. (2003) pp. 1109-1122.
4. A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. McEvoy, M. Mogensen, S.C. Singhal and J. Vohs, *Nature Mater.* (2004) 317.
5. R.V. Wandekar, B.N. Wani, and S.R. Bharadwaj, *Solid State Sciences*, 11 (2009) 240
6. S. Manoharan and K.C. Patil, *J. Am. Ceram. Soc.*, 75 (1992) 1012
7. S.R. Jain, Adiga, K.C. and V.R. Pai Vernekar, *Combust. Flame*, 40 (1981) 71-79
8. R.V. Wandekar, Ph.D Thesis, (2007) Mumbai University.
9. P. Courty, B. Delmon, C. Marcilly, A. Sugier, (1968) Fr. Patent 1604707, Mentioned in ref: R.A. Rocha, E.N.S. Mucillo, *Mater. Res. Bull.*, 38 (2003) 1979
10. R. Steinberger-Wilckens, L.G.J. De Haart, I. C. Vinke, L. Blum, A. Cramer, J. Rimmel, G. Blass, F. Tietz, and W.J. Quadackers, in N. Sammes, et al (eds) "Fuel Cell technologies: State and Perspectives" Springer, (2005) pp 123-134
11. R.N. Basu, G. Blass, H.P. Buchkremer, D. Stover, F. Tietz, E. Wessel and I.C. Vinke, *J. Eur. Ceram. Soc.* 25 (2005) 463
12. R.N. Basu, A. Das Sharma, A. Dutta, and J. Mukhopadhyay, *Int. J. Hyd. Energy* 33 (2008) 5748
13. S.C. Singhal, *Solid State Ionics*, 135 (2000) 305
14. *The CRC Handbook of Solid State Electrochemistry* (Ed by) P.J. Gellings and H.J.M. Bouwmeester, CRC Press Boca-Raton (1997)
15. C.S. Tedmon, H.S. Spacil and S.P. Mittoff, *J. Electrochem. Soc.* 116 (1969) 1170
16. Y. Ohno, S. Nagata and H. Sato, 3 (1981) 439
17. H.S. Isaacs and L.J. Olmer, *J. Electrochem Soc.* 129 (1982) 436
18. E. Pollert, S. Krupicka and E. Kuzmicova, *J. Phys. Chem. Solid* 43 (1982) 1137
19. R.V. Wandekar, B.N. Wani and S.R. Bharadwaj, *J. Alloys and Compound* 433 (2007) 84
20. D.J. L. Brett, A. Atkinson, N.P. Brandon and S.J. Skinner, *Chem Soc Rev.*, 37 (2008) 1568
21. J. Schoonman, *Solid State Ionics*, 135 (2000) 5
22. H.L. Tuller, *Solid State Ionics*, 131 (2000) 143
23. R.V. K. Wandekar, B.N. Wani and S.R. Bharadwaj, *Solid State Sci.*, 12 (2010) 8
24. R.M. Ormerod, *Chem. Soc. Rev.*, 32 (2003) 17
25. D.L.J. Brett, A. Atkinson, D. Cumming, E. Raminéz-Cabrera, R. Rudkin and N.P. Brandon, *Chem. Engg. Sci.* 60 (2005) 5649
26. S. Mc Intosh and R.J. Gorte, *Chem Rev.* 104 (2004) 4845
27. B. Viswanathan and M. Aulice Scibioh, *Fuel Cells: Principles and Applications*, CRC press, January 2008.

Challenges in PEM Fuel Cell Development



Dr. K. S. Dhathathreyan received B.Sc. (Hons) and M.Sc. in Chemistry from Bangalore University and PhD from Indian Institute of Science, Bangalore. He was a recipient of the Alexander von Humboldt Fellowship and has worked at the University of Goettingen and Max-Planck Institute. He held postdoctoral positions at the University of Groningen, The Netherlands and University of Calgary, Canada. He has been engaged in R&D and demonstration of various Hydrogen Technologies. He worked at SPIC Science Foundation for 14 years and presently he is an Associate Director at ARC-International, Hyderabad, an autonomous R&D Centre of the Department of Science and Technology, Govt. of India and heads ARCI's Centre for Fuel Cell Technology located in Chennai.

After obtaining PhD from IIT, Madras, Dr. N. Rajalakshmi worked as post doctoral fellow in TH Darmstadt, Germany and University of Geneva, Switzerland for 8 years, on various aspects of hydrogen economy. She has vast experience in PEMFC technology both in Material aspects and Engineering issues from SPIC science foundation and Center for Fuel cell Technology for the past 15 years. Presently, she is a senior scientist at CFCT, unit of ARCI, DST at Chennai. She is a reviewer for many journals, member of International Association of Hydrogen energy, Materials Research Society of India.



Abstract

Polymer Electrolyte Membrane Fuel Cell (PEMFC) has been in the forefront of development for low capacity (< 100 kW) stationary applications, transportation application and few niche applications (military, marine, railway, submarine) in recent years. A variant of PEMFC is the Direct Methanol Fuel Cell (DMFC) which is being projected for many portable applications. Owing to the apparent simplicity of its construction, a large number of research groups are engaged in basic research as well as applied research and development in PEMFC. PEMFC has been the choice of teaching aid for imparting knowledge of fuel cells to undergraduate students.

Although PEMFC has been known since the GEMINI flight in the 1960s, a renaissance in PEMFC development came about with the availability of Nafion^R series of membranes from DuPont and introduction of platinum

electro-catalyst supported on high surface area carbon in the 1980s.

Billions of dollars have been invested / committed worldwide and a large number of demonstrations have been carried in different application regimes, with almost all the global auto industries / manufacturers involved in developing vehicles powered by PEMFC.

During the last few years, India has attracted many foreign companies for joint demonstration of PEMFC especially in telecom industry and to some extent in decentralized power generation. Although PEMFC has shown remarkable potential in a number of application areas, several challenges remain to make these fuel cells a commercial reality.

In addition to such challenges listed by many leading international research groups, Indian scientists/ technologies face additional challenges to successfully bring PEMFC into Indian market. This

Dr. K. S. Dhathathreyan and Dr. N. Rajalakshmi, Centre for Fuel Cell Technology, ARC-International, IIT-M Research Park, Phase-I, 2nd Floor, 6, Kanagam Road, Taramani, Chennai 600 113; E-mail: ksdhatha@arci.res.in; lakshmiaja2003@yahoo.com

paper elaborates on all these challenges. The challenges are to be considered as opportunities for researchers in this field. The objective of this article is not to review the work reported in literature on individual aspects but to elaborate on specific challenges.

Introduction

PEMFC is the most investigated fuel cell system in recent times in many different applications, owing to its advantages like easy start up, modularity, high power density, ambient temperature operation etc. The commonly used electrolyte in PEMFC is Nafion^R manufactured by DuPont and the electrode substrates are basically carbon based and they are either woven carbon cloth or carbon paper. Depending on the fuel to be used in the PEMFC, the requirements for electro catalysts are completely different. The anode electro catalysts are Pt supported on carbon for hydrogen fed fuel cell and Pt-Ru for reformat fuel. The reformat normally contains 10 to 100 ppm of CO even after purification and this has detrimental impact on fuel cell performance as the strong adsorption of CO onto Pt reduces the catalytic activity. The electro catalysts for oxygen reduction being Pt supported on carbon, Pt Black, Pt-M alloys where M being transition metals. The simplest case is the operation with pure hydrogen and oxygen or air. Cells with high power density and very low degradation have been already demonstrated. The most important materials under development for PEMFC stacks are the ion conducting membrane, bipolar plates, and electro catalysts for the fuel & air electrode targeted at cost reduction and increasing the durability.

The state-of-the-art advances in PEMFC have been described in detail by several recent reviews [1-4], on special topics such as electrodes [5] and catalysts [6-12]. Litster and McLean [5] provide an overview of not only the PEMFC electrode design and fabrication but also assembly methods, identifying those that have been shown to produce effective electrodes and those that have high future potential. In general, proton conductivity of Nafion type polymers with perfluorinated polymer chain back-bone and sulfonic groups, normally used in PEMFC, increases as the hydration level of the polymer increases with H₂O:SO₃ ~15:1 and conductivity ~10⁻¹S/cm under operational

conditions. Materials with low equivalent weight and short distances between hydrophilic side groups typically exhibit high conductivity. The relative humidity has a greater impact on conductivity than the temperature, even at temperatures above 90°C, where the conductivity drops dramatically due to dehydration. Although increased water content is beneficial for the conductivity, it increases swelling of the membrane resulting in dimensional instabilities. Excellent reviews of new membrane materials development are available [13-21].

The membrane and electrode assembly (MEA) is the 'heart' of the PEMFC. Its structure and composition are of vital importance to minimize all contributions of over potential and maximize the power density; to minimize the noble metal loading, for effective thermal and water management, and to attain lifetimes of PEMFCs. There needs to be an extension of the three dimensional zone in the electrode by the impregnation of the proton conductor so that the utilization of the electro catalyst is similar to that in a fuel cell with a liquid electrolyte (e.g. phosphoric acid, potassium hydroxide) which can lead to high power density PEMFCs. It is worthwhile stressing at this point that minimizing ohmic over-potentials is vital for attaining high power densities; and this was made possible by using supported membranes (prepared by impregnation of Nafion into micro porous Teflon mesh, invented by W.L. Gore and associates and by deposition of very thin active layers (about 10 nm), containing only the carbon supported platinum nanocrystallite and Nafion, directly on the supported membrane. This process reduced the contact resistance. Thus, this MEA has shown the best PEMFC performance to date and is being widely used by fuel cell developers in USA and Japan.

The bipolar plates are the lungs of the fuel cell [3, 22, 23]. The bulk of the stack cost as well as the weight of the fuel cell stack comes from the bipolar plates which are conventionally made from electro graphite which is impervious to the gases at the operating conditions. Much effort is being expended on the development of low cost bipolar plates. Besides the conductivity required for these materials to function as bipolar plates, the other major property requirement is the corrosion resistance and the

material has to withstand the oxidative and reductive atmosphere in the fuel cell under acidic conditions.

Cost and Lifetime

Two of the major challenges to widespread use of fuel cell are cost and lifetime, which are inter-related. For example, adding more catalyst to a fuel cell increases catalyst lifetime but increases fuel cell cost. Similarly, increasing a fuel cell membrane's thickness increases its lifetime but also increases its cost. Thus, a complex balance exists between the cost and lifetime of a PEM fuel cell. To improve the durability of PEM fuel cells, researchers are studying the factors that determine a PEM fuel cell's lifetime, so that the lifetime can be increased without increasing cost or losing performance. Studies have shown that several factors can reduce the useful life of a PEM fuel cell, including platinum-particle dissolution and sintering, carbon-support corrosion, and membrane thinning [24-26]. Lifetime can also be reduced by efforts to maximize the initial performance of a fuel cell component. For example, decreasing the equivalent weight of the polymer electrolyte typically increases the membrane's proton conductivity but also increases its water uptake and gas permeability and thus degrades its mechanical properties.

Cost is a barrier for all types of Fuel Cells across all applications. Today, many fuel cells cost about US\$ 3000 /kW. For stationary power generation the cost should be brought down to US\$ 100-200 /kW and for transportation the cost has to be reduced to US\$ 35-40 /kW to compete with the gasoline ICE. Reducing costs is not easy when only a small number of fuel-cell systems are being made. Because of the nonstandard size and specialized requirements of components for Fuel Cell systems, costs are unusually high at low volumes. Cost reductions must be realized in raw materials, manufacturing of fuel cell stacks and components, and purchased components. Raw materials costs must be reduced by a combination of alternative (lower cost) materials, quantity pricing, and reduction in required amounts of expensive materials. Manufacturing cost reductions can be partly realized from classical learning curve gains. However, it will likely require introduction of new and innovative manufacturing technologies or designs requiring simpler manufacturing processes.

Cost reduction can also be achieved by improving performance, simplifying design and operation. High performance is required to improve power plant packaging (volume and weight) for a given power output.

Balance of System Components

All types of Fuel Cell systems require the successful development and integration of Balance of System (BoS) components such as heat exchangers, air supply system, compressors, sensors, power converters and controllers. Premature failure of these components is not uncommon, which limits system durability and reliability. Presently used BoS are not developed for fuel cell use except for power controllers.

Thermal and Water Management

Thermal and water management are important for PEM Fuel Cells, which operate at relatively low temperature and require humidification of the air and fuel supplies to prevent performance degradation. A complicating factor is thermally integrating the low-operating temperature PEM Fuel Cell with the high-temperature fuel processor, particularly on-board a vehicle where issues of waste heat rejection from the system and maintaining positive water balance on-board the vehicle become critical design and operating issues. In recent times efforts to develop fuel processors for automotive applications has come down. Fuel cell system must be designed as a whole, not as a collection of stand-alone parts. Fuel cell design can therefore be thought of as optimization problem. The merit function [Fig.1] in this optimization process being the power density obtained at given cost, weight and life-time. This merit function is the focal point for the technology push [27].

In general, the challenges for large scale deployment of PEMFC technology can be broadly classified into the following dimensions eventually aimed at cost reduction and increased life:

- Materials development
- Stack design
- System Integration and Operation of the system
- The broader challenge of fuel supply

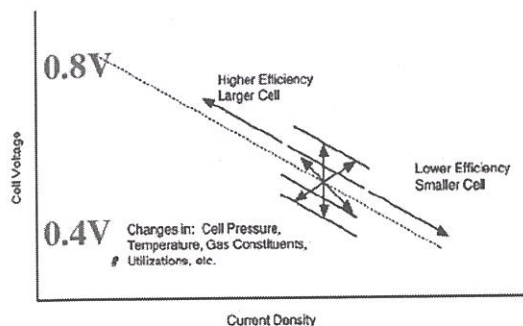


Fig. 1 Optimization trade off in a PEMFC system [27].

There are also scale-up issues. While many high performing catalysts have been reported, there is a lacuna on reports of scaling up these catalyst syntheses to large scale. Similarly, a fuel cell developer has to worry about scaling up of each and every component, be it the electrode, the process for making the electrodes, small single cell to large area single cells and eventually the stack. The other areas where not much information is reported are the sealants, gaskets & methods for making them in large quantities; balance of systems such as the air movers and fuel supply mechanism besides the power controllers. In this article, some of the issues not articulated in detail elsewhere, will be discussed.

Challenges in PEM Fuel Cell Materials Development

The types of materials used in PEMFC vary in nature [physical characteristics, electrical, thermal and mechanical properties and include organic materials such as the membrane, gaskets and the binders, carbon-based materials such as high surface carbon powders, woven or non woven carbon fabric or paper, carbon-based bipolar plates, metals such as Pt, Ru, Co, Ni used as catalysts and S.S or coated metal plates as bipolar plates. Hence the performance of the PEMFC depends on averaging the characteristics of the various components. So, development of any new material for any one function of the fuel cell e.g., new membrane should take into account the interplay of such membrane with other components of the fuel cells with which it is in contact, when the fuel cell is operated. This is one of the major gaps in many research reports. In recent times, there are a number of publications on

developing high temperature membranes for use in PEMFC purportedly to overcome the issues of water management and to facilitate higher temperature operation to improve the oxygen reduction kinetics and to increase CO tolerance. But in most of these works, it is observed that Nafion is still used as a binder for fixing the electrode to the membrane. Nafion may be a necessity, not only to facilitate the three phase boundary formation in the catalyst layer but also to overcome the H_2O_2 attack on the polymer electrolyte. One more issue with most alternative proton conducting polymer electrolytes which are mainly aromatic hydrocarbon and more hydrophilic than Nafion [28] is that liquid water is more easily formed in the electrode which might block the transport of reactants (fuel and oxidant). If different polymers are employed in the catalyst layer and the electrolyte membrane, there is the problem of compatibility of the polymer membrane and the catalyst layer [29]. It has been found [30] that the interfacial resistance is larger for a MEA consisting of Nafion-based catalyst layers and non-Nafion membrane than all-Nafion one, and that the degradation rate for the former is much larger than the latter. If the polymers in the catalyst layer and the membrane are the same one, regardless of it being Nafion or non-Nafion, it seems that the interfacial resistance can be lowered to some extent [31]. The exact origin of the increased interfacial resistance between Nafion-based catalyst layers and non-Nafion membranes remains unknown. The larger interfacial resistance is perhaps due to the different chemistry of the two polymers [29]. The larger degradation rate of non-Nafion-membrane MEA is probably due to the different rates of swelling/contraction of different polymers, which results in the de-lamination of MEA in the cycle of hydration-dehydration [32]. It has been reported [28] that modifying polyaromatic electrolyte membranes with fluorine and other functional groups can decrease the interfacial resistance in the MEA consisting of the Nafion-based catalyst layer and non-Nafion membrane. It is reasonable to assume that a fluorinated copolymer could be more compatible with highly fluorinated Nafion than a non-fluorinated copolymer [29]. It can be speculated that the chemical similarity of the polymers in the catalyst layer and in the membrane is important for a good binding of the two parts (the catalyst layer and the membrane) and thus lower the interfacial

resistance in the resultant MEA. It should also be emphasized that if an alternative membrane material does emerge, considerable R&D will still be necessary to optimize and manufacture the new membrane-electrode assembly (MEA). It has taken many years for Nafion-type MEAs to be developed, although some of the expertise gained may be able to be transferred to the new system.

Secondly, the corrosion issues of the carbon-based components, especially the catalyst and GDL that emanate at high temperature operation, are not taken into account in the studies reported with high temperature membranes. Highly-dispersed platinum on carbon black (furnace black) has normally been used for the PAFC. Experience shows that in this type of cell, the carbon cathode is subject to degradation and loss of carbon by an electrochemical oxidation mechanism. The degradation of PEMFC cathodes has not, until recently, been such a concern because of the relatively low operating temperature. As developers seek to raise the operating temperature, however, cathode degradation could become more important.

In general, many of the studies reported in literature are mainly "isolated" performances rather than "interactive" investigations. Three types of materials are being investigated for oxygen reduction: (i) heat-treated macrocyclic compounds of transition metals (ii) ruthenium-based chalcogenides and (iii) palladium alloys catalysts. Among these classes, most promising catalysts are palladium alloys and high loaded RuSe/C. Palladium and ruthenium are more preferable for general usage in fuel cell devices, due to lower price and higher mining capacity, in comparison with platinum. Most of the studies using these catalysts have been carried out using rotating electrodes, but there are not many examples of any of these used even in single cell studies or in real applications. Pt supported on carbon is still the ORR catalyst of choice.

Development of carbon-polymer composites as bipolar plates as a replacement for the expensive electro graphite for use in PEMFC is another subject which has resulted in many publications. Composites are an alternative to graphite and offer a reduction in weight and an improvement in manufacture as they can be extruded or molded to any shape, reducing manufacturing time and cost.

But the main issue is that the conductivity of these materials will always be less than the electro graphite, owing to the presence of binders. A high loading of filler is required in order to increase the electrical conductivity, while insufficient binder will lead to poor mechanical properties. In addition, they offer lower thermal conductivity and limited operating temperature range. Recently, nanocomposite materials have been reported using fillers such as carbon nanotubes, graphitic powders and silver-coated glass, which can offer improved mechanical properties and in particular, increased conductivity.

Reports on use of conducting polymers as binder are again blinded by the fact that these conducting polymers could undergo oxidative decomposition in the fuel cell environment. Use of conducting polymers as coating on metal plates faces similar issues.

So, the challenge in developing new, low cost materials for use in PEMFC is not just developing materials but also investigate its properties/performance in conjunction with properties of other materials used in the cell as well as the operating environment of the fuel cells.

Challenges in Fuel Cell Stack Development

The major challenges in stack design are uniformity of cells, power density, stack cost, size and weight, effect of contaminants etc., Similarly the challenges in operation are water management, catalyst poisoning, carbon corrosion, durability, stability, operating conditions etc., while there are a large number of single cell studies, reports on stack development/stack design are not available freely in open literature. A fuel cell stack designer/developer faces several challenges and many-a-time a heuristic approach is followed initially, which is followed by modeling and eventual stack design. The designs and therefore design criteria greatly depend on application. There are number of trade-offs in designing the fuel cell stack. In many an instance, it is not possible to translate the idealized single cell performance to stack level, mainly because it is very difficult e.g. to maintain the humidity within the cells in a stack, a luxury enjoyed in single cell studies.

