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Alternate Electrolyte Materials for Intermediate Temperature Solid Oxide Fuel Cells

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The solid oxide fuel cell (SOFC) employs yttria-stabilized zirconia (YSZ) as the oxide ion conducting electrolyte. Because of the life limiting problems associated with the high temperature of operation (1273 K) of the YSZ electrolyte based cells, attempts are being made to develop alternate electrolytes which have oxide ion conductivity values comparable with that of YSZ at intermediate temperature (around 1073 K, Intermediate Temperature Solid Oxide Fuel Cell - ITSOFC). Partially substituted barium cerate perovskites were reported to have adequate ionic conductivity at 1073 K. Similarly, $LaGaO_3$ materials were also reported to have comparable ionic conductivity values. In this paper the fundamental aspects, problems and prospects of using $LaGaO_3$ based electrolytes in ITSOFC system and their systematic evolution in their eventual application are presented and discussed.

Introduction

Fuel cells are electrochemical devices, which offer the direct conversion of a variety of fuels into electrical power. Over all these years, several types of fuel cell systems were under development owing to their environmental compatibility, potential for use in stationary/ distributed electric power stations as well as in transportation applications. As it stands today, six different types of fuel cells, namely, solid polymer electrolyte fuel cells (SPEFC), alkaline fuel cells (AFC), direct methanol fuel cells (DMFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) are the main systems under development. SOFC systems have several distinct features such as very high-energy conversion efficiency, use of non-precious materials, no liquids involved in the fuel cell, adaptation to a variety of fuels and invariant electrolyte [1,2]. SOFC systems are based on stabilized zirconia electrolyte, Ni-YSZ cermet as anode and $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) as cathode. However, they pose very critical requirements on materials.

Intermediate temperature solid oxide fuel cells (ITSOFC)

The high temperature operation of SOFC causes many serious problems such as severe restrictions on the choice of materials, electrode sintering programmes, interfacial diffusion between electrodes and electrolyte, and mechanical stresses due to difference in their thermal expansion coefficient values. The thermal compatibility of the LSM cathode – YSZ interface is not good enough on prolonged operation of SOFC systems resulting in the formation of new inter-metallic compounds across the interface leading to performance degradation due to rise in the cell resistance with time [3]. In view of this, current focus is on the