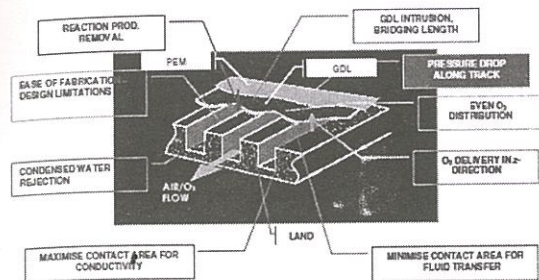


Fig. 2 Factors influencing PEMFC Performance

Although the drivers and system design for both stationary and transport sectors are similar in principle, the main differences are in the choice of fuel, power conditioning, ease of start up, noise level, operating conditions, lifetime, size, weight, heat removal etc. In addition, there are design options depending on the application for stationary power generation e.g. grid connection, nominal power output, load following, cogeneration capabilities etc. For the transportation applications, a fundamental difference can be made between passenger vehicles (car, auto rickshaw, mini van) and commercial vehicles, which rigidly determine many physical parameters such as electric motor, power output of the fuel cell, space requirement etc. In addition, the requirement of batteries and/or super capacitors adds to the complexity of the design. Hence the fuel cell power systems need to be designed for a variety of applications, namely stand-alone, grid parallel, grid independent, backup power energy generators, fuel cell vehicles, hybrid vehicles etc.

Fuel cell systems are complex entities. The complexity is hidden in the microscopic details [Fig. 2], mostly inaccessible to the experimental "eye". More specifically, fuel cell operation entails circulation of protons, electrons, reactants and water, with the processes in the structural elements of the cell, coupled strongly and non-linearly to each other. The fundamental difficulties associated with fuel cell design stem from this non linear coupling [33].

A fuel cell stack is designed depending on the required power output based on which the area of the cells and the number of cells in the stack are determined. Some of the challenges in fuel cell stack

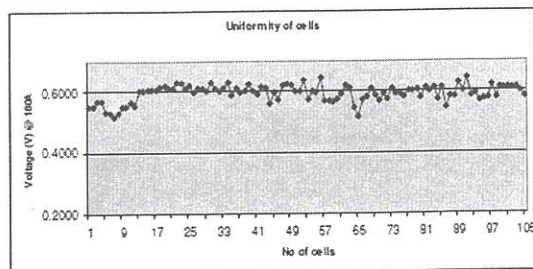


Fig. 3 Variation in cell voltage in a stack with large number of cells (Source: Unpublished data, CFCT, ARCI)

design are uniformity of cells, power density, water management etc., and these are discussed below.

Uniformity of Cells Performance

A fuel cell stack is an assembly of a large number of cells put together using bipolar plates as building blocks. Although all the individual elements in a stack are made by the same process/procedure, the cell voltages of these cells could be different [Fig. 3] during operation. A large number of parameters can cause non uniformity in performance. These include the flow field designs, cell configuration, location & number of coolant plates, temperature variations within the stack, temperature variation within the single cell assembly etc.

Uniform reactants flow-distribution within each flow field plate can be obtained by careful computational fluid dynamic techniques and experimental validation. A typical CFD analysis of a flow field design with respect to velocity distribution is shown in Fig. 4.

However, such models have to be accepted with caution because in many cases these are developed with flow and velocity as primary criteria without taking into account the electrochemical reaction that takes place in the cells and water vapor/liquid water in the gas streams.

The fuel cell stack performance is limited by performance of the weakest cell in the stack and the location of such a cell is not always constant when one makes a large number of stacks. This is one of the major challenges for a fuel cell stack designer i.e.

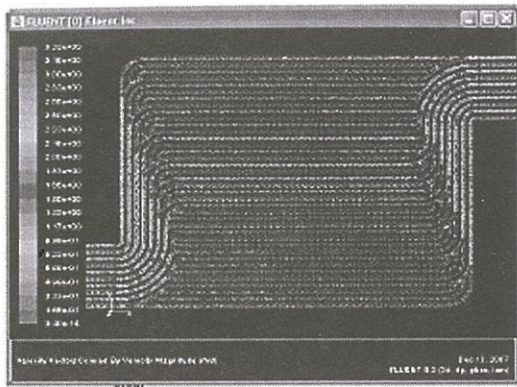


Fig. 4 CFD analysis of a Flow field design (Source: Unpublished data, CFCT, ARCI)

ensuring that all the cells in a stack assembly perform in the same way under all operating conditions.

Fuel cells develop heat while they generate electric power. The heat is removed by either forced air cooling or by circulating coolant fluids such as water. Although, in principle every cell has to be cooled, a fuel cell designer, in the interest of the fuel cell stack weight and cost, has to arrive at an optimum coolant flow field plate design and its position within the stack. This aspect can lead to variation in stack temperature at different locations. The challenge for the fuel cell engineer is to design the flow field in such a way that it can carry enough fluid to cool the stack uniformly.

Presently, almost all the components, except Catalyst Coated Membranes (CCM) and Gas Diffusion Layers (GDL) of the fuel cell are hand-made or at best, made by semi-automated processes. The stacks are assembled manually. The fabrication of components and assembly requires skilled technicians. Mass production techniques, quality control and automated stack assembly are required to be developed to ensure uniform performance of the individual cells in a stack.

Humidification & Water Management

Water management is one of the major challenges in the operation of a fuel cell stack. PEMFC working at temperatures $\approx 80^{\circ}\text{C}$ under atmospheric pressure often involves a dual phase

water system, i.e. liquid water/water vapor; when the humidification is too high, water condenses and the electrodes are flooded, which makes water management difficult. The membrane's ionic conductivity is a strong function of its hydration state. Although water is produced in the cathode, some water still has to be brought into the fuel cell to prevent the membrane drying. The form of water depends on local conditions inside the cell: gas flow rate, pressure and temperature. The stack design, selection and control of operating conditions affect water management and therefore the stack performance.

When operated with humidified reactants, the operating temperature, rate of flow of reactants and nature of Gas Diffusion Layer (GDL) play a major role in maintaining the humidity level in the membrane. On the contrary, operating the stacks using dry reactants pose a different set of challenges. In laboratory experiments external humidifiers [1] of various types can be used. But for standalone power generation systems and in order to reduce the parasitic losses, humidification segments made from graphite plates and membrane are built as part of the stack (internal humidification). In this concept, a portion of the membrane is set aside to humidify the inlet gases and liquid water is injected directly into this inactive portion of the stack. In another method, dry gas is passed through a separate section of the stack to condition the gas before it enters the electrochemically active portion of the cell. The advantage is that the gases are conditioned inside the stack, and the gas temperatures will be very close to the temperatures of the fuel cell stack itself. However, a portion of the electrochemically active section of the stack must be set aside for humidification purposes, which reduces the power density of the stack. Further, these arrangements introduce complexities with respect to the rate of flow of the reactants and introduce unwarranted pressure drops. This is one of the engineering challenges, fuel cell designer encounters.

Operating Conditions

Operation with low relative humidity of the gases at the stack inlet is preferred because it simplifies the system (humidification of reactant gases and water recovery). PEM fuel cells are operational even at room temperature, but the typical

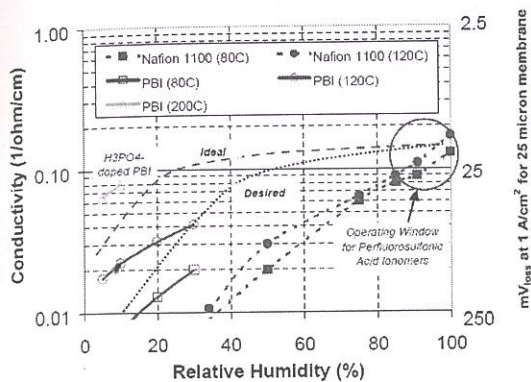


Fig. 5 Relationship between proton conductivity and adjoining gas stream relative humidity at various temperatures for perfluorosulfonic acid (1100 EW) and phosphoric-acid-doped polybenzimidazole. Curves are also shown for materials that would enable and be ideal for system simplification. [34]

operating temperature is between 60 and 80°C. In order to reduce the size of the heat rejection equipment there is a lot of R&D on high-temperature membranes that would allow operation at 130 - 140°C [17, 18]. Because of the rapid drop-off in conductivity with decreasing relative humidity for PFSA ionomers, they are typically operated in the high-RH window as shown in Fig. 5. [34]

The role of the system built around such a membrane is to provide the 100% RH environment so that the membrane/electrode can efficiently conduct protons with minimum voltage loss. However, maintaining 100% RH in the gas streams is problematic from the system point-of-view. The membrane RH requirement drives high-pressure operation (resulting in higher compressor auxiliary loads), low temperature operation (resulting in lower system heat-rejection rates), and increased RH in inlet streams (resulting in higher complexity and cost due to humidification/condensation requirements). Although Fig. 5 indicates that PFSA conductivity at 120°C for current ionomers is above 0.1 S/cm at 100% RH, this is an impractical operating region from a system point-of-view based on the calculations from system pressure and water addition capability. One of the challenges is defining

a suitable RH at 120°C at which the 0.1 S/cm target can be achieved.

At present, phosphoric-acid doped polybenzimidazole (PBI), first identified by Case Western Reserve University, is under active development which allows operation at temperatures up to approximately 200°C with conductivity of 0.06-0.08 S/cm, RH of 5-10%. However, the reported conductivity drops rapidly as a function of temperature, reaching 0.01-0.02 S/cm at 15-30% RH and 80°C. This is problematic from an automotive system start-up point-of-view. Additional issues with PBI have been stability in the presence of liquid water and inefficient cathode structures resulting in low a real power density.

Alternatively in the long run, the system would obviously benefit from membranes that required no external humidification. Operation with low relative humidity of the gases at the stack inlet is preferred because it simplifies the system (humidification of reactant gases and water recovery). PEM fuel cells are operational even at room temperature, but the typical operating temperature is between 60 and 80°C. When operating with dry reactants, the rate of water generated at the cathode needs to be equilibrated with rate of heat generated. The operating condition need to be effectively identified without damaging the endurance of cells, as one can see the humidity response shown in Fig. 6 for stacks operating at various current densities. In addition, the starting humidity of the reactant also plays a vital role in maintaining water balance depending on stack capacity.

Power Density

PEM Fuel cells have achieved > 1 Wcm² peak power, but in normal operation ($V_{\text{cell}} \sim 0.6$ V), the achievable power density is 0.6 - 0.7 and 0.3 to 0.4 Wcm² in high efficiency operation ($V_{\text{cell}} \sim 0.7$ V). Fig. 7 shows typical fuel cell and fuel cell stack performance. The goal of fuel cell development is to keep increasing power density and also to attain the same performance obtained in a single cell. This is possible through improvements in key materials, such as catalyst and electrolyte, as well as through improvements in fuel cell design. Operating the stacks at low power density leads to increased durability but at high cost while operating at high

power density leads to less cost and less durability. In addition the degradation of the stack also depends on whether the system is operated continuously or cycled with various start stop cycles as in the case of transport applications. Hence depending on the application, life-time of the stacks varies. For example in the case of transport application, high power density is required due to less available space and life-time is expected to be 5000 hours, whereas for stationary application, where space is not a constraint, the life-time is expected to be 40,000 hours. The volume, size, shape and weight of the fuel cell play a very important role for most mobile applications. Automotive fuel cell stacks have gravimetric and volumetric power density > 1 kW/kg and > 1 kW/l, respectively. However, the

power density is significantly lower for smaller stacks of < 10 kW capacity.

Durability

For any application of PEM fuel cells, several hours of continuous or intermittent operation has to be demonstrated. It has been found that the operating conditions have a strong effect on durability decay rates [24]. The exact mechanism(s) of PEM fuel cell low durability or failure is (are) not yet well understood. At present, the researchers have attributed the durability decay to hydrogen crossover, fluoride emissions rate, Pt particle size distribution etc. There are also several possible PEM fuel cell failure mechanisms, such as: manufacturing defects, unwanted chemical reactions caused by contaminants or by-products, stability of the electro-catalysts, membrane stability, mechanical clamping, thermal effects due to insufficient local heat removal rate etc. To prevent catalyst poisoning and carbon corrosion, non noble metal catalysts, alternative support materials are being investigated. Unfortunately, none of these catalysts has reached the level of a Pt-based catalyst in terms of catalytic activity, durability and chemical/electrochemical stability. Much more research is needed to produce commercially valid non-noble electro catalysts.

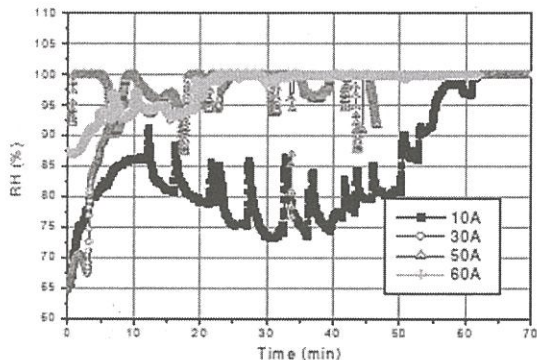


Fig. 6 Humidity response with respect to current [Source: Unpublished data, CFCT, ARCI]

Challenges in Fuel Cell System Development – System Integration

A fuel cell stack needs a supporting system in order to be operational. Besides the fuel cell stack, the fuel-cell system also incorporates several

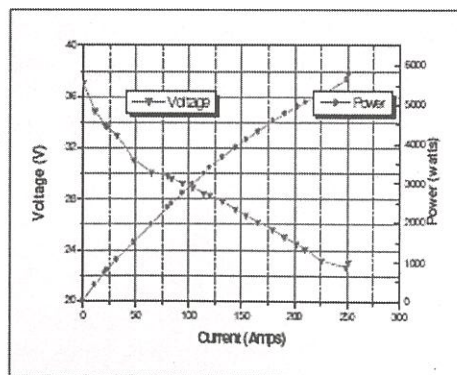
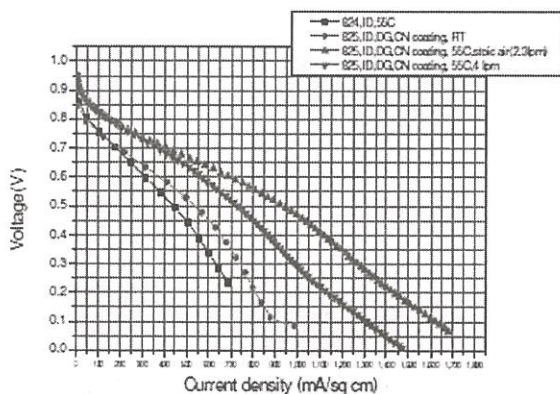


Fig. 7 Typical fuel cell performance (left: single cell, right: stack) [Source: Unpublished data CFCT, ARCI]

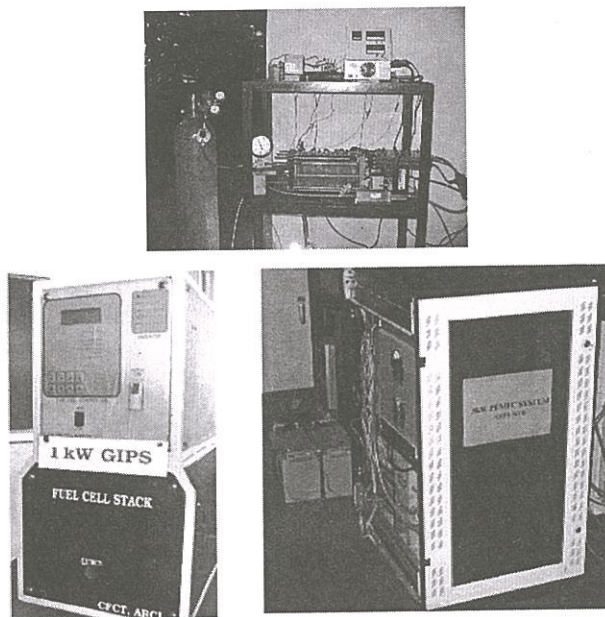


Fig. 8 A typical fuel cell set up and packaged fuel cell systems 1 kW and 5 kW [Source: Unpublished data CFCT, ARCI]

balance-of-system (BoS) components such as pumps, valves, heat exchangers, piping and power controllers.

Fig. 8 shows a typical laboratory set up for a fuel cell system and a packaged system. System design and its complexity also depend on application. Fuel cell system integration is a very complex subject as the integration involves several time contacts for the response of the individual components which is based on their own dynamics.

Although many application demonstrations have used off-the shelf components many of the failures in fuel cell demonstration have come from these components which necessitates development of suitable components which can operate for longer duration without maintenance. Each and every one of these BoS systems requires intense R&D and in India very few laboratories are involved in these developments. A fuel cell developer in India, therefore, has to necessarily depend on imported components which come with their own limitations. Many-a-time, a fuel cell designer in India has to modify his/her design of the fuel cell stack depending on the availability of these components. Given below are some of the major challenges in

BoS. Many of these BoS required are common to all types of fuel cells.

Heat Exchangers

Even though PEMFC is a very efficient system, there is still 40-50% of the energy produced as heat. The ratio of electrical power to heat is about 1:1 when the fuel cell is operated at average cell voltage of 0.65 V. Cooling plates inserted in the fuel cell stack assembly remove the heat either using liquid coolant and some times air. Current PEMFC systems run at a maximum of 80°C because operation above that temperature requires too much system support of the membrane. Also, current membranes have glass transition temperatures in the range of 80-120°C and are thus subject to creep and hole-formation at temperatures in that range. The challenge for the fuel cell engineer is to dissipate this heat quickly. Traditionally, FC designer has used heat exchangers used in automobile industries to remove this heat. Unfortunately, it turns out that the heat rejection rate of automotive radiators is insufficient to reject continuous full power waste heat loads with the 80°C source temperature [1]. It requires a novel complex cooling system with a large dimension and weight, e.g. the cooling system in the

state-of-the-art fuel cell cars accounts for about 50 wt% of the total weight of the fuel cell system. Although fuel cell vehicles are inherently more efficient than the internal combustion engine (ICE), the ICE has a thermal system packaging advantage. This is because the ICE rejects approximately one-third of its waste heat in the exhaust stream (vs. <10% for the PEMFC). Thus, the heat flow to be dissipated by the cooling system is approximately double as compared to that of the combustion engine [35].

Technological Limits of Cooling [36]

It is crucial that a sufficient air mass flow be available to accomplish the required cooling. Besides the exchange rate of the heat exchanger (ideal exchange rate = 1), a significant criterion is the expenditure of flow rate required to achieve this exchange rate. Development of heat exchangers for engine cooling in vehicle is aimed at the most favorable design of pressure loss / heat transfer ratio possible. A mechanically assembled aluminum radiator has a lower power than brazed aluminum radiator whose performance is surpassed by brazed copper/brass radiators. It is also known that radiators with counter current are better than cross current flow mode for the air. However space limitations in a vehicle do not allow counter current flow mode.

A fuel cell driven vehicle uses more than one coolant flow to cool down: fuel cell stack coolant and a coolant for the electronic components. There are wide varieties of possible configuration. One such possibility is given in Fig. 9.

When selecting a fan arrangement for high-capacity cooling modules, contradictory requirements have to be linked. On the one hand, at low driving speeds, with the associated low support by dynamic pressure for air circulation, a relatively high fan speed is required to circulate a large volume of air. A typical situation is the uphill ride of a fully loaded vehicle. The operating point, and thus the airflow result from the intersection of the characteristic of the cooling unit and that of the fan. Therefore a steep fan characteristic is desirable. On the other hand, great dynamic pressure results from high driving speeds. This leads to a displacement of the cooling unit characteristic, which will now intersect with the fan characteristic in an area where

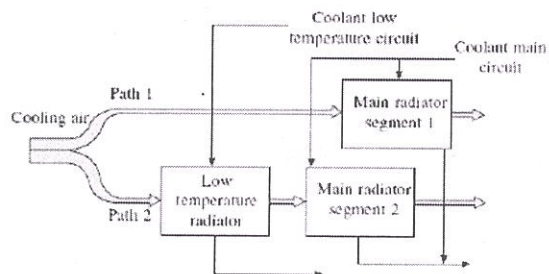


Fig. 9 Basic configuration for analysis of interaction between the main and low temperature radiator [37]

the fan is building up low pressure only or is even overblown. In order to obtain the highest possible airflow under these conditions, the fan characteristic should be as flat as possible, or even better, no fan should be available at all. A reconciliation of these contradictory requirements is required.

Many PEM fuel cell systems have been reported wherein a single air blower is used to feed the reactant gas as well supply the air to cool the stack. The thermal load can be managed simply by using fans without any water cooling system, the air-cooled PEMFC is widely used in sub kW and around 1 kW systems. The performance of an air-cooled system is highly dependent on ambient temperature and humidity. Air-cooled systems are expensive to build as each cell has to have channels for the anode and cathode plates for the cooling air to flow. In case of tropical and sub tropical countries, air cooling concept has to be thought very seriously as the temperature is about 35°C on an average.

Air Supply Systems

Air management in a fuel cell system could comprise of compressor/expander, filters, humidifier, mass flow sensor and water separator depending on the design of the fuel cell system and application. The options that have been used for supplying air are: air compressor, fan and blower, membrane or diaphragm pumps. Air is required not only for supplying reactant oxidant but also for cooling purposes and to cater to fuel processor needs, if used. Fuel cells operating at higher pressure (using an air compressor) show improved performance compared to those operating on air

blowers. For a stationary application of fuel cells, commercially available air compressors can be easily used. In case of transport applications, the common compressors are not suitable. Extensive research is being carried out to develop air supply system where the energy requirement is less and large volume air can be supplied and the system is compact in design. Root compressors, Lysholm or screw compressor, centrifugal or radial type compressors, axial flow compressors have all been tried each having its own set of advantages and disadvantages [38]. However the parasitic losses encountered with use of air compressors are high. In many an instance it is difficult to get an air compressor suitable for particular capacity fuel cell stacks (leading to over designing). On the other hand, fuel cell stacks operating with air blowers are bulky. The blowers have limited pressure-range and the flow rate can drop to zero if the back pressure rises to even 50 Pa (0.5 cm of water). In addition, the fuel cell air flow field plate has to be redesigned to accommodate the low pressure air supplied by the air-blower. In systems which require humidified air, a fuel cell engineer has to design a humidifier which would work on low pressure air. In addition, a load-following air supply system would be useful in reducing parasitic losses. However such load-following variable speed blowers/compressors are not readily available. Cunningham [39] in his analysis of air supply options for FCV found that: (i) the same peak P_{net} can be achieved with both a blower (low pressure) and a compressor (high pressure), but the required fuel cell stack sizes are different. For the same peak P_{net} of 86 kW, 16.3% more operating PEM cells were needed in the stack for the blower application (500 vs. 430 cells with a constant active area of 490 cm²). The blower system was able to obtain the same net power by operating just above ambient pressure at the stack and providing sufficiently higher air mass flow rates compared to that of the compressor for much of the P_{net} range (ii) the parasitic loads for the blower are significantly less than that of the compressor at the high P_{net} region. Power spent on compression can be recovered if the system is equipped with expander on the same shaft of the compressor.

These challenges are not trivial. One of the reasons for high cost of the present day fuel cell

systems is the non availability of fuel cell specific components.

A critical need in fuel cell systems for vehicles is an efficient, compact, and cost-effective air management system to supply air preferably at about 2.5 atm. Because no off-the-shelf compressor technologies are available to meet the stringent requirements of fuel cell air management, several compressor and blower systems are currently being developed. The efficiency, reliability and durability of compressors depend on effective lubrication or friction and wear reduction in critical components such as bearings and seals. Conventional oil or grease lubrication of compressor components is not desirable because such lubricants can contaminate and poison the fuel cell stack.

Power Controllers

The subject of power control systems for fuel cells is quite complicated. Fuel cells produce variable DC power. The power from fuel cells although is similar to battery, the voltage characteristics for battery and fuel cell are entirely different as shown in Fig. 10.

A fuel cell system is designed depending on the end use. PEMFC can generate high current density but at low voltages. In order to make use of this variable DC power, DC-DC converters and inverters are required. A power electronics professional would prefer a high voltage input which necessarily means having a large number of cells connected in series. However, to minimize the flow distribution and mechanical engineering issues, a fuel cell engineer would prefer a compact stack with

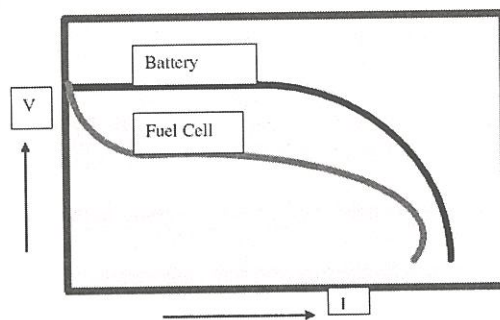


Fig. 10 Voltage-Current characteristics of fuel cell battery

less number of cells. A large variation in fuel cell terminal voltage from no load to full load, results in larger voltage ampere rating of the power conditioning unit. Off-the-shelf power controllers used in conventional UPS systems are not suitable for use with fuel cells as $i-v$ characteristics are totally different. Any new power converter developed should be able to handle high current at low voltages. Presently all the DC-DC converters and inverters are custom built, most of them operating at an efficiency of $\sim 80\%$. There is requirement for these power electronic devices with higher efficiency.

In addition to the DC-DC converter and inverter, the power control device should also provide interface for powering parasitic loads such as blowers, compressors, pumps, fans etc and these interfaces could be 12V DC, 24 V DC, 48 V DC. In addition to these requirements, the power controller should also have provision for charging the batteries (trickle charge, controlled charge etc.) normally used to start up the fuel cell system. In applications where the fuel cell is used along with other energy systems, the fuel cell power control system has to be designed in such a way that the fuel cell stack is protected from other power devices. The power controller should also have provision to charge super-capacitors if they are used to take care of surge current on transient loads. More detailed investigations are required in using super-capacitors along with fuel cells. The power conditioning design depends also on operating mode, like grid parallel, grid support, stand alone or back-up power. The ability to carry unbalanced load due to switching characteristics of the electronic circuitry due to unequal load should also be taken into account.

System Efficiency

The fuel cell system efficiency is lower than the stack efficiency due to power requirements for auxiliary components and due to power conversion. A well designed fuel cell system is expected to use not more than 10% of the fuel cell output power for auxiliary components. The efficiency of power conditioners like inverters and converters should be relatively high and also their operating range of voltage and current and configurations need to be optimized for the given application. Generally, Systems with a reformer should reach 40%

efficiency while the hydrogen fueled systems should have efficiency around 50%.

Other Issues

In addition to several challenges mentioned above, the PEM fuel cell must be able to run continuously as generators of premium power for base, back-up, and peak-shaving loads in cooperation with the electric grid.

Fuel Issues

In order to bring the fuel cell systems to the market, hydrogen should be widely available fuel, or fuel cell systems may be equipped with a reformer that generates hydrogen-rich gas from hydrocarbon fuels. This poses several challenges to the fuel cell stack and system design. Carbon monoxide, even in small quantities, is a poison for Pt catalyst at normal operating temperatures. Controlling a fuel cell/reformer system in variable power mode and maintaining low CO level all the time, is a very challenging task. In addition, several other contaminants may be generated in the reforming process, which may have a detrimental effect on fuel cell stack performance and durability. The U.S. Department of Energy in August 2004 reduced substantially the support for onboard reformer development, putting more emphasis on on-board hydrogen-storage development, yet another critical issue for fuel cell acceptance. With respect to infrastructure, hydrogen or hydrogen-rich fuels must be widely available and priced like commodities. This may require a hydrogen infrastructure, although other possibilities are emerging. External fuel processors (reformers) are also the subject of intensive development around the world. A variety of innovative compact reformers using diffusion-bonded printed-circuit components or micro-channel designs, also illustrate the impact of materials technology on this aspect of fuel-cell systems.

Miniaturization

To compete with current battery technology, portable power Fuel Cell applications for consumer electronics require miniaturization, shock and vibration resistance, orientation insensitivity, and passive operation. Components and subsystems are required.

Codes and Standards

Some commonly agreed measures for system efficiency are power density, dynamic behavior, durability. This requires a harmonized testing procedures, both for the entire Fuel Cell systems and for the system components under a variety of boundary conditions: e.g. Different applications; Different stack concepts; Type of fuels and quality. Till recently no standardized test procedures for Fuel Cells, stacks, and systems existed. The same applies for their assessment against user requirements in the stationary, transport and portable applications. In practice, many laboratories and manufacturers have developed their own test protocols to meet their needs and those of their customers, showing clearly the need for harmonization of testing procedures and measurement methods to ensure a smooth introduction of the technology and to provide equal opportunities for the market operators and a decent and confident comparison basis for the customers.

Conclusions

Fuel cells are being developed and have been demonstrated in many applications like clean transportation, clean power generation, distributed power generation and military applications. Fuel cells are versatile, efficient, clean and modular. There are a few technical challenges but there are no 'showstoppers.' Fuel cells are close to commercialization and there are some niche markets which could enable early penetration, particularly those that do not need hydrogen infrastructure like stationary power, back-up power, niche transportation such as forklifts.

As PEMFC commercialization approaches, the need for product and manufacturing engineering is obviously increasing. However, the need remains for aggressive research and development focused on new fuel cell materials, particularly if the technology is to meet demanding requirements. Improved polymer electrolyte and catalyst materials will have the largest impact on PEMFC commercialization. The process of materials discovery will be most efficient if materials developers focus on making materials and obtaining ex-situ data. A reliable and time-effective method should be developed for novel material screening. The emphasis should be placed on simulating real fuel cell working

conditions and the relationship between the working conditions and the cell related properties. After obtaining promising materials, the projects involving implementation in MEAs can be launched. This approach will allow polymer scientists and electro-catalyst experts to focus their efforts on discovering materials and avoid wasting their efforts on the time-consuming and potentially misleading process of MEA preparation.

From the Indian perspective, although there are many reports on developing new materials, system development remains a neglected area. Even with materials development, a few of them have reached the level of large scale production.

Fuel cells with their applications may actually be the main driver for hydrogen economy together with electricity from clean renewable energy sources and satisfy all the energy needs. Changing of the entire energy system is a huge task on global level, which may take several decades to complete.

References

1. K. S. Dhathathreyan and N. Rajalakshmi, Polymer Electrolyte Membrane Fuel Cell, in Recent Trends in Fuel Cell Science and Technology, Edited by S. Basu Copyright © 2006, Anamaya Publishers, New Delhi, India.
2. N. Rajalakshmi and K.S. Dhathathreyan, "Present Trends in Fuel Cell Technology Development", NOVA Science Publishers Inc., NY, USA (2008)
3. V. Mehta, J.S. Cooper, J. Power Sources 114 (2003) 32
4. F. de Bruijn, Green Chem. 7 (2005) 132
5. S. Litster, G. McLean, J. Power Sources 130 (2004) 61
6. J.S. Lee, N.D. Quan, J.M. Hwang, S.D. Lee, H. Kim, H. Lee, H.S. Kim, J. Ind. Eng. Chem. 12 (2006) 175
7. H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Appl. Catal. B-Environ. 56 (2005) 9
8. E.S. Smotkin, R.R. Diaz-Morales, Ann. Rev. Mater. Res. 33 (2003) 557
9. E. Antolini, J. Mater. Sci. 38 (2003) 2995 ; E. Antolini, Mater. Chem. Phys. 78 (2003) 563

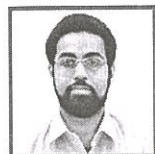
10. L. Zhang, J.J. Zhang, D.P. Wilkinson, H.J. Wang, *J. Power Sources* 156 (2006) 171
11. Z. Shi, J.J. Zhang, Z.S. Liu, H.J. Wang, D.P. Wilkinson, *Electrochim. Acta* 51 (2006) 1905
12. F. Bensebaa, A.A. Farah, D.S. Wang, C. Bock, X.M. Du, J. Kung, Y. Le Page, *J. Phys. Chem. B* 109 (2005) 15339
13. M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chem. Rev.* 104 (2004) 4587
14. Q.F. Li, R.H. He, J.O. Jensen, N.J. Bjerrum, *Chem. Mat.* 15 (2003) 4896
15. J. Roziere, D.J. Jones, *Ann. Rev. Mater. Res.* 33 (2003) 503
16. G. Alberti, M. Casciola, *Ann. Rev. Mater. Res.* 33 (2003) 129
17. S.J. Hamrock, M.A. Yandrasits, *Polym. Rev.* 46 (2006) 219
18. A.M. Herring, *Polym. Rev.* 46 (2006) 245
19. Zhang J, Xie Z, Zhang J, Tang Y, Song C, Navessin T, Shi Z, Song D, Wang H, Wilkinson DP. High temperature PEM fuel cells. *Journal of Power Sources* 2006; 160 (2) 872
20. Savadogo O. Emerging membranes for electrochemical systems: Part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications. *Journal of Power Sources* 2004; 127 (1–2) 135
21. Kerres J, Ullrich A. Synthesis of novel engineering polymers containing basic side groups and their application in acid–base polymer blend membranes. *Separation and Purification Technology* 2001 (22–23)1
22. Barbir F. *PEM Fuel Cells: Theory and Practice*. Elsevier, Academic Press: Burlington, 2005
23. Hermann A, Chaudhuri T, Spagnol P. Bipolar plates for PEM fuel cells: a review, *International Journal of Hydrogen Energy* 2005; 30(12)1297
24. R. Borup et al. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation, *Chem. Rev.* 107 (2007) 3904
25. Chalk, S. G.; Miller, J. F. J. *Power Sources* 159 (2006) 73
26. Fowler, M.; Mann, R. F.; Amphlett, J. C.; Peppley, B. A.; Roberge, P. R. In *Handbook of Fuel Cells, Fundamentals, Technology and Applications*; Vielstich, W., Gasteiger, H. A., Lamm, A., Eds.; 2003; Vol. 3, p 663
27. *Fuel Cell Hand Book* (5th ed.) by EG & G Services, Parsons Inc. Science Applications International Corporation, October 2000.
28. M.A. Hickner, B.S. Pivovar, *Fuel Cells* 5 (2005) 213
29. M.A. Hickner: *Transport and Structure in Fuel Cell Proton Exchange Membranes*, PhD Thesis, Virginia Polytechnic Institute and State University, 2003
30. M.A. Hickner, B.S. Pivovar, *Fuel Cells* 5 (2005) 213
31. S. von Kraemer, M. Puchner, P. Jannasch, A. Lundblad, G. Lindbergh, *J. Electrochem. Soc.* 153 (2006) A2077
32. E.B. Easton, T.D. Astill, S. Holdcroft, *J. Electrochem. Soc.* 152 (2005) A752
33. *Development of Biomimetic™ Flow Field Plates for PEM Fuel Cells*, Alan Chapman and Ian Mellor, 8th Grove Symposium, Sep. 2003 London, UK.
34. Hubert A. Gasteiger, Mark F. Mathias, *Fundamental research and development challenges in polymer electrolyte membrane fuel cell technology*.
35. Walter J, *Modellierung eines Brennstoffzellen Antribesstrangs VDI Berichte Nr. 1565: (2000) 355*
36. M.F. Mathias, R. Makharia, H.A. Gasteiger, J.J. Conley, T.J. Fuller, C.J. Gittleman, S.S. Kocha, D.P. Miller, C.K. Mittelsteadt, T. Xie, S.G. Yan, P.T. Yu, *Interface* 14 (2005) 24
37. Rogg S, Höglinger M, Zwitter E, Pfender C, Kaiser W and Heckenberger T, *Cooling Modules for Vehicles with a Fuel Cell Drive, FUEL CELLS*, 3 (2003) 153
38. Cunningham J M, *Air System Management for Fuel Cell Vehicle Applications*, MS Thesis, University of California, Davis, USA, 2001.

Fabrication of Anode Supported Solid Oxide Fuel Cell



Dr. Rajendra N. Basu is a Scientist-F and Head, Fuel Cell and Battery Division of Central Glass and Ceramic Research Institute, CSIR, Kolkata and working in the area of Solid Oxide Fuel Cell, Li-ion Battery and Mixed Ionic and Electronic Conductor (MIEC)-based Dense Ceramic Membrane. After obtaining PhD in 1988 from Indian Institute of Technology, Kharagpur, he carried out postdocs (6 years) from the Pennsylvania State University (USA), Forschungszentrum Jülich (Germany), McMaster University (Canada), Oita University (Japan) and Physikalisch Technische Bundesanstalt (Germany). He has been conferred with national and international awards such as DAAD, JSPS (Senior), MRSI Medal etc. He is a Fellow of West Bengal Academy of Science & Technology, India.

Dr. Abhijit Das Sharma, Scientist-El, obtained his M.Sc (Chemistry) from IIT, Kharagpur in 1987 and Ph. D from Jadavpur University in 1993. He joined CGCRI, Kolkata in 1997 and has been working on different aspects of solid oxide fuel cell, the cell fabrication and glass-based high temperature sealants in particular. His other areas of research interest are ceramic capacitors, high temperature superconductors and MIEC-based dense membrane for gas separation. He has published more than 30 papers in International journals and has 8 Indian patents to his credit.



Shri Jayanta Mukhopadhyay is presently a Scientist-B in Fuel Cell & Battery Division of CGCRI, Kolkata. He obtained his B. Tech in Chemical Technology and M.Tech in Ceramic Engineering in the Year of 2000 and 2002, respectively from University of Calcutta. He was the topper in B. Tech and M. Tech. Before joining CGCRI, he was a R&D Scientist at ARCI, Hyderabad. He has about 20 research publications and two patents to his credit. His present research activities include improved SOFC cathodes by novel powder processing techniques, functional anodes, SOFC stack engineering, mixed ionic and electronic conductor (MIEC)-based membrane for hydrogen separation etc.

Dr. Atanu Dutta, worked as researcher in Fuel Cell and Battery Division of CGCRI, Kolkata. He worked on intermediate and low temperature solid oxide fuel cells and various new cathode materials. He was awarded PhD degree (Materials Science) in 1995 by Indian Institute of Technology, Kharagpur. He is an ICTP Fellow and worked at University of Roma, TorVergata, Roma, Italy for more than one year. He also has a postdoctoral research experience for three years at Oita University and Kyushu University, Japan. Presently, he is a Professor in the Department of Physics, VIT University, Chennai Campus, India.



Abstract

Using inexpensive and simple processing techniques, anode-supported planar single cells of dimensions 5 cm × 5 cm × 1.5 mm and 10 cm × 10 cm

× 1.5 mm have been fabricated. The process involves room temperature lamination of several porous layers of tape cast NiO-YSZ together with a dense layer of YSZ electrolyte followed by co-firing. The half-cell fabrication is optimized while the

Dr. R.N. Basu, Dr. A. Das Sharma, Shri J. Mukhopadhyay and Dr. Atanu Dutta⁺, Fuel Cell and Battery Division, Central Glass and Ceramic Research Institute, Kolkata 700 032, Council of Scientific & Industrial Research (CSIR), India; ⁺Present address: Department of Physics, VIT University, Chennai Campus, Chennai 600 048; E-mail: rnbasu@cgcri.res.in / rajenbasu54@gmail.com

electrolyte thickness is lowered down from 40 μm down to 10 μm . The fabricated single cells with screen printed La(Sr)MnO₃ (LSM)-YSZ as cathode active layer and LSM as current collector layer shows very high electrochemical performance without any active layer on the anode side of the fabricated cells. The single cells are tested with hydrogen on the anode and oxygen on the cathode sides. The current density and power density of a typical coupon cell of diameter 16 mm (with YSZ thickness 10 μm) is found to be $\sim 1.7 \text{ A/cm}^2$ and $\sim 1.2 \text{ W/cm}^2$ respectively at a cell voltage of 0.7V measured at 800°C. Single cells have also been fabricated using nanocrystalline cobalt doped lanthanum ferrite (LSCF) based mixed ionic and electronic (MIEC) cathode materials and gadolinium doped ceria (CGO) based interlayers. The syntheses of both the cathode and the interlayer materials are carried out using low temperature combustion technique. Using LSCF and CGO combination, the current density of a typical coupon cell (with YSZ thickness 10 μm) is as high as $\sim 2.4 \text{ A/cm}^2$ with a power density of $\sim 1.7 \text{ W/cm}^2$ (at 0.7 V and 800°C) using hydrogen as fuel and oxygen as an oxidant. At 800°C the area specific resistance (ASR) value, evaluated from the current-voltage plot, is found to be as low as 0.205 $\Omega\text{-cm}^2$ and 0.17 $\Omega\text{-cm}^2$ for the cells with LSM based cathode current collectors and LSCF based cathode current collectors respectively. The performances of both the variety of cells are found to be almost size independent having excellent repeatability.

Keywords

Anode-supported, Planar SOFC, Processing, Tape casting, Co-firing, Nanocrystalline cathode, High performance

Introduction

Solid oxide fuel cells (SOFCs) are considered to be one of the most promising power generation technologies for the future due to its high efficiency, extremely low level of pollution and fuel flexibility. In a SOFC, the oxygen ions (O²⁻) are conducted from the porous air electrode (cathode), where they are formed, through a gas-tight, ceramic, oxygen-ion conducting electrolyte to the porous fuel electrode (anode). There, they react with the fuel, such as

hydrogen, natural gas, coal gas to deliver electrons to the external circuit and produce electricity. The state-of-the-art materials for SOFC are 8 mole % yttria stabilized zirconia (8YSZ) as the electrolyte, NiO-YSZ as the anode and La(Sr)MnO₃ (LSM) as the cathode¹. Improvement in single cell power output coupled with long term stability for such a cell has been the subject of intensive research and accordingly, a lot of developments have been made both in SOFC materials and design [1-3].

Among the various designs, the planar anode-supported thin film electrolyte design, originally introduced by Forschungszentrum Jülich, Germany, is recently followed by many of the SOFC developers because of several advantages associated with this design [4]. Generally electrolyte-supported cells and electrode-supported cells are the two possible configurations of a planar design that are under development. 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 cell have to be operated at a very high temperature of around 1000°C in order to have sufficiently low resistance of the electrolyte. This hinders the commercialization of SOFC due to the necessity of using costly construction materials to withstand such a high temperature. In order to avoid this, the SOFC operating temperature should be lowered. However, as the ionic conductivity of the 8YSZ electrolyte decreases with decreasing temperature, simply lowering of the operating temperature of SOFC will lead to an increase in resistance of the electrolyte causing very low power output. 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, use of metallic interconnects which are much easier to fabricate compared to their ceramic counterpart that are required for 1000°C operation. 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). However, in such a configuration, the major technical challenge involves fabricating a pinhole and crack-free dense layer of YSZ electrolyte of thickness 50 µm 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 loss.

For the fabrication of such (NiO-YSZ/YSZ) half-cells, conventionally the porous anode-support is fabricated first over which the YSZ layer is developed subsequently using different fabrication techniques such as electrochemical vapour deposition, chemical vapour deposition, spray pyrolysis, sol-gel coating, vacuum slip casting, screen printing etc. [5-11] On the other hand, cofiring of the half-cell consisting of NiO-YSZ anode and YSZ electrolyte reduces the number of processing steps and is more advantageous from the view point of cell fabrication. In this regard, tape casting is a simple, cost-effective and up-scalable technique that can be used to fabricate such a half-cell by co-firing a laminated block consisting of several layers of NiO-YSZ with an YSZ layer. Although co-firing makes the process simpler but camber and/or breakage of the half-cell may occur during high temperature (> 1300°C) processing of the same due to differential thermal expansion coefficients and sintering shrinkages among the components viz. NiO-YSZ and YSZ. Hence, meticulous optimization of different processing parameters such as tape casting slurry composition, heat-treatment schedule etc. is required to obtain a defect-free and flat half-cell. Another problem associated with the development of single cell of SOFC is that during fabrication of the strontium doped lanthanum manganite (LSM) cathode if the processing temperature is more than 1150°C, the LSM reacts with the adjacent YSZ electrolyte to form insulating layers like lanthanum zirconate, strontium zirconate, at the interface causing poor cell performance [12]. Thus it is a major challenge to restrict the processing temperature within 1150°C during fabrication of the LSM cathode. Thus the design of the electrodes and their microstructure are some of the critical parameters upon which the

performance of the completed single cell (obtained upon fabrication of the cathode layer over the half-cell) depends⁷. In order to have enhanced cell performance, normally two active layers e.g., anode active layer and cathode active layer are used between the anode-electrolyte and cathode-electrolyte interfaces respectively [6-9, 13]. These layers are believed to increase the triple phase boundary (TPB) lengths with consequent enhancement in electrochemical reactions on each side of the electrolyte and reduce the polarization losses. Several reports are available in the literature describing the performance of such anode-supported SOFC [14-20]. The present work reports the use of inexpensive, simple and up-scalable processing techniques, such as tape casting and screen printing, for the fabrication of anode-supported planar SOFC where separate anode active layer has not been applied. 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 and electrochemical performance studies using both LSM based conventional cathode as well as LSCF based nanocrystalline MIEC cathodes.

Experimental

Fabrication of Single Cell

The flow chart for the fabrication of anode-supported single cell is shown in Fig. 1. The first major step during the fabrication process is the development of the anode-supported half-cell (NiO-YSZ/YSZ). As mentioned earlier, tape casting technique is used extensively for the same. For tape casting slurry preparation, nickel oxide and 8 mol% yttria stabilized zirconia (YSZ) powder mixture (in 60:40 mass ratio) is first ball milled for about 20 h in an azeotropic mixture of toluene and ethanol using menhaden fish oil as dispersant followed by addition of optimized amounts of polyvinyl butyral binder, benzyl butyl phthalate plasticizer and graphite porosifier and further ball milling for another 20–24 h. The homogeneous slurry of NiO-YSZ thus obtained, is then cast under the doctor blade of a laboratory type tape casting machine. After drying, a flexible green sheet of NiO-YSZ (~ 100 µm thick) is obtained. Similarly, green sheets of YSZ electrolyte is obtained by casting YSZ slurry that is formed in

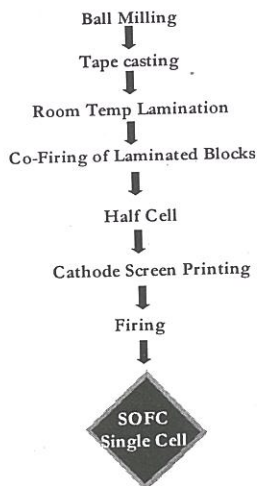


Fig. 1 Flow chart of the fabrication of anode-supported single cells

the same way as in the case of NiO-YSZ except that no porosifier is added in this case. During casting of YSZ slurry, however, the blade gap has been reduced so as to vary the electrolyte thickness and to fabricate thinnest possible electrolyte sheet. The green sheets of NiO-YSZ anode as well as YSZ electrolyte are then cut to the required size. Several numbers of the cut sheets of NiO-YSZ are then laminated at room temperature together with an YSZ sheet on top. The monolithic block of NiO-YSZ/YSZ, thus formed, is then co-fired above 1300°C with an intermediate binder burn out step so as to obtain the sintered half cell. The LSM-YSZ based active layer and LSM based current collector layer (CCL) are then applied on the YSZ surface of the half cell by screen-printing technique. For the cells with nanocrystalline LSCF based cathodes, doped ceria based materials was used as an interlayer onto which LSCF based cathodes are applied by screen printing technique to fabricate the single cells.

The LSM powder used for active layer as well as CCL has been prepared using an auto-ignition technique. In this process, a precursor solution containing lanthanum (III) nitrate hexahydrate, strontium (II) nitrate and manganese (II) acetate tetrahydrate with La:Sr:Mn = 0.65:0.3:1.0 together with acetic acid monohydrate is sprayed into the reaction chamber of an in-house built spray

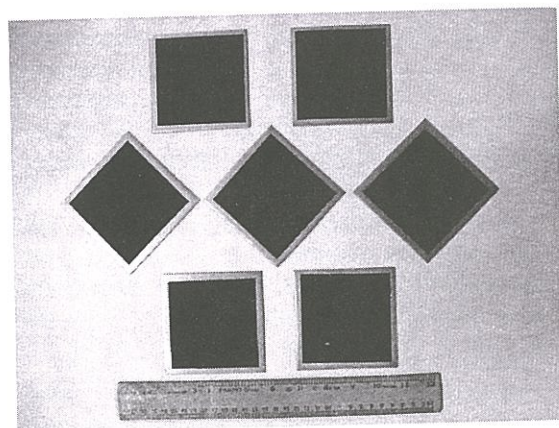


Fig. 2 Photographs of the fabricated 10 cm x 10 cm SOFC anode-supported single cells

pyrolyser (heated to about 300°C) where the spray mist undergoes a controlled oxidation-reduction reaction leading to the formation of an ash precursor. Upon calcination, the ash yields phase pure oxide. For active layer application, the calcination temperature is 800°C whereas for CCL, the ash is calcined at 950°C so as to obtain optimized particle size for the active layer and CCL respectively as reported by Haanappel et al. [7] For screen printing application, a viscous paste of the active layer is prepared by mixing LSM and YSZ powder (in 50:50 mass ratio) with a suitable organic vehicle. Similarly, a viscous paste of CCL (containing only LSM powder) is also prepared. Prior to screen printing, the half-cells are thoroughly cleaned with acetone in an ultrasonic bath followed by drying. At first a thin active layer of LSM-YSZ is screen printed on the YSZ surface of the half cell. After drying, a relatively thicker layer of CCL (LSM) is screen printed over the active layer. Both the layers are then cofired above 1100°C . Fig. 2 shows the photographs of few representative cells fabricated in this investigation. For the synthesis of cobalt doped lanthanum ferrite, stoichiometric amounts of lanthanum (III) nitrate hexahydrate, strontium (II) nitrate, iron (III) nitrate nonahydrate and cobalt (II) nitrate hexahydrate are used as the raw materials. Using these raw materials, nanocrystalline LSCF based materials are synthesized through an auto combustion technique with L-alanine as fuel [21]. The auto combustion technique is also used for the synthesis of the gadolinium doped ceria (CGO)

interlayer materials, using cerium nitrate and gadolinium nitrate as the metal source and citric acid as fuel. For the fabrication of single cell, a thin layer of CGO interlayer (in the form of thick paste) is screen printed first on the YSZ surface of the half cell followed by sintering above 1250°C. A relatively thick layer of the LSCF based cathode paste is then screen printed over the sintered CGO surface and again sintered above 1000°C.

Microstructural Characterization

The microstructures and morphology of the cells have been studied extensively. For this purpose, cells (both half and single) are sectioned and epoxy-mounted. After proper curing of the epoxy, the samples are polished down to 0.5 µm and the cross sections are examined under a scanning electron microscope, SEM (Leo, S430i, U.K.).

Electrochemical Characterization

In order to evaluate the electrochemical performance, single cell in the form of coupon cell (~16 mm diameter and 1.5 mm thick) cut from larger area cells of dimension 10 cm x 10 cm x 1.5 mm is placed between two alumina tubes kept inside a vertical split type furnace. Platinum meshes are used as current collectors both at the cathode and the anode and proper electrical contact is made through platinum lead wires. The sealing of the gas compartment on the anode side is made by using a ring-shaped glass seals which is kept pressed by the alumina tubes and upon heating to about 1000°C; the glass softens to form a gas-tight seal. The whole assembly is then cooled down to 800°C and a flow of gaseous argon is introduced at the anode side and oxygen at the cathode side. The reduction of NiO to metallic Ni for the anode of the single cells is then achieved by gradual replacement of argon with hydrogen (saturated with 3 vol% water vapour). During testing, both oxygen and hydrogen flow rate is set and maintained at 100 sccm with the help of electronic mass flow controllers (MKS Instruments, USA). The current density as a function of cell voltage is evaluated under different applied loads across the cell and measurements are carried out sequentially at 800, 750 and 700°C.

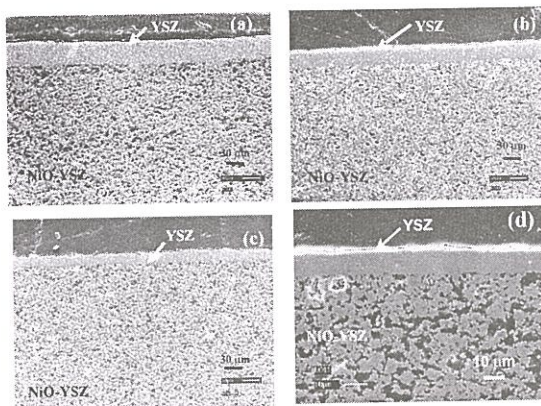


Fig. 3 SEM image of polished cross section of sintered half cells with different YSZ thicknesses: (a) 40 µm, (b) 30 µm, (c) 20 µm and (d) 10 µm

Results and Discussion

Microstructure of SOFC Half- and Single Cell

A major emphasis is given during this investigation to optimize the processing parameter so as to obtain the thinnest possible YSZ layer in the anode-supported half-cell. Fig. 3 shows the microstructures of such sintered half-cells having different YSZ thicknesses. A dense YSZ layer, well adhered to the porous NiO-YSZ substrate, can be observed in all the cases. It may be mentioned here that due to the handling problem associated with the corresponding YSZ green tapes, we could not lower the thickness of the sintered YSZ electrolyte below 20 µm during the initial stages of our developmental work. However, with further optimization of process parameters, the slurry formulation in particular, it has been possible to fabricate half-cells with very thin (~10 µm) and dense YSZ film with reproducible quality. The microstructures of the single cells with LSM-YSZ based cathode active layer, LSM based cathode current collection layer and LSCF based MIEC cathodes with CGO based interlayers are given in the Fig. 4a and Fig. 4b respectively. The anode is found to be highly porous which is essential for gas-phase reaction to occur at the electrolyte/electrode/gas triple phase boundary. On the other hand, the active layer on the cathode side (~10 µm) is relatively less porous than the CCL (~50

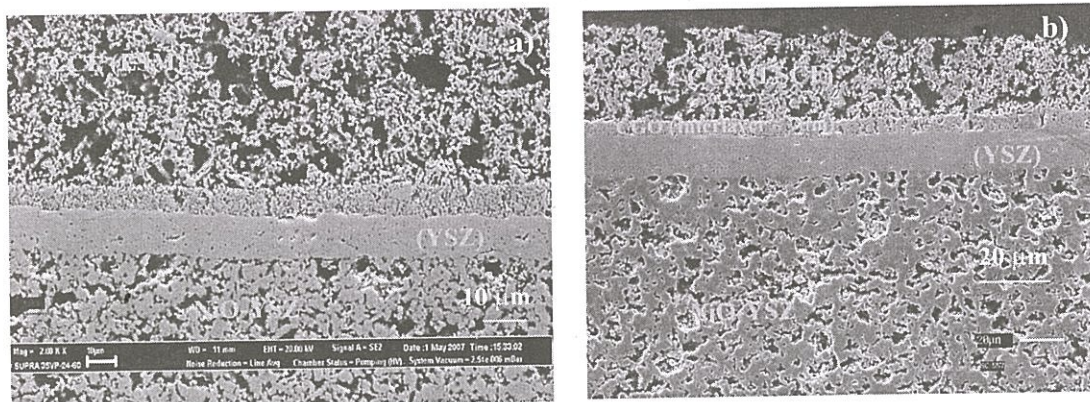


Fig. 4 SEM image of polished cross section of sintered single cells with different cathodes: (a) LSM-YSZ Cathode Active Layer and LSM as Cathode Current Collection Layer (b) LSCF based MIEC Cathodes with CGO based Interlayer

μm). High porosity at CCL is also essential for reducing the cathode overpotential and thus to increase oxygen reduction kinetics at the active layer/YSZ electrolyte interface.

Electrical Conductivity of SOFC Cermet Anode and Half cell

The electrical conductivity of the Ni-YSZ anode substrate has been studied for samples from various batches and from different portions of the 10 cm × 10 cm anode substrate. The conductivity at 800°C is found to be > 500 S/cm. Uniformity of the conductivity (± 20 S/cm) value is observed among the different samples studied. A typical $\ln(\sigma T)$ vs $1/T$ Arrhenius plot in the temperature range 550-800°C is shown in Fig. 5. A linear decrease in electrical conductivity with temperature in the plot indicates that the conductivity is predominantly metallic in nature. From the slope of the line in Fig. 5, the activation energy for electronic conduction is calculated to be about 0.1 eV which is typical for Ni-YSZ cermet anode having a Ni content of 40 vol% [22]. In addition, the electrical conductivities of Ni-YSZ/YSZ (20 μm) half-cells have also been studied during the present investigation. In this case, it has been observed that with the increase of temperature the conductivity increases continuously and at 800°C the value is found to be ~ 0.02 S/cm. Since the Ni-YSZ anode cermet with 40 vol% Ni content shows a very high conductivity value which is metallic in nature, the observed low conductivity

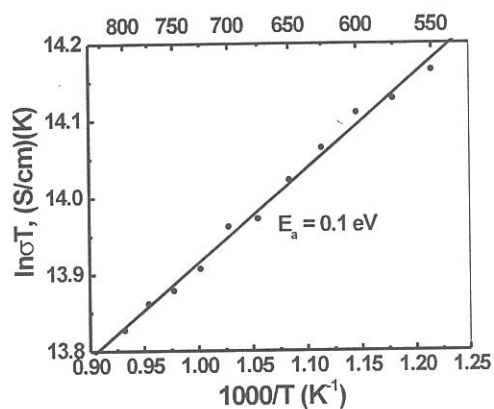


Fig. 5 Arrhenius plot of the temperature dependent electrical conductivity of a typical Ni-YSZ anode prepared by tapecasting and lamination processes

value and the increase of the same with increasing temperature in case of the half cell suggests that the conductivity, in this case, is solely controlled by the thin YSZ electrolyte. The observed stable conductivity data of the half cell also indicates that the thin YSZ film supported on the porous Ni-YSZ anode is defect free.

Electrochemical Performance of SOFC Single Cell

Table 1 shows the comparative electrochemical performance of the coupon cells

TABLE 1. Electrochemical performances of anode-supported SOFC single cells (at 800°C, 0.7 V) with variable YSZ thickness

Electrolyte Thickness (μm)	Current density (A/cm^2)	Power density (W/cm^2)
40	1.00	0.70
30	1.20	0.84
20	1.35	0.95
10	1.7	1.2

derived out from 10 cm \times 10 cm single cells having different YSZ thicknesses (10-40 μm) at 800°C. As expected, the electrochemical performance improves with a decreasing electrolyte thickness and for the cell having YSZ thickness of 20 μm , a high current density of 1.35 A/cm^2 with a power density $\sim 0.9 \text{ W}/\text{cm}^2$ is achieved at a cell voltage of 0.7V at 800°C. The electrochemical performance curves for the coupon cells are shown in Fig. 6. The electrochemical performance of single cell with lowest possible YSZ film thickness (10 μm), as achieved under the present investigation, has also been tested. As shown in Fig. 7, a dramatic improvement of cell performance is observed. Current density as high as $\sim 1.7 \text{ A}/\text{cm}^2$ with a corresponding high power density of $\sim 1.2 \text{ W}/\text{cm}^2$ are obtained at 800°C and 0.7 V. Although similar high performance of SOFC is reported in the literature, [7, 15, 16, 23, 24] in all those cases the fabricated cell requires an active layer on the anode side. However, under the conditions of the present investigation, the anode-cermet has such a microstructure that, even without any active layer, fuel oxidation occurs favorably at the anode-electrolyte interface so that the resistive and polarization losses are low on the anode side of the cell. Following the method of Kim et al.¹⁴, the current density dependant area specific cell resistance (ASR) ($\Omega\text{-cm}^2$) is calculated from the linear portion of the I-V curves at all the operating temperatures in case of coupon cells. Table 2 shows the ASR values obtained for cells with 20 μm and 10 μm thin YSZ films respectively. The obtained cell ASR value which is essentially ohmic in nature,

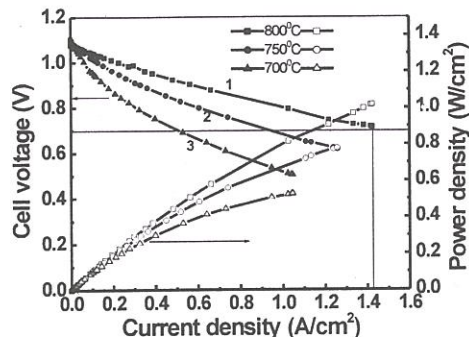


Fig. 6 Cell voltage and power density as a function of current density for an anode-supported single coupon cell ($\sim 16 \text{ mm}$ dia.) with YSZ electrolyte thickness of 20 μm measured at 800, 750 and 700°C

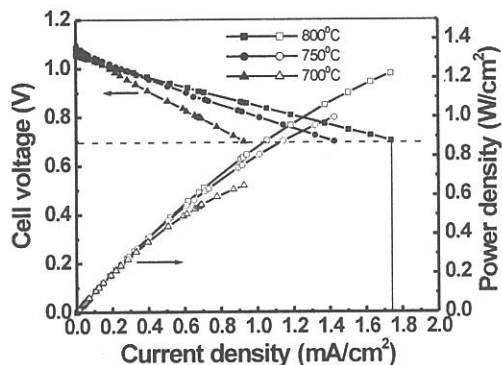


Fig. 7 Cell voltage and power density as a function of current density for an anode-supported single coupon cell ($\sim 16 \text{ mm}$ dia.) with YSZ electrolyte thickness of 10 μm measured at 800, 750 and 700°C

include resistance of the electrolyte, electrodes, interfaces between the electrodes and the YSZ electrolyte. It is well known that the electrolyte and the cathode resistances increase while the anode resistance decreases as the temperature decreases. Thus, the overall ASR of the cell increases as the temperature decreases. While varying thickness of the electrolyte from 20 μm to 10 μm all the other processing parameters are kept unchanged. In spite

TABLE 2. Area specific resistance, calculated from the linear portion of the I-V characteristics at different temperatures for anode-supported SOFC single cells with varied YSZ thickness

Operating temperature (°C)	Area specific resistance ($\Omega\text{-cm}^2$)	
	Cell with 20 μm YSZ	Cell with 10 μm YSZ
800	0.262	0.205
750	0.418	0.274
700	0.511	0.420

of that a change of ASR value with temperature decrease is not comparable. In fact, with 20 μm YSZ the cell shows ASR value of $\sim 0.262 \Omega\text{-cm}^2$ and with 10 μm YSZ the cell shows the ASR value of $\sim 0.205 \Omega\text{-cm}^2$ at 800°C. While studying the effect of YSZ electrolyte thickness on cell performance Zhao and Virkar [25] also concluded that cell performance does not depend much on the electrolyte ohmic resistance in low thickness level and morphology and /or microstructures of different layers may vary significantly even in identical fabrication steps to influence the cell performance. Figure 8 shows single-cell performance with current-voltage (I-V) and current-power (I-P) characteristics having LSCF based cathodes with CGO based interlayers. In these cells, CGO interlayer is sintered at $\sim 1300^\circ\text{C}$. It can be seen that while cell with such nanocrystalline LSCF based MIEC cathode produces a current density as high as $\sim 2.4 \text{ A/cm}^2$ with a power density of $\sim 1.7 \text{ W/cm}^2$ when measured at 800°C at a cell operating voltage of 0.7V. As the operating temperature decreases, the cell characteristics changes in similar fashion in all the cells. The enhancement of the electrochemical performance of the single cells using such MIEC cathodes is believed to be primarily due to higher electrocatalytic activity of the cathodes leading to a reasonably high electrochemical oxygen reduction reaction (ORR) of the oxidant fed at the cathode.

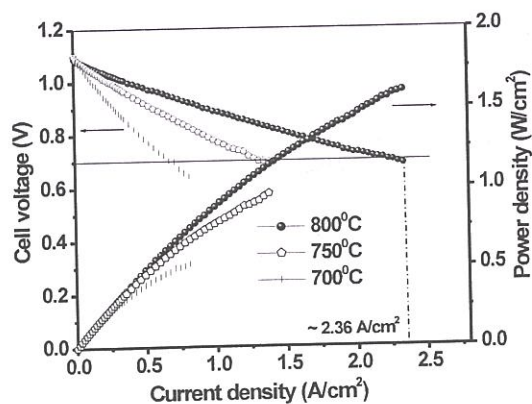


Fig. 8 Cell voltage and power density as a function of current density for an anode-supported single coupon cell ($\sim 16 \text{ mm}$ dia.) with YSZ electrolyte thickness of 10 μm and CGO based Interlayer and LSCF based MIEC cathode measured at 800, 750 and 700°C

Conclusions

Using simple and inexpensive techniques YSZ-based anode-supported single cell is fabricated after optimizing various process parameters including screen printing of cathode and cathode active layer. These processing techniques produce dense gas-tight YSZ thin film well bonded to the support cermet anode. The microstructure of the single cells is found to be very much helpful to obtain high SOFC performance. Under the conditions of the present investigation, high current density has been obtained even without using any active layer on the anode side of the fabricated cell. Thus, a current density as high as $\sim 1.7 \text{ A/cm}^2$ with power density of $\sim 1.2 \text{ W/cm}^2$ at 800°C and 0.7V, is successfully demonstrated using the fabricated cell with thinnest possible YSZ thickness ($\sim 10 \mu\text{m}$) as obtained. The same anode-supported single cell when tested with nanocrystalline LSCF based cathodes with CGO based interlayers are found to perform much better and a current density as high as $\sim 2.4 \text{ A/cm}^2$ with power density of $\sim 1.7 \text{ W/cm}^2$ is achieved at 800°C and at 0.7 V. It is also observed that the performance of the cell is size independent. The primary reason for such high performance is believed to be because

of the higher ORR of LSCF based MIEC cathodes at the cell operating temperature than LSM based conventional cathode. The area specific resistance (ASR) obtained from the linear portion of current-voltage trace show relatively low resistive loss at different operating temperatures. As the electrolyte thickness decreases the ASR value decreases showing the reduced effect of electrolyte resistance contribution.

Acknowledgments

The authors acknowledge CSIR-NMITLI Project for financial support and Director, CGCRI for his kind permission to publish this work.

References

1. S.C. Singhal and K. Kendall, "High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications" Ed. Elsevier, UK (2003).
2. L. Blum, W.A. Meulenberg, H. Nabelek, R. Steinberger-Wilckens; "Worldwide SOFC technology overview and benchmark", *Int J Appl Ceram Tech*, 2 (2005) 482-92.
3. R.N. Basu; Recent Trends in "Fuel Cell Science and Technology: Materials for Solid Oxide Fuel Cell", Ed. S. Basu p. 284, Anamaya Publisher, New Delhi and Springer, New York (2006).
4. T. Ishihara; "Handbook of Fuel Cells, Fuel Cell Technology and Applications: Part 2", Ed. W Vielstich, A. Lamm and H.A. Gasteiger, (2003) p. 1109, John Wiley & Sons Ltd., England.
5. B.C.H. Steele; "Materials for IT-SOFC stacks: 35 years R&D: the inevitability of gradualness" *Solid State Ionics* 3-20 (2000)134.
6. A. Hagen, R. Bardfod, P.V. Hendriksen, Y.L. Liu, S. Ramousse; "Degradation of anode supported SOFCs as a function of temperature and current load" *J. Electrochem Soc* 153 - 6 (2006) A1165-71.
7. V.A.C. Haanappel, J. Mertens, D. Rutenbeck, C. Tropartz, W. Herzhof, D. Sebold, F. Tietz; "Optimization of processing and microstructural parameters of LSM cathodes to improve the electrochemical performance of anode-supported SOFCs", *J. Power Sources*141 (2005), 216-26.
8. H.Y. Jung, W-S. Kim, S-H. Choi, H-C Kim, H-W. Lee, J.H. Lee; "Effect of cathode current-collecting layer on unit-cell performance of anode-supported solid oxide fuel cells", *J Power Sources*; 155, (2006), 145-51.
9. R. Muccillo, E.N.S. Muccillo, F.C. Fonseca, Y.V. Franc, T.C. Porfirio, D.Z. Florio de, M.A.C. Berton, C.M. Garcia;. *J. Power Sources*; 156 (2006) 455-60.
10. L. Besra, C. Compson, M. Liu; "Electrophoretic deposition of YSZ particles on non-conducting porous NiO-YSZ substrates for solid oxide fuel cell applications" *J Am Ceram Soc* 89 (2006) 3003-09.
11. R.N. Basu, G. Blass, H.P. Buchkremer, D. Stöver, F. Tietz, E. Wessel, I.C. Vinke; "Simplified processing of anode-supported thin film planar solid oxide fuel cells" *J Eur Ceram Soc*25 (2005) 463-71.
12. J.W. Fergus; "Electrolytes for solid oxide fuel cell" *J Power Sources* 162 (2006) 30-40
13. Y.K. Lee, J.Y. Kim, Y.K. Lee, I. Kim, H.S. Moon, J.W. Park, C.P. Jacobson, S.J. Visco; "Conditioning effects on La_{1-x}Sr_xMnO₃-yttria stabilized zirconia electrodes for thin-film solid oxide fuel cells" *J Power Sources* 115 (2003) 219-28.
14. J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, S.C. Singhal; "Polarization effects in intermediate temperature, anode-supported solid oxide fuel cells" *J Electrochem. Soc* 146-1, (1999) 69-78.
15. K.J. Yoon, P. Zink, S. Gopalan, Uday B. Pal; "Polarization measurements on single-step co-fired solid oxide fuel cells" *J Power Sources* 172-1 (2007) 39-49.
16. F. Zhao, A.V. Virkar; "Dependence of polarization in anode-supported solid oxide fuel cells on various cell parameters", *J Power Sources* 141 (2005) 79-95.

17. C. Wang, W.L. Worrell, S. Park, J.M. Vohs, R.J. Gorte; "Fabrication and performance of thin-film YSZ solid oxide fuel cells" *J Electrochem Soc* 148-8 (2001) A864-68.
18. R. Barfod, M. Mogensen, T. Klemenso, A. Hagen, Y.L. Liu, P.V. Hendriksen; "Detailed characterization of anode-supported SOFCs by impedance spectroscopy" *J Electrochem. Soc* 154-4 (2007) B371-78.
19. R.N. Basu, A. Das Sharma, A. Dutta, J. Mukhopadhyay, H.S. Maiti; "Development of anode-supported planar SOFC using inexpensive and simple processing technique" *Electrochemical Society Transactions* 7 (2007) 227-34.
20. R.N. Basu, A. Das Sharma, A. Dutta, J. Mukhopadhyay; "Processing of High Performance Anode-supported Planar Solid Oxide Fuel Cell", *Int. J. Hydrogen Energy*, 33 (2008) 5748-5754
21. Atanu Dutta, Jayanta Mukhopadhyay, R.N. Basu; "Combustion Synthesis and Characterization of LSCF based Materials as Cathode of Intermediate Temperature Fuel Cell", 29 *J. European Ceram. Soc.*, (2009) 2003-2011
22. D. Montinaro, V.M. Sglavo, M. Bertoldi, T. Zandonella, A. Aricò, M.Lo Faro, V. Antonucci; "Tape casting fabrication and co-sintering of solid oxide "half-cells" with a cathode-electrolyte porous interface. *Solid State Ionics*" 177 (2006) 2093-7.
23. Y. Jiang, A.V. Virkar; "Fuel composition and diluent effect on gas transport and performance of anode-supported SOFCs" *J Electrochem Soc* 150-7 (2003) A942-A951.
24. H. Moon, S.D. Kim, S.H. Hyun, H.S. Kim; "Development of IT-SOFC unit cells with anode-supported thin electrolytes via tape casting and co-firing" *Int J Hydrogen Energy* 33 (2008)1758-68.
25. F. Zhao, A.V. Virkar; "Dependence of polarization in anode-supported solid oxide fuel cells on various cell parameters" *J Power Sources* 141 (2005) 79-95.

Fabrication of Cathode Supported Solid Oxide Fuel Cell



Dr. Deep Prakash obtained his B.E. (Hons.) in Metallurgical Engineering from National Institute of Technology (then REC), Durgapur, India and joined BARC Training School, Mumbai in 1991 as 35th Batch Trainee Scientific Officer. He was awarded Ph.D. from Indian Institute of Technology, Bombay. He worked as post-doctoral fellow from November 2005 to October 2006 at Institut des Materiaux Jean Rouxel, Nantes, France and as Research Fellow from October 2006 to October 2007 at University of St. Andrews, Scotland, UK. Currently he is Scientific Officer in the Energy Conversion Materials Section, BARC. His areas of interest are chemical synthesis of functional ceramics, shaping and fabrication of components, electrical characterization of SOFC materials and devices, thermoelectric materials and devices. He is life member of Powder Metallurgy of India and Indian Institute of Metals.

Shri P.K. Sinha graduated in Chemical Engineering from Ranchi University and joined Beryllium Pilot Plant, BARC in 1985. He has worked in development of beryllium technology in India and made outstanding contributions in powder metallurgy of beryllium. He is currently heading Energy Conversion Material Section, Materials Group, BARC. His area of interest involves the development of composite materials and shape forming through powder metallurgy route. He is a life Member of Powder Metallurgy Association of India.



Introduction

It may not be an overstatement to say that the SOFC is regarded as one of the most promising renewable energy technologies for futuristic energy generation. This is due to the fact the technology is very promising not only being environmentally benign, but also possesses immense potential for utilization of various fuels (fuel flexibility); ability to adapt to distributive power generations, thus cutting down overall transmission losses; and posing innovative design approaches to realize a spectrum of power packs from few watts to megawatts level [1-4]. All these factors have pushed research and developmental efforts for commercially viable integrated SOFC systems for stationary as well as automotive applications [5-6].

Since the advent of solid oxide fuel cells technology, various designs and configurations have been invented and are under development. Though the essential feature of all these designs remains a gas-tight electrolyte layer sandwiched between

porous layers of cathode (air electrode) and anode (fuel electrode), depending upon the shape, the designs are termed as tubular, planar, spiral, honeycomb etc [7-10]. Further, the design configuration is also classified based on the major component, which generally imparts strength and structural support to all other components, and therefore termed as electrolyte, anode or cathode supported. Since it is beyond the scope of the present paper to discuss design features of various configurations, the text is restricted to cathode supported SOFC cells.

This paper presents an overall view of various designs and fabrication methods for manufacture of cathode supported SOFC, being pursued at various laboratories as well as commercial enterprises.

Salient Features of Cathode supported SOFC

As the name suggests, cathode supported configuration of SOFC consists of thicker cathode

Dr. Deep Prakash and Shri P.K. Sinha, Energy Conversion Materials Section, BARC, Vashi Complex, Navi Mumbai 400705;
E-mail: deep_prakash@rediffmail.com

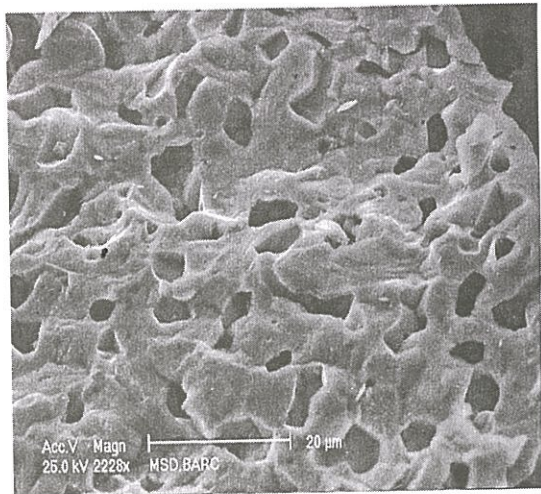


Fig. 1 Microstructure of cathode in a cathode-supported tubular SOFC cell

(air electrode) which acts as main structural component. The cathode thickness is generally of the order of 1 mm. The dense, gas-impermeable electrolyte layer is then applied on the cathode, followed by porous anode layer. Besides the cathode being thicker in dimensions, the cathode supported SOFC has some salient features which are described below.

Redox Stability

One of the major advantages of cathode supported design is that the anode layer can be much thinner, typically from 50-100 μm . Such thin anodes are easier to give rise to redox stability in the cell [11]. In order to enhance service life of the SOFC, or for commercial usage, a strong redox stability is a must. It may be noted that reduction of NiO in the SOFC anode gives rise to Ni, which is responsible for anodic reaction. Anode re-oxidation, which occurs above $\sim 500^\circ\text{C}$ is associated with significant volume increase. Repeated cycles of oxidation-reduction build up cracks in the anode resulting in failure of the components. A thin anode layer in this regard is much preferred due to its better stability. The microstructure of anode is also required to be finer with smaller pores than that of anode supported cells.

Cathode Microstructure

On the other hand, the thicker cathode requires enough porosity or permeability for oxygen to reach to the electrolyte – cathode interface, and therefore, cathode should have porous structure with large pores. Various types of pore-formers or a combination of them have been in use for designing cathodes with higher performance [12-13]. For a higher cathode performance, large area of triple-phase boundaries (TPB) is required. This is generally achieved by mixing fine particle of YSZ with LSM in intimate mixtures. The microstructure significantly effects cathodic performance, as evidenced by using electrical impedance spectroscopy. In order to combine benefits of large TPB which also has finer microstructure and thus small size pores, and larger pores for facilitating oxygen / air to the interface, use of graded porosity is prevalent. Fig. 1 shows a typical microstructure in a cathode supported cell.

Cathode Electrolyte Interaction

Interaction of cathode with electrolyte during manufacturing as well as in-service, is one of the major performance limiting concerns, particularly for cells with YSZ as electrolyte and LSM as cathode. It has been well proven that reaction of YSZ with LSM at temperatures beyond 1350°C give rise to insulating phases such as $\text{La}_2\text{Zr}_2\text{O}_7$ [14-15]. Occurrence of this phase reduces the conductivity of cathode which in turn gives rise to large parasitic resistance and finally resulting in loss of power output from the device. Maneuvering chemical composition of LSM, viz. incorporation of 'A'-site deficiency in the composition of $(\text{La,Sr})\text{MnO}_3$ has been reported to avoid formation of zirconate phases [16]. Incorporation of interlayer such as gadolinia doped ceria (GDC) between cathode and electrolyte has been actively pursued to avoid formation of undesirable phases [17]. Further, research is also being carried out on materials such as cobaltites, nickelates and ferrates to replace LSM and thus overcome the problem of LSM-YSZ interaction [18-19].

Cathode Supported Designs

The cathode supported designs of SOFC can be classified into following broad categories:

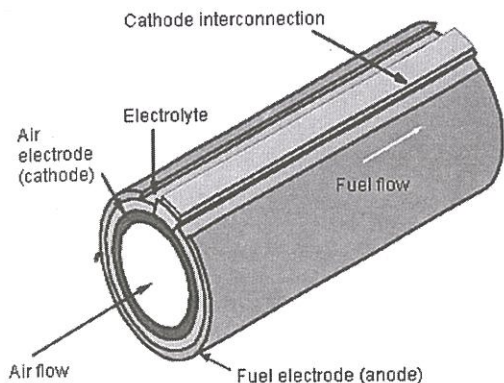


Fig. 2 Schematic of cathode supported tubular SOFC cell of Siemens

- (i) Tubular
- (ii) Micro-tubular
- (iii) Honeycomb
- (iv) Delta tubes

The tubular design is the most popular for cathode supported cells. This concept was first used by Westinghouse (later Siemens-Westinghouse). Fig. 2 shows a typical cathode supported cell. The cathode tubes are manufactured by extrusion process. In order to make tubes of LSM by extrusion, the powder is mixed with suitable binder and additives, along with pore formers and extruded into tubes of required dimensions, followed by sintering. During sintering, the binder and pore formers evaporate giving rise to porous tubes. The porous tubes are then applied with dense strip of interconnect (doped lanthanum chromite) using plasma spray process. The interconnect is essential for series connection of tubes. Subsequently, dense coating of electrolyte is applied on the LSM part of the tubes, masking the interconnect. Siemens has developed electro-chemical vapor deposition (ECVD) process for electrolyte coating. The process yields thin (~5-10 μm) layer of impervious YSZ electrolyte. The outside part of tubes is finally coated with NiO-YSZ composite which results in Ni-YSZ anode during in-situ reduction. Current design of Siemens has tube nominal diameter 2.2 cm and length 59 cm. One single tube gives 210 W dc power, and a bundle of 24 cells is 5 kW. Fig. 3 shows a stack of tubular cells as manufactured by Siemens [20].

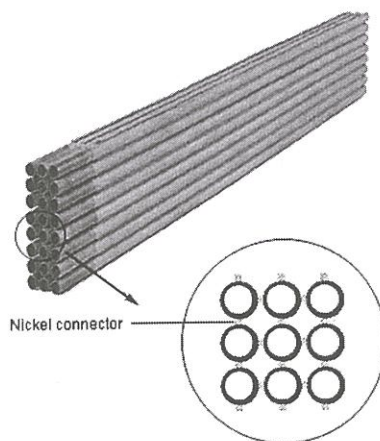


Fig. 3 Stack of tubular SOFC cell of Siemens [20]

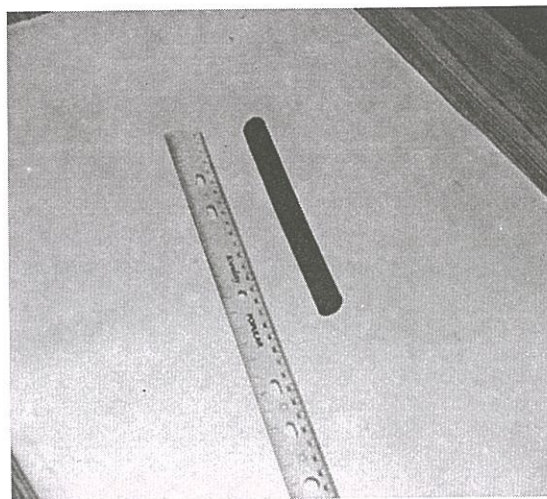


Fig. 4 One-end closed tube of LSM made by CIP

Another method of preparing one-end closed tubes is cold iso-static pressing (CIP) technique. In this technique, the powder is filled in flexible rubber moulds with metallic mandrels and iso-statically pressed. The green tubes are sintered to obtain sintered porous tubes. One-end closed tubes made by CIP are shown in Fig. 4.

Various techniques are being developed for obtaining dense, impervious electrolyte coating on porous LSM tubes, besides the ECVD process. These include dip coating, electrophoretic deposition and spray-deposition [21-22].

pre-commercial trials are carried out in several laboratories all over the world. Research is in progress to enhance power output by maneuvering microstructures as well as to find better cathode materials.

Acknowledgements

Authors are thankful to Dr. A.K. Suri, Director, Materials Group, BARC and Dr. S. Banerjee for valuable guidance, constant encouragement and support. We are also thankful to Dr. S. Ramanathan, MPD, Shri P. Raghunathan, HWD, Dr. John T. John, MSD and Drs. T. Mahata, A. Sinha, S.R. Nair, P.K. Patro, and Shri R.K. Lenka, ECMS for many thought provoking discussions.

References

1. M.F. Akorede, H. Hizam and E. Pouresmaeil, Distributed energy resources and benefits to the environment, *Renewable and Sustainable Energy Reviews*, 14, 724-734, (2010)
2. B. Rohland, J. Nitsch and H. Wendt, Hydrogen and fuel cells – the clean energy system, *J. Power Sources*, 37, 271-277, (1992)
3. J.T.S. Irvine, The Bourner lecture – Power sources and the new energy economy, *J. Power Sources*, 136, 203-207, (2004)
4. N.Q. Minh, Ceramic fuel cells, *J. Am. Ceram. Soc.*, 76, 563-588, (1993)
5. M.C. Williams, J.P. Strakey, S. C. Singhal, U.S. distributed generation fuel cell program, *J. Power Sources*, 131, 79-85, (2004)
6. S.C. Singhal, Solid Oxide Fuel Cells for stationary, mobile and military applications, *Solid State Ionics*, 152-153, 405-410, (2002)
7. R.J. Kee, A.M. Colclasure and H. Zhu, Fuel Cells – Solid Oxide Fuel Cells: Cells and Stacks, *Encyclopedia of Electrochemical power sources*, 51-62, (2009)
8. V. Lawlor, S. Griesser, G. Buchinger, A.G. Olabi, S. Cordiner, D. Meissner, Review of the micro-tubular solid oxide fuel cell Part I. Stack design issues and research activities, *J. Power Sources*, 193, 387-399, (2009)
9. R. P. O'Hayre, S.-W. Cha, W. Colella and F.B. Prinz, *Fuel Cell Fundamentals*, John Wiley & Sons, New York, (2006)
10. S.C. Singhal and K. Kendall, *High Temperature Solid Oxide Fuel Cells – Fundamentals, Design and applications*, Elsevier, Oxford, UK, (2003)
11. S. Linderoth and A. Smith, in *Worldwide SOFC overview from a scandinavian and a European perspective*, in *Advances in Solid Oxide Fuel Cells III*, N.P. Bansal, J. Salem, D. Zhu (Eds.), American Ceramic Society, 3-16, (2008)
12. Deep Prakash, R K Lenka, A K Sahu, P K Patro, P K Sinha, and A K Suri, Effect of cathode functional layer on the electrical performance of tubular solid oxide fuel cell, *Proc. Conf. ASME 8th International Conference on Fuel Cell Science, Engineering and Technology*, Brooklyn, New York, USA, June 14-16, (2010)
13. Deep Prakash, R.K. Lenka and P.K. Sinha, Evolution of microstructure in SOFC electrodes, *Proc. Conf. Microtexture and Microstructure*, Microstructure-2009, November 27-28, Mumbai, India, (2009)
14. H. Yoltolrawa, N. Sakai, T. Kawada and M. Dokiya, *J. Electrochem. Soc.*, 138(9), 2719-2727, (1991)
15. T. Kenjo and M. Nishiyama, LaMnO₃ air cathodes containing ZrO₂ electrolyte for high temperature solid oxide fuel cells, *Solid State Ionics*, 57, 295-302, (1992)
16. M. Dokiya, N. Sakai, T. Kawada, H. Yokokawa, T. Iwata and M. Mori, in *Solid Oxide Fuel Cells I*, ed. S. C. Singhal, The Electrochemical Society Proceedings, Pennington, NJ, PV 89-11, 325-336, (1989)
17. S.P. Simmer, J.W. Templeton and J.W. Stevenson, Electrochemical characterization of modified LSM cathodes, in *Advances in Solid Oxide Fuel Cells III*, N.P. Bansal, J. Salem, D. Zhu (Eds.), American Ceramic Society, 3-16, (2008)
18. R.K. Lenka, P.K. Patro, T. Mahata, D. Prakash, A.K. Tyagi and P.K. Sinha, *Synthesis and*

- characterization of $GdCoO_3$ as a cathode material for solid oxide fuel cell, International Conference on Electroceramics (ICE-2009), New Delhi, (2009)
19. C. Amow and S.J. Skinner, J. Solid State Electrochem., 10, 538-546, (2006)
 20. <http://www.energy.siemens.com/us/pool/hq/power-generation/fuel-cells/principle-behind/modular-bundle-large.jpg>
 21. A.K. Sahu, A.Ghosh, A.K. Suri, Characterization of porous lanthanum strontium manganite and development of yttria stabilized zirconia coating, Ceramics International, 35, 2493-97, (2009)
 22. P.K. Patro, Deep Prakash, P.K. Sinha, B.P. Sharma, 8-YSZ electrolyte coating on SOFC cathode substrate using spray deposition technique, Proc. National Conference on Recent Advances in Surface Engineering (RASE-2009), 26-27 Feb, Bangalore, India, (2009)
 23. T. Yamaguchi, A.M. El-Toni, T.Suzuki, Y. Fujishiro, M. Awano and S. Shimizu, Development of fabrication technology for honeycomb-type SOFC with integrated multi micro-cells, in Advances in Solid Oxide Fuel Cells III, N.P. Bansal, J. Salem, D. Zhu (Eds.), American Ceramic Society, 41-47, (2008)
 24. [http://www.netl.doe.gov/publications/proceedings/04/seca-wrkshp/SECA Program Overview - Surdoval.pdf](http://www.netl.doe.gov/publications/proceedings/04/seca-wrkshp/SECA%20Program%20Overview%20-%20Surdoval.pdf)
 25. http://www.siemens.com/innovation/pool/en/publikationen/publications_pof/pof_spring_2007/technology_for_the_environment/fuel_cell_power_plants/pof107art42_bild1_1446125.jpg

Alternate Possibilities for Electrodes and Membranes for Direct Methanol Fuel Cells



Dr. B. Viswanathan completed his graduation (1961) and post-graduation (1964) from Madras University and did his Ph.D. (1969) from IIT, Madras. He has been Professor with the Chemistry Department of IIT, Madras and is currently Professor at the National Centre for Catalysis at IIT, Madras. He has been the recipient of several Awards and honors, such as, Fellowship of Max. Planck Society (1977, 1983) Alexander Von Humboldt Foundation Fellowship (1971), MRSI Medal (1998), Tamilnadu best Scientist Award (1994) etc. His research interests are in the fields of fuel cells, hydride batteries, electrochemistry, hydrogen energy, molecular catalysis, Materials Science, theoretical chemistry etc. He has more than 350 journal publications, more than 100 symposium presentations, over 30 books and an equal number of patents to his credit.

Abstract

Direct methanol fuel cells (DMFC) are one of the viable alternatives to the hydrogen oxygen fuel cells which can be easily adapted to the existing infrastructure of distribution and storage. Unlike the hydrogen oxygen fuel cells in its various forms, DMFC has not received considerable attention. However, like the hydrogen oxygen fuel cells, the commercialization of DMFC has also met with considerable barriers and two of the important aspects of DMFC are the electrodes for both fuel oxidation and also for oxygen reduction and the membrane. In the case of the membrane, the available Nafion membranes allow the cross over of methanol from anode to cathode thus not only inhibiting the cathodic reduction of oxygen but also generate mixed potential which is affecting the efficiency of the resulting Fuel cell. The purpose of this presentation is to examine the alternate possibilities for these two applications in DMFC. However the alternatives considered are only meant to give one the direction for future research and they are not the end of the search itself. The alternatives proposed for the anodes are directed to functionalization of the support so as to sustain appropriate nanosize of the Pt clusters. The cathode selection is based on non noble metal cluster systems which possess similar properties like that of Pt. The

search for alternate membranes based on hybrid systems has been pursued vigorously. However the hybrid membranes may not compete with Nafion in the values of conductivity but can exhibit better 'selectivity', a compound property reflecting proton conductivity and methanol cross over.

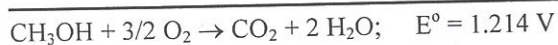
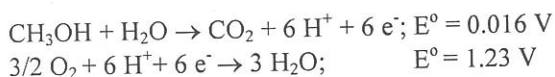
Introduction

Fuel cells have been conceived to be possibly clean, efficient and silent energy conversion technology, which possibly can meet the various demands for energy even though not fully [1]. The anxiety and expectations with respect to their commercial introduction in transport sector and stationary applications have to be put off (from 2003 and 2001 respectively) since a viable and commonly adoptable technology has not yet evolved for this energy conversion device [2]. However, there are indications that this technology may become viable in the near future though the date of adaptation has been put off a number of times in the past and may possibly happen in the future too. There are a number of barriers for commercial adaptation of fuel cells. In this presentation, it is the intention to bring out two important aspects of Direct Methanol Fuel Cells (DMFC) that may be primarily contributing to the barrier for early commercialization.

Dr. B. Viswanathan, National Centre for Catalysis Research, Indian Institute of Technology, Madras, Chennai 600 036;
Email: bvnathan@iitm.ac.in

Before one considers the two important aspects (considered in this presentation) namely development of cost effective, efficient and catalytically most active electrodes and viable membranes, it is necessary that some details of DMFC is considered. In Fig 1 a general schematic representation of a DMFC is shown.

The electrochemical reactions taking place in DMFC can be written [3] as:



It is seen that DMFC provides similar voltage like that of hydrogen oxygen fuel cell and also has the flexibility that the existing infra structure for distribution and consumption can be easily adapted for the change over to methanol from the current liquid fuels [1]. Technically speaking DMFC is similar to Polymer Electrolyte Membrane Fuel Cells (PEMFC), though instead of hydrogen, one employs methanol and hence produces carbon dioxide. It is possible to develop DMFC for some portable applications in the range of 1-100W. [3]

Seats of Electrochemical Reactions in Fuel Cells

In any electrochemical cells, the electron transfer reactions occur at the electrode/ electrolyte interface. In the fuel cells the oxidation of the fuel occurs at the anode and the reduction of the oxidant (molecular oxygen) takes place at the cathode. It is generally perceived that the oxidation of the fuel is important and hence more attention is given for the development of suitable catalyst containing electrodes for the oxidation of methanol. The design and development of suitable anodes for methanol fuel cell had been one of the prime tasks of researchers. They have brought into application the concepts available in the catalytic oxidation of methanol for designing suitable anodes for DMFC. However there are various other limitations for the development of viable DMFC. In Table 1 these have been listed for convenience [4].

Any fuel cell electrode development has to start with the development of suitable support for effectively dispersing the noble metal and also to functionalize them for subsequent interaction and

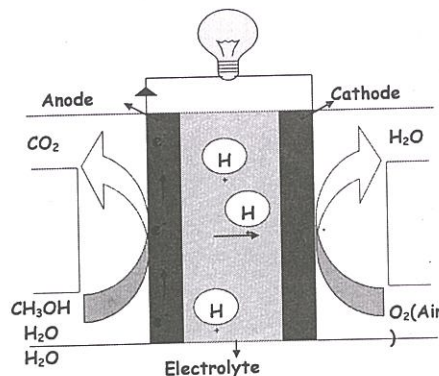


Fig. 1 A schematic diagram of a Direct Methanol Fuel Cell. (Reproduced from B. Viswanathan, M. Helen and S. Srinivasa Murthy, 'Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel' (2005) 61.)

TABLE 1. Limitations in the development of a viable DMFC

- Sluggish methanol oxidation (anode) kinetics:
 - 6 electron transfer
 - formation of CO as an intermediate in the multi-step methanol oxidation mechanism – poisoning of catalyst
- Large methanol crossover through the membrane:
 - Linked to the electro osmotic drag
 - decreases fuel efficiency
 - may poison the cathode
 - creates mass transport problems at cathode layer by wetting hydrophobic gas channels, leading to increased flooding
- Cost of electro-catalysts

activation of the fuel molecule. The conventional support in fuel cells is carbon. The desirable characteristics of carbon supports are summarized in Table 2.

TABLE 2. The Role and characteristics of Carbon support for fuel cell applications

- High surface area (the desirable ranges are 1000s m²/g)
- High dispersion of noble metal particles to reduce the extent of noble metal loadings (in DMFC normally 1.5mg/cm² are employed)

- Avoid the agglomeration of the metal particles during operation, functionalize the noble metals so that they provide effective sites for activation of fuel molecules
- Good stability of electro-catalysts for long term use in fuel cells
- Improved activity of electro-catalysts through the metal support interaction
- Lower the resistance of mass transport – avoid any physical control of the electrochemical reaction
- Always superior to the respective unsupported systems
- Shorten the time of DMFC commercialization
- Electrochemical properties – carbon materials have a wide electrochemical potential window enabling a variety of substrates or fuels to be employed.
- Carbon supports have desirable chemical properties especially considerable corrosion resistance
- Appropriate electrical properties for use as electrodes - Good conductivity
- Mechanical properties - Dimensional & mechanical stability and Light weight & adequate strength

Among the various types of carbon materials available today carbon nanostructures have received considerable attention as electrochemical electrode support due to the desirable characteristics given in Table 3 [5].

TABLE 3. Characteristics of Carbon nanotubes as an electrode support in fuel cells

- Mesoporosity (2-50 nm)
- Improved mass transfer
- Better dispersion
- Surface bound groups
- High accessible surface area
- High purity → avoids self-poisoning
- Good electronic conductivity

Alternate Anodes for DMFC

Having decided on the nature of the carbon support for fuel cell applications a synthetic strategy has been evolved for the development of anodes for DMFC which consisted of preparing the functionalized carbon nanotubes and loading the noble and other active species on them. Four

different kinds of nitrogen containing carbon precursors are chosen to make nitrogen containing carbon nanotubes [6]. The details of the synthesis strategy adapted are given elsewhere [4, 7, and 8]. The results obtained using in the oxidation of methanol on these materials as supports for Pt are given in Table 4.

It is seen that the Pt loaded on nitrogen containing carbon nanotubes shows higher activity for methanol oxidation as compared to the catalyst where Pt is loaded on commercial carbons without nitrogen and also even in nitrogen containing carbons, there is an optimum amount of nitrogen where the dispersion of Pt (in terms of size and activity) is best suited for methanol oxidation.

TABLE 4. Electro-catalytic activity of the Pt/N-CNT electrodes in comparison with commercial catalysts for methanol oxidation [7,8].

Electrode	Nitrogen content	Activity I_p (mA/cm ²)
Pt	-	0.076
GC/ETek 20% Pt/C Naf	-	1.3
GC/CNT-Pt PPP-Naf	0.0	12.4
GC/CNT-Pt PVP –Naf	6.63	16.2
GC/CNT-Pt PPY –Naf	10.5	21.4
GC/CNT-Pt PVI-Naf	16.7	18.6

PPP - poly (paraphenylene); PVP- Poly (vinylpyrrolidone); PPY – Polypyrrole; PVI - Poly (vinylimidazole).

When normally alloy system is employed as anodes like Pt-Ru, the main focus appears to exploit the bifunctional mechanism so that the formed CO could be removed and oxidized at the alternate metallic sites. However, it is also possible to use unconventional supports like metal oxide nanotubes like TiO₂ or WO₃ which will facilitate the spillover route (both hydrogen and oxygen) and thus can be expected to exhibit enhanced anodic oxidation activity. In order to test this hypothesis, titanium oxide nanotubes were preformed in the pores of alumina membrane and then subsequently loaded with Pt using H₂PtCl₆. Similar strategies were

adapted for the preparation of other oxide nanotubes. The results obtained on these types of systems are given in Tables 5 and 6 [4].

TABLE 5. The activity of Pt/TiO₂ nanotube for electrochemical oxidation of methanol

Electro-catalyst	Anodic scan peak potential (V) vs. Ag/AgCl	Anodic peak current density (mA cm ⁻²)
Bulk Pt	—	0.16
20 % Pt/C	0.762	1.3
Pt/TiO ₂ nanotube	0.680	13.2

TABLE 6. Electro-catalytic activity of Pt/WO₃ nanorods and Pt/C for methanol Oxidation

Electro-catalyst	Pt loading µg/cm ²	Specific activity mA/cm ²
Pt/C	20	29.5
Pt/WO ₃ nanorods	20	62.0

The promotion effect of TiO₂ nanotubes in the methanol oxidation can be rationalized on the basis of Strong Metal Support Interaction (SMSI) as well as the OH adsorption on Ti ion site facilitating the oxidation of CO on Pt sites which are otherwise poisons the metallic sites and thus renders these metallic sites unsuitable for methanol oxidation. A pictorial model of these postulates is given in Fig.2.

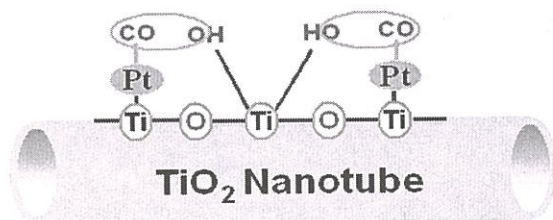
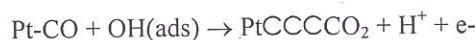


Fig. 2 A possible mechanism for the removal of CO poisoning intermediates during methanol oxidation over TiO₂ nanotube supported Pt catalysts.

The step envisaged is:



OH (ads) forms on TiO₂ surface and oxidizes Pt-CO by a combination of metal support interaction (SMSI) and OH adsorption on TiO₂.

It is possible that a variety of other exotic anode electro-catalyst may be developed with increased activity and also considerably reducing the noble metal loading (say in sub-milligram scale) without sacrificing the activity and long term stability of the electrodes.

Recent Developments in Cathode for DMFC

As pointed out, it is the oxygen reduction reaction that is sluggish and requires development of most efficient catalysts. Designing catalysts that can operate efficiently and last a long time is a barrier to making fuel cell technology commercially viable. Though platinum is the natural choice its cost and also its life time are the two limiting factors. In spite of all the developments, nearly upto 40% of the fuel cell's efficiency is lost in the cathode. Hence, according to Shouheng Sun (Professor at Brown University) the cathode reaction [9] "is a crucial step in making fuel cells a more competitive technology with respect to internal combustion engines and batteries". The group at Brown University has designed an exotic catalyst system based on the core shell model where in the core is generated from iron pentacarbonyl and shell of platinum was obtained by the decomposition of platinum acetylacetonate, thus effectively reducing the extent of use of platinum to the extent of 30%. These authors have claimed that the catalyst system that they have developed is 12 times more active and is stable over 10,000 cycles which are remarkable considering the current status of the possible oxygen reduction electrodes available today. In fact as early as 2000, Jens Rostrup-Nielsen has pointed out that the designing of effective catalyst for the oxygen reduction reaction is a dream for the researchers for over past five decades. Numerous reports have dealt with the preparation and functioning of noble and non-noble metal based catalysts (especially the control of the size of the metal particles) for oxygen reduction reaction. Among them Pt-Ir showed the highest voltage of 1.75 V (at 80°C / 1 mg/cm² loading) [10].

Materials with physical and chemical properties approximating to those of noble metals and whose electronic configuration is related to the noble metals are being explored. So far the general criteria for choosing the materials for ORR include high electronic conductivity, thermal stability and also the chemical stability in acidic environment. The suitability of the noble metal based catalysts has been evaluated by several research groups. All these studies based on noble metal catalysts could only improve and enhance the output voltage by only 0.2 V. However, the aimed improvements in the fuel cell output is overshadowed by the attended increase in cost as a result of the complex methods of preparation and also the instability of the catalyst to the unfavourable environment of the reaction. Non noble metal based materials are abundant in nature and also are cost effective than the noble metal based materials. The search for the non noble metal based materials is important due to the fact that they do not lose their reactivity and the productivity when they are employed in the methanol based fuel cells. Venkateswara Rao [11] has carried out ORR on various sizes of Pt particles supported on carbon [2.0, 2.5, 3.5, 4.0, 5.0 and 6.0 nm]. The Pt/C catalysts were synthesized and their reactivity was measured. The highest ORR activity (4.3 mAcm^{-2} at 0.7 V NHE) was exhibited by Pt with a particle size of 3.5

nm. In addition some complexes of Pt have also been studied for more than two decades. According to Yang et al., [12] ORR has been carried out on Pt and Pt Ni complexes. The observed results indicated that the output voltage is only 0.9 V which is numerically greater than the reports of Stamenkovic et al [13], and Mukerjee and Srinivasan. [14]. The bi-functional mechanism of Pt/Ru catalyst has been studied extensively. According to these studies a Pt/Ru ratio 90:10 is the most effective stoichiometry for methanol electro-oxidation. Two effects were considered for the superior activity of binary Pt-Ru catalysts: the ligand effect and the bifunctional mechanism. Chalcogens appear to have most of the features expected for ORR catalyst. Since the complex Pt-Ru-chalcogen showed enhancement in the ORR activity, several groups have worked on similar materials and the variation in composition of the constituents and preparation methods have been documented [11]. In spite of all these efforts, there are still some aspects of oxygen reduction reaction that have to be fully understood.

Recently, taking clue from biological systems, various nitrogen containing complexes have been tried as catalysts for ORR [15]. The tetramethoxyphenylporphyrin and phthalocyanine complexes of iron and cobalt have been examined as

TABLE 7. Estimated metal and nitrogen content, on set potential for oxygen reduction and ORR activity of catalysts generated from Fe- and Co- TMPP systems and that of commercial Pt Catalyst.

	Metal loading (%)	Nitrogen content (%)	Onset Potential in mV versus NHE	ORR activity at 700 mV versus NHE in mAcm^{-2}
CDX1-FeTMPPCl (UT)	2.01	2.0	+810	0.2
CDX2-FeTMPPCl(UT)	2.03	2.0	+830	0.4
CDX1-FeTMPP (HT)	1.96	1.9	+840	4.2
CDX2-FeTMPP (HT)	1.97	1.9	+870	4.9
CDX1-CoTMPP (UT)	1.98	2.0	+740	0.2
CDX2-CoTMPP (UT)	1.97	2.0	+760	0.3
CDX1-CoTMPP (HT)	1.89	1.9	+795	3.2
CDX2-CoTMPP (HT)	1.93	1.8	+860	4.5
Pt/Vulcan XC72R (E-TEK)	2.67	—	+915	4.9

UT= untreated; HT= heat treated; (FeTMPPCl = $(\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{FeCl})$); CDX1 is a commercial carbon as received sample from Columbian Chemicals company and CDX2 is the same oxidized carbon- support)

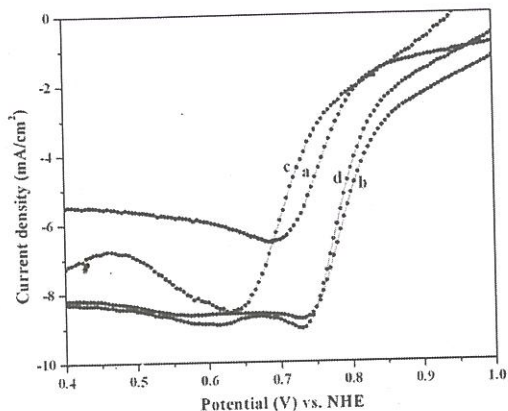


Fig. 3 Polarization curve of heat-treated MTMPP ($M = \text{Fe}$ and Co) supported on as-received and oxidized carbon catalysts: (a) CDX1-FeTMPPCl(HT), (b) CDX2-FeTMPPCl(HT), (c) CDX1-CoTMPP(HT) and (d) CDX2-CoTMPP(HT) in O_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$; Scan rate – 10 mV s^{-1}

ORR electrodes, especially the heat treated samples which could generate the metal nitrogen clusters which exhibited considerable ORR activity.

Typical results obtained for ORR activity of iron and cobalt tetramethoxy phenyl porphyrin complexes are given in Table.7. The point that emerges from the results given in this table is that the heat treated tetramethoxyphenylporphyrin complexes of iron and cobalt show ORR activity comparable to that commercial Pt catalyst thus showing that it is possible to generate appropriate non noble catalyst systems for oxygen reduction reaction in Fuel cells. It is also to be noted that the activation barrier may be reduced on non-noble metal catalyst systems as compared to the commercial Pt catalysts.

The diffusion limited plateau polarization curves for carbon supported catalysts are shown in Fig. 3. The model proposed by Jiang and Anson [16] shows that the plateau is inclined when the distribution of active sites is less uniform and the reaction is slower. A steep reduction wave similar to that observed on Pt catalysts is seen on these catalysts systems which have been supported on HNO_3 treated oxidized carbon. It has been deduced that the presence of quinone type species with well

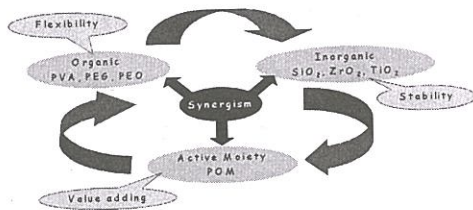


Fig. 4 The synthetic strategy employed for the preparation of hybrid membranes (Adopted from S. Shanmugam, Some device applications of (embedded) metal oxygen cluster compounds. PhD thesis, Indian Institute of Technology, Madras (2004).

dispersion of MN_4 species may be responsible for the observed ORR activity. The surface oxygen functionalities generated by the nitric acid treatment may be facilitating the dispersion of MN_4 type species without much agglomeration of the active species.

It is therefore possible that alternate Oxygen Reduction electrodes without the use of noble metals can be successfully developed and exploited in DMFC.

Studies for Membrane Development

In order to avoid the complete monopoly of Nafion membranes, the concept of hybrid membrane has been introduced. The conceptual framework for this development is shown in Fig. 4.

The development of hybrid membranes with inorganic organic components with active moiety has gone through a step wise process as shown in Fig. 5 in order to eliminate the drawbacks normally found in the developed membranes. In this exercise, the methanol cross over from anode to cathode has to be considerably reduced as compared to what is achieved in commercial Nafion 115 membranes.

Various types of membranes have been developed for deployment in DMFC. Poly vinyl alcohol (PVA)-based systems [17] have been tried but the strong hydrophilic characteristics and the swelling behaviour in aqueous solutions have been

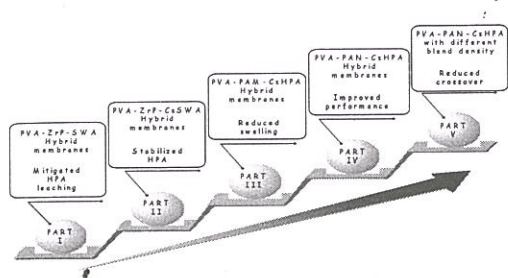


Fig. 5 The five-step process for the development of hybrid membrane.

the main drawbacks for their direct use in DMFC. A set of hybrid membranes with different blend ratio of PVA and polyacrylonitrile with proton conductors based on heteropoly acids has been designed and prepared. The properties of the developed membranes are given in Table 8, together with the values for Nafion.

Using these hybrid membranes, methanol cross over studies have been carried and the results obtained for some typical systems are shown in Fig. 6. and follows the order PVA-PAN--

CsSTA-Glu < PVA-PAN--CsPTA-Glu < PVA-PAN--CsPMA-Glu < Nafion 115. The selectivity defined as the ratio of conductance and the methanol cross over is also another parameter for selecting membranes for DMFC application. The data for the hybrid membranes are shown in Fig. 7. All the designed membranes outperformed Nafion 115. The high selectivity of the hybrid membranes is attributed to the dense interpenetrating network that is formed, leading to low methanol permeability.

Epilogue

The purpose of this presentation is to provoke alternative thinking for the conventional Pt based electrodes and Nafion membranes for DMFC. The postulates and principles enumerated in this presentation are only indicative conceptual possibilities and certainly not the exhaustive listing. It is clear that alternative most active, efficient, cost effective electrodes and membranes may be developed in the future and the DMFC will become a viable alternative energy source.

TABLE 8. Water uptake, Methanol uptake, Swelling and Ion-Exchange Capacity (IEC) values for different hybrid membranes compared with that of Nafion 15

Membrane	Water uptake (%)	Methanol uptake (%)	Swelling (%)	IEC meq.g ⁻¹
Nafion 115	22	80	12	0.9
PVA(90)-PAN(10)-CsPMA-Glu	46	5.7	4	0.61
PVA(80)-PAN(20)-CsPMA-Glu	30	4.2	2.4	0.59
PVA(70)-PAN(30)-CsPMA-Glu	21	2.2	2	0.55
PVA(90)-PAN(10)-CsPWA-Glu	34	6.5	3.6	0.7
PVA(80)-PAN(20)-CsPWA-Glu	27	4.9	2.2	0.65
PVA(70)-PAN(30)-CsPWA-Glu	18	3	1.7	0.62
PVA(90)-PAN(10)-CsSWA-Glu	30	8	2.4	0.74
PVA(80)-PAN(20)-CsSWA-Glu	25	6.5	2	0.7
PVA(70)-PAN(30)-CsSWA-Glu	16	4.6	1.3	0.7

CsPMA: CSPWA and CsSWA – Cesium salt of phosphomolybdic acid; phosphotungstic acid and silicotungstic acid respectively. Glu - glutaraldehyde

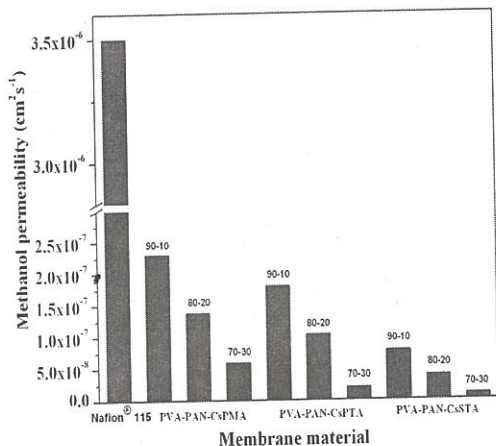


Fig. 6 Methanol permeability of hybrid membranes with different blend density compared with that of Nafion 115.

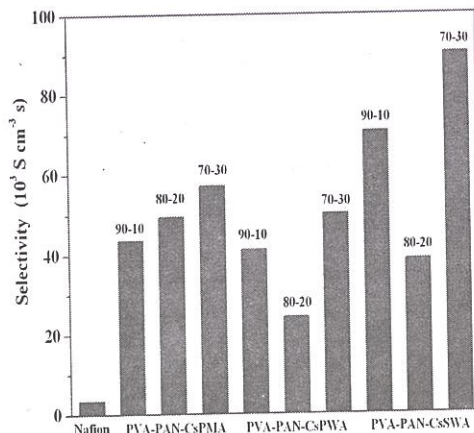


Fig. 7 Selectivity of hybrid membranes compare with that of Nafion 115.

Acknowledgment

It is a pleasure to record our grateful thanks to the Department of Science and Technology, Government of India for the creation of the National Centre for Catalysis Research. Thanks are also due to the former colleagues of NCCR for their contribution in the experimental part of the work reported in this paper.

References

1. B.Viswanathan and M Aulice Scibioh, Fuel Cells: Principles and Applications, CRC press, January 2008.
2. Frank de Bruijn, The current status of fuel cell Technology for mobile and stationary applications, Green Chem., &, 132 (2005).
3. Heinzl, C. Hebling, M. M ler, M. Zedda, C. M ler, Fuel cells for low power applicaitons, J Power Sources, 105, 250 (2002).
4. T. Maiyalagan, Electro-catalytic support for noble metals for exploitations as electrodes for fuel cells. PhD thesis, Department of Chemistry, Indian Institute of Technology, Madras.(2007)
5. Man-Yin Lo, I-Husan Liao, Chun-Chieh Huang, Key issues in the preparation DMFC electro-catalysts, Int. J. Hydrogen energy 32, 731 (2007)
6. Roy,S.C., A.W. Harding, A.E.Russell, and K.M. Thomas, Spectroelectrochemical study of the role played by carbon functionality in fuel cell electrodes, J Electrochem.soc., 144, 2323 (1997)
7. Maiyalagan, T. and B. Viswanathan, Template Synthesis and Characterization of Nitrogen Containing Carbon Nanotubes. Mater. Chem.Phys., 93, 291-295 (2005).
8. Maiyalagan, T., B. Viswanathan. and U.V. Varadaraju , Nitrogen containing carbon nanotubes as supports for Pt–Alternate anodes for fuel cell applications. Electrochem. Commun., 7, 905-912. (2005).
9. <http://www.physorg.com/news193937033.html>; C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, "Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction", J. Am. Chem. Soc. 2007, 129, 6974; C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, "A General Approach to Size and Shape Controlled Synthesis of Pt Nanoparticles and Their Catalysis for Oxygen Reduction Reaction", Angew. Chem. Int. Ed. 2008, 47, 3588.
10. Millet, P., R. Durand and M. Pineri (1990) Preparation of new solid polymer electrolyte

- composites for water electrolysis. *Int. J. Hydrogen Energy*, 15 (4) 245. 10.1
11. Venkateswara Rao, Ch., On the search for efficient catalysts for oxygen reduction reaction, Ph. D., thesis, IIT Madras (2008).
 12. Yang, H., W. Vogel, C. Lamy, and N. A. Vante (2004) Structure and Electrocatalytic Activity of Carbon-Supported Pt/Ni Alloy Nanoparticles Toward the Oxygen Reduction Reaction. *J. Phys. Chem. B*, 108 (30), 11024.
 13. Stamenkovic, V., T. J. Schmidt, P. N. Ross, and N. M. Markovic., (2002) Surface Composition Effects in Electrocatalysis: Kinetics of Oxygen Reduction on Well-defined Pt₃Ni and Pt₃Co Alloy Surface. *J. Phys. Chem. B*, 106 (46), 11970.
 14. Mukerjee, S., and Supramaniam Srinivasan, Enhanced electro catalysis of oxygen reduction on platinum alloys in proton exchange membrane fuel cells, *Journal of Electroanalytical Chemistry*, 357, (1-2), 201 (1993).
 15. Venkateswara Rao, Ch., and B. Viswanathan, Oxygen reduction by FeN₄ - a DFT study, *Indian J Chem., Sec A* 43A, 2333 (2004).
 16. Jiang, R., and F C Anson, The origin of inclined plateau currents in steady state voltammograms for electrode processes involving electrocatalysis, *J. Electrochem. Soc.*, 147, 4605 (1991).
 17. Helen, M., Development of Hybrid Membranes for Application in Direct Methanol Fuel Cells, Ph.D. Thesis submitted to the Indian Institute of Technology, Madras April 2009.

Development of Membranes for Polymer Electrolyte Membrane (PEM) Fuel Cells



Dr. S. Prabhakar, Head Separation Technology Section, Desalination Division graduated from the 16th batch of Training school in chemistry and later obtained master's degree in Chemical Engg from IIT, Madras. He has been one of the pioneers in membrane desalination in India. He has been associated with development and deployment of membrane based technologies for desalination, water purification and other separation applications. He was responsible for the development of indigenous spiral wound membrane elements and membrane casting machine. He has pioneered the application of membrane processes for radioactive waste treatment. He is a member of Technology Innovation Committee under Water Augmentation & Renovation (WAR) programme of DST. His current research interests include membrane development for fuel cells, bipolar electrolysis and fractionation of seawater through membrane processes. He has more than 75 publications and three patents to his credit.

Dr. Hemant S. Sodaye is a M.Sc. and Ph.D. in chemistry from Mumbai University (1998) and joined BARC as Dr. K. S. Krishnan Research Associate in 2000. His studies are in the field of ion exchange membranes used as solid polymer electrolyte (SPE) in the fuel cell. His postdoctoral research work was at Osaka University at Japan where he studied the degradation of polymer electrolyte membranes. Presently he is working in the field of development of alternate solid polymer electrolyte (SPE) membranes for polymer electrolyte membrane fuel cells (PEMFC) in order to replace Nafion. His research also involves, development of membrane electrode assemblies for the PEMFC. He is also engaged in the development of bipolar membranes for production of acid and base from waste salt stream.



Dr R.C. Bindal is a Senior Scientist in the Desalination Division of BARC. He has been associated with the development of different types of membranes and membrane-based water purification devices. He is instrumental in developing five different water purification/industrial effluent treatment technologies including the technologies for microorganism, fluoride and arsenic decontamination. Currently his area of interest includes development of inorganic and mixed matrix nanocomposite membranes for radioactive waste treatment and gas permeation studies. He is member of several professional bodies associated with water technologies. He has got three patents and more than 40 publications to his credit.

Dr. P.K. Tewari Head, Desalination Division (BARC) and Professor Homi Bhabha National Institute, has been involved in guiding research & development activities in desalination & water purification technologies and membrane development for various applications. He is a member of Research Advisory Committee of Department of Drinking Water Supply (DDWS) and several other committees. Dr. Tewari has over one hundred and twenty (120) research publications to his credit in journals, proceedings, books and encyclopaedia. He is a member of Editorial & Scientific Committee of 'International Journal of Nuclear Desalination' and member of editorial board of 'Desalination and Water Treatment' journal. He is receipt of several awards and felicitations in India and abroad.



Dr. S. Prabhakar, Dr. H.S. Sodaye, Dr. R.C. Bindal and Dr. P.K. Tewari, Desalination Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085; E-mail: sprabha@barc.gov.in

Introduction

Fuel cells have emerged as an alternative source of energy/energy conversion devices in portable as well as stationary mode. A variety of fuel cells such as phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC) etc. have been developed and a few of them are commercially available. Other than PAFC, all the commercially available fuel cells such as MCFC or SOFC operate at high temperatures and therefore their use remains limited to stationary power generation applications. Electrolyte leakage is a major drawback of the liquid electrolyte fuel cells. Proton Exchange Membrane Fuel Cells (PEMFCs) otherwise known as solid polymer electrolyte fuel cells can operate at temperatures close to 80°C. It has large number of applications in civil, aviation and military areas both in portable and stationary power generation mode. Constant research and development activities across different laboratories of the world are in progress to prepare cost effective eco-friendly membranes to make affordable PEMFCs. This article provides a brief overview of the development of PEMFC, particularly with the emphasis on membrane development.

Polymer Electrolyte Membrane Fuel Cell

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The basic physical structure or building block of a fuel cell consists of an electrolyte sandwiched between two porous electrodes, the anode and the cathode (Fig. 1(a)). The key components of the fuel cells are the electrolyte (Fig. 1(b)), the electrode layer (cathode and anode) which forms the integral part of the electrolyte and known as membrane electrode assembly (Fig. 1(c)), the gas diffusion layer made up of porous carbon and bipolar plates to make contact with the adjacent fuel cells when connected in series.

The anode and cathodes have Pt or Pt/Pd metal catalyst to facilitate the reactions. At anode the hydrogen is oxidized to produce protons ($H_2 \rightarrow 2H^+ + 2e^-$), the electron travels through the external circuit whereas the proton diffuses through the electrolyte to the cathode and reacts to form water ($2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$). One of the key

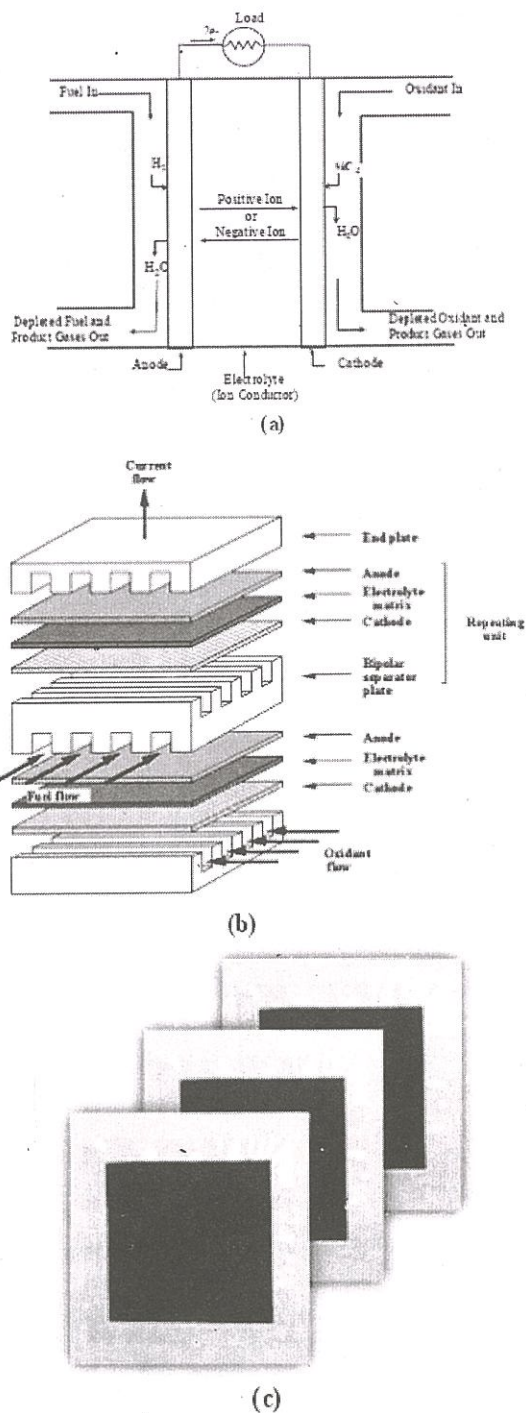


Fig. 1 (a) Schematics and (b) parts of Fuel Cells and (c) membrane electrode assembly

components in this cell is the solid polymer electrolyte (SPE) which is also known as polymer electrolyte membrane and therefore the cell is known as Polymer Electrolyte Membrane Fuel Cell (PEMFC).

Advantages

Solid membranes similar to ion exchange membranes and capable of transporting ions would be ideally suited as solid polymer electrolyte in the fuel cells. The disadvantages of the liquid electrolyte fuel cells are circumvented by the use of the electrolyte in the solid form. The advantages of using solid polymer electrolyte over that of the liquid electrolytes are

- No electrolyte leakage and the associated problems of corrosion.
- No change in the concentration of the electrolyte either by dilution by water generated at cathode or by drying due to high temperature.
- No special requirement of sealing
- Solid polymer electrolyte membrane act as separator for hydrogen and oxygen preventing their mixing
- Having a low permeability for gases, prevent gas crossover
- Fuel cells can be handled ruggedly in field conditions (e.g., dropping from helicopter) without suffering from mechanical failure such as liquid spillage.
- Simplified electrodes manufacturing process.

History of Development of SPE

The initial stages of electrolyte membrane development for fuel cell started in 1959 with phenol-formaldehyde membranes. These membranes had low mechanical strength and lifetime of 300-1000 h with power density of 0.05-0.1 kWm⁻² [1]. Later partially sulfonated polystyrene membranes were developed to improve the power density to about 0.4-0.6 kWm⁻². [2]. However, these membranes were brittle and lead to mechanical failure of the fuel cells. Cross-linked polystyrene-divinylbenzene sulfonic acid membranes resulted in the improvement of the mechanical strength and lifetime of the fuel cells. They exhibited lifetime in the range of 1000 to 10,000 h at a power density of 0.75-0.8 kWm⁻² [3]. Although there are few anion exchange membranes

being developed as solid polymer electrolyte, this article essentially deals with the research in the area of cation exchange membranes. The R&D efforts were directed towards to achieve

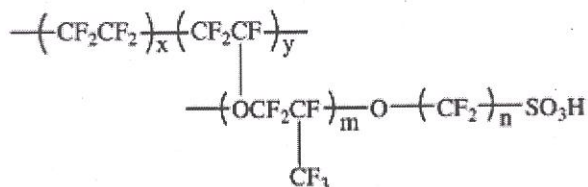
- High proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity
- Hydration: proton transport takes place as H₃O⁺ in the membrane; therefore, higher conductivity is obtained at higher hydration. Drawback of very high hydration is cathode flooding due to electro-osmotic drag of water which increases with hydration.
- Adequate mechanical strength and stability to avoid mechanical failure in the fuel cells and prevention of accidental mixing of gases.
- Lower thickness: implies lower membrane resistance, faster water equilibration, also reduces electro-osmotic drag.
- Chemical and electrochemical stability under operating conditions, e.g., stability to peroxides which are produced due to fuel crossover.
- Form stability: Low swelling/deswelling, to maintain form stability and good moisture control. Large volume/area change during swelling or deswelling results in rupture and mechanical failure of the fuel cells.
- Extremely low fuel or oxygen by-pass to maximize columbic efficiency as well as reduce peroxide formation, which lead to chemical degradation of the membrane and reduction in the membrane life time.
- Low cost: this is extremely important for commercialization of the fuel cells.

In 1970 Du Pont De Nemours Co. invented perfluorosulfonated membrane named "Nafion®" that not only showed a two-fold increase in the specific conductivity of the membrane but also extended the lifetime by four orders of magnitude (10⁴-10⁵ h).

Perfluorosulfonated Membranes

Perfluorosulfonated membranes were synthesized from tetrafluoroethylene as a starting material. These membranes have a PTFE like backbone with side chains terminating with sulfonic acid groups. Besides Du Pont, Asahi glass and Dow chemicals also developed similar membranes. However, the length of the side chains and the distance between the side chains were different (Table 1) [3]. The equivalent weight of these

TABLE 1. Schematic structure of perfluorosulfonic acid membranes manufactured by different companies.



Structure parameter	Trade name and type	Equivalent weight	Thickness (μm)
$m = 1, x = 5-13.5,$ $n = 2, y = 1$	DuPont		
	Nafion 120	1200	260
	Nafion 117	1100	175
	Nafion 115	1100	125
$m = 0, 1, n = 1-5$	Nafion 112	1100	80
	Asashi Glass		
	Flemion-T	1000	120
	Flemion-S	1000	80
$m = 0, n = 2-5,$ $x = 1.5-14$	Flemion-R	1000	50
	Asashi Chemicals		
$m = 0, n = 2,$ $x = 3.6-10$	Aciplex-S	1000 ~ 1200	25 ~ 100
	Dow Chemical		
	Dow	800	125

electrolyte membranes ranged from 800 to 1200 g/equivalent of protons in dry form. Thickness was in the range of 50 to 260 μm . Apart from perfluorosulfonated membrane like Nafion there are several other electrolyte membranes made from either perfluorinated or non fluorinated chemicals and are commercially available. Some of these electrolyte membranes are given in Table 2 [3]. These membranes were thoroughly studied for their structure by various experimental techniques, e.g., small angle X-ray scattering. The structure of the perfluorosulfonated polymer was found to be unique. A schematic of the cluster network model is depicted in Fig. 2 [4]. The backbone PTFE like structure forms the hydrophobic moieties and the side chains forms the partially hydrophilic region. The sulfonic acid groups forms clusters in the presence of water. The overlapping clusters form a transport channel responsible for the proton transport in the membrane. Since the proton transport takes place through the cluster region, the

conductivity is highly sensitive to the water content of the membrane.

Development of Alternate SPE

The fluorinated polymers have shown the best of the performance in the fuel cells (>5000 hrs of operation). However, there is a need to develop alternate non fluorinated polymers. Besides high cost, the fluorinated membranes contribute to environmental burden during their preparation as well as disposal of the polymers. It is recently reported that fluorinated compounds such as hydrofluoric acid and other fluorinated fragments [5] are released in the water during operation as well. There has been a constant effort to develop new types of electrolytes and is evident from the increasing number of publications over the years (Fig 3). Some of these electrolytes have been classified based on the polymer types or methods of preparation and shown in Fig. 4. The method of preparation of these polymers is tabulated in Table 3.

TABLE 2. Commercially available SPE materials

Membrane	Membrane Type	IEC meq./gm	Thickness (mm)	Gel water (%)	Conductivity (S _{cm}) at 30°C 100% RH	Manufactured by
K101	Sulfonated Polyarylene	1.4	0.24	24	0.0114	Asahi Chemical Industry Company Ltd., Chiyoda-ku, Tokyo, Japan
CMV	Sulfonated polyarylene	2.4	0.15	25	0.0051	Asahi Glass Company Ltd., Chiyoda-ku, Tokyo, Japan
DMV	Sulfonated polyarylene	-	0.15	-	0.0071	
Flemion	Perfluorinated	-	0.15	-	-	
MC 3470	-	1.5	0.6	35	0.0075	Ionac Chemical Company, Syborn Corporation, USA
MC 3142	-	1.1	0.8	-	0.0114	
61AZL386	-	2.3	0.5	46	0.0081	Ionics Inc., Watertown, MA 02172, USA
61AZL389	-	2.6	14.2	48	-	
61CZL386	-	2.7	0.6	40	0.0067	
N 117	Perfluorinated	0.9	0.2	16	0.0133	Du Pont Company, Wilmington, DE 19898, USA
N 901	Perfluorinated	1.1	0.4	5	0.01053	
R-1010	Perfluorinated	1.2	0.1	20	0.0333	Pall RAI Inc., Hauppauge, NY 11788, USA

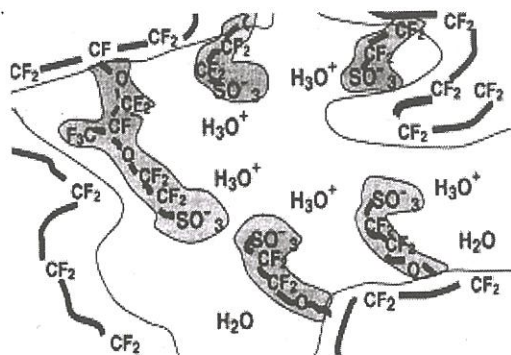


Fig. 2 Phenomenological sketch of the nano structure in NAFION.

Initial development of the solid polymer electrolyte started with partially sulfonated polymers, e.g., partially sulfonated polystyrene. However, these sulfonated polymers displayed weak mechanical property. The mechanical strength and chemical stability [6] were improved by grafting onto fluorinated polymers such as poly(vinylidene fluoride) or fluoro-ethylene-propylene copolymer (FEP). The polystyrene based polymers suffered degradation due to peroxide attack on the α carbon atom. M/s Ballard Power overcame this issue by replacing the hydrogen by fluorine, i.e. α, β, γ -trifluorostyrene, which offered excellent stability.

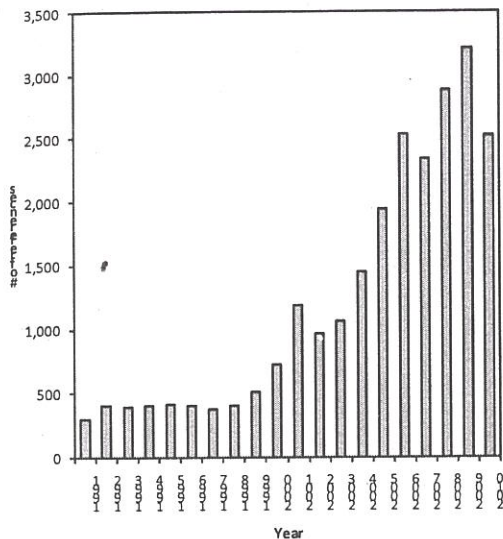


Fig. 3 The number of references found in the scientific database 'Scienccdirect' by using the combination of the words: 'polymer', 'fuel' and 'cell'

Desalination Division of BARC, on the other hand prepared poly(α -methyl styrene) in the laboratory which was then partially sulfonated to produce the polymer [7]. Sulfonated poly(ether etherketone) (SPEEK) which was also studied, showed improved degradational stability. The conductivity of these polymers were lower. However, attempts to improve the ion exchange capacity and hence the conductivity resulted in the solubility of the polymer at higher temperature. This difficulty was overcome by cross linking of PEEK or SPEEK with divinyl benzene (DVB). Parallely, composite membranes were prepared to improve the stability. The results showed that the structures of composite membrane made from combination of SPEEK (acid) and poly benzimidazole(PBI) (base) became more compact than that of SPEEK, due to the acid-base interaction between the sulfonic acid groups and amine groups, which could lead to the increase of mechanical properties and the reduction of excess swelling.

High Temperature SPE

Membranes operating above 100 °C are preferred since fuel cell is more CO-tolerant,

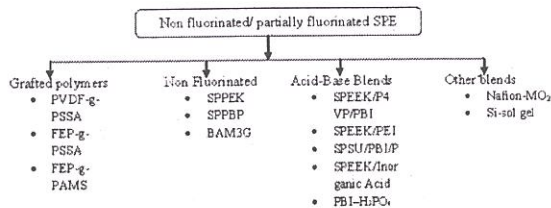


Fig. 4 Classification of different types of solid polymer electrolyte being developed.

however, Nafion like membranes in which the proton transport primarily depends on the water content, conductivity decreases rapidly above 90 °C. It was found that composite membranes such as SPEEK-PBI[8] or Nafion-PBI can be used above 100°C. The majority of the new ionomers developed currently are based on different arylene main-chain polymers, which are characterized by excellent thermal, chemical, and mechanical properties. Some of these ionomers are shown in Fig. 5. Hybrid membrane systems such as Nafion -silica [9] through sol-gel process suitable for high temperature operation are also reported.

Degradation of Solid Polymer Electrolyte

Durability of the membranes in the fuel cell still remains an unresolved issue even in case of Nafion. The thermal stability/electrochemical stability are the one of the key factors governing the life time of the membrane in the fuel cell. Electrolyte degradation in polymer electrolyte fuel cells occurs due to in-situ formation of small amounts of hydrogen peroxide (H₂O₂). It is generally accepted that the degradation mechanism involves the decomposition of H₂O₂, which produces radicals (OH•, OOH•) that attack the chemical bonds in Nafion membrane [22]. Significant degradation of the membrane results in pinhole formation [23] thus mixing of gases and reduction in overall efficiency of the fuel cells. The degradation of electrolyte especially occurring with loss of sulfonic acid sites increases the resistance of the membrane. In the other hydrocarbon membranes, the H₂O₂ formed attacks the α -carbon atom that results in loss of the sulfonic acid groups increasing the membrane resistance. The degradation may be initiated from polymer defects, e.g., polymer end groups that

TABLE 3. Different membranes and their detail description.

Sl. No.	Membrane	Description
Perfluorinated Membranes/Partially fluorinated polymers		
1	Gore-Select membrane	Composite membrane; a base material preferably made of expanded PTFE that supports perfluorinated sulfonic acid resin, PVA etc. [10]
2	BAM3G (Ballard Inc)	Polymerization of α,β,β -trifluorostyrene and subsequent sulfonation [11]
Grafted Polymers		
3	α,β,β - Trifluorostyrene grafted membrane	Grafting of α,β,β -trifluorostyrene and PTFE/ethylene copolymers
4	Styrene grafted and sulfonated poly(vinylidene fluoride) membranes [PVDF-g-PSSA]	Pre-irradiation grafting of styrene onto a matrix of PVDF after electron beam irradiation. The proton conductivity can be increased by crosslinking with DVB [12]
Non fluorinated		
5	α -methyl styrene blend PVDF	Partially sulfonated α -methyl styrene composite with PVDF [7]
6	Sulfonated Poly(ether etherketone) (SPEEK)	Direct sulfonation of PEEK in conc. sulfuric acid medium [13]
7	Sulfonated poly(ether sulfone)	Partially sulfonated polysulfones [14]
8	Sulfophenylated polysulfone	Sulfophenylation of polysulfone [15]
9	Methylbenzenesulfonated PBI/methylbenzenesulfonate poly(p- phenylene terephthal amide) membranes	These alkylsulfonated aromatic polymer electrolyte possess very good thermal stability and proton conductivity when compared to PFSA membranes, even above 80 °C [16]
10	Sulfonated naphthalenic polyimide membrane	Based on sulfonated aromatic diamines and dihydrides. Its performance is similar to PFSA [17]
11	Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP)	Derived from poly(p-phenylene) and structurally similar to PEEK. Direct sulfonation to produce the electrolyte. [18]
12	Poly(2-acrylamido-2-methylpropanesulfonic acid)	Made from polymerization of AMPS monomer. AMPS monomer is made from acrylonitrile, isobutylene and sulfuric acid [3]

TABLE 3. (Contd.)

Sl. No.	Membrane	Discription
Acid base blends		
13	Imidazole doped sulfonated polyetherketone (SPEK)	Complexation with imidazoles to obtain high proton conductivities [19]
14	Sulfonated Poly(ether etherketone) (SPEEK)-PEI	Sulfonated Poly(ether etherketone) (SPEEK)-Poly ethylene imine (PEI) blended [20]
15	Sulfonated Poly(ether etherketone) (SPEEK)-PBI blend	Composite membranes based on highly sulfonated PEEK and PBI [8]
16	PBI-H ₃ PO ₄	PBI doped with phosphoric acid [21]

maybe different than the main chain and unstable towards degradation. The initial degradation sites form the active centers for further degradation and then the process accelerates.

Conclusion

Constant efforts are in progress to increase the thermal, chemical stability of polymer electrolytes without compromising the conductivity. Large number of polymers including aromatics in combination with organic/inorganic acids is being investigated. However, a cheaper and durable electrolyte is still not available. The areas of improvement include resistant to peroxide degradation, stability and performance at high temperatures, higher conductivity etc.

References

- 1 H.J.R., Magnet C. Berger (Ed.), in: "Handbook of Fuel Cell Technology", Prentice-Hall, Englewood Cliffs, NJ, USA, 1968, p. 425.
- 2 J.O'M. Bockris, S. Srinivasan, "Fuel Cells: Their Electrochemistry", McGraw-Hill, New York, 1969.
- 3 B., Smitha, S. Sridhar, A.A. Khan, Journal of Membrane Science, 259 (2005) 10–26
- 3 M. Wakizoe, O.A. Veleev, S. Srinivasan, Electrochim. Acta, 40 (1995) 335

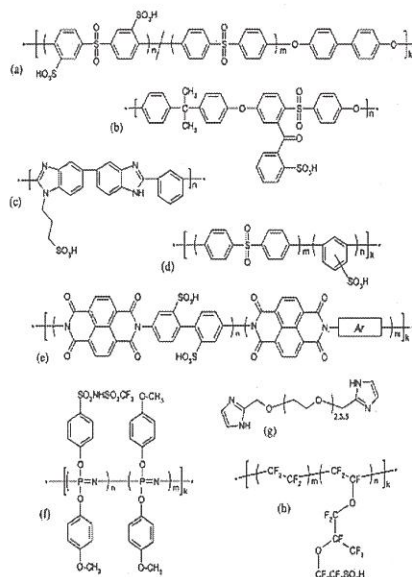


Fig. 5 Examples of proton conducting polymers under development as PEM materials: (a) sulfonated poly(arylene ether sulfone); (b) sulfophenylated polysulfone; (c) sulfopropylated PBI; (d) sulfonated poly(arylene-co-arylene sulfone); (e) sulfonated naphthalenic polyimide (Ar, various aromatic moieties); (f) poly(aryloxyphosphazene) having sulfonimide units (g) imidazole-terminated ethylene oxide oligomers; and (h) Nafion marketed by the DuPont company.

- 4 H.G. Haubold, T. Vad, H. Jungbluth, P. Hiller, *Electrochim. Acta*, 46 (2001) 1559–1563.
- 5 Yoko Akiyama, Hemant Sodaye, Yuji Shibahara, Yoshihide Honda, Seiichi Tagawa, Shigehiro Nishijima, *Polymer Degradation and Stability*, 95(1) (2010) 1-5.
- 6 Felix N. Büchi., Bhuvanesh Gupta, Otto Haas, Günther G. Scherer, *Electrochimica Acta*, 40(3) (1995) 345-353.
- 7 H. S. Sodaye, S. Prabhakar, P. K. Tewari, National Seminar on Membrane science & technology: Challenges and opportunities, Regional Research Laboratory: Jorhat February 12-13, 2004.
- 8 Haiqiu Zhang, Xianfeng Li, Chengji Zhao, Tiezhu Fu, Yuhua Shi and Hui Na, *Journal of Membrane Science*, 308(1-2) (2008) 66-74.
- 9 N. Miyake, J. S. Wainright, R. F. Savinell., *J Electrochem Soc* 2001;148:A898 –A904.
- 10 Bahar B., Hobson A.R., Kolde J.A., Zuckerbrod D., US Patent, 5,547,551 (1996).
- 11 Wei J., Stone C., Steck A., US Patent 5,422,411 (June 1995)
- 12 Heitala S., Paronen M., Holmberg S., Nasman J., Juhanoja J., Karjalainen M., Serimaa R., Tivola M., Lehtinen T., Parovuori K., Sundholm G., Ericson H., Mattsson B., Torell L., Sundholm F., *J. Polym. Sci.* 37 (1999) 1741–1753.
- 13 Helmer-Metzman F., Osan F., Schneller A., Ritter H., Ledjeff K., Nolte R., Thorwirth R, US Patent 5,438,082 (August 1995).
- 14 Wang F, Hickner M, KimYS, Zawodzinski TA, McGrath JE., *J Membr Sci* 2002;197:231–42.
- 15 Lafitte B, Karlsson LE, Jannasch P. ,*Rapid Macromol Commun* 2002;23:896 –900.
- 16 Rikukawa M., Sanui K., *Prog. Polym. Sci.* 25 (2000) 1463–1502.
- 17 Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M., *Polymer* 2001;42:359–73.
- 18 Lawrence R., US Patent 4,214,969 (July 1980)
- 19 Kreuer K.D., *J. Membr. Sci.* 185 (2001) 13.
- 20 Kerres Jochen, Ullrich Andreas, Meier Frank and Hüring Thomas, *Solid State Ionics* Volume 125, Issues 1-4, 1999, Pages 243-249
- 21 Tingelöf Thomas, Ihonena K. Jari , *Journal of Membrane Science* Volume 313, Issues 1-2, 10 April 2008, Pages 86-90
- 22 Yoko Akiyama, Hemant Sodaye, Yuji Shibahara, Yoshihide Honda, Seiichi Tagawa, Shigehiro Nishijima, *Polymer Degradation and Stability*, 95(1) 2010, 1-5
- 23 Haolin Tang, Shen Peikang, San Ping Jiang, Fang Wang and Mu Pan, *Journal of Power Sources*, 170(1), 85-92

For Limited Circulation Only

Printed & Published by :

Dr. A.V.R. Reddy, Secretary, Indian Association of Nuclear Chemists and Allied Scientists (IANCAS)
(Registration No. MAH / 232/1984 GBBSD) on the behalf of IANCAS, C/o. Radiochemistry Division ,
Bhabha Atomic Research Centre, Mumbai 400 085

Printed at

Perfect Prints, 22/23, Jyoti Industrial Estate, Nooribaba Dargah Road, Thane 400 601.
Tel. (022) 2534 1291 Telefax : (022) 2541 3546, E-mail : perfectprints@gmail.com

Edited by

R.V. Kamat, Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085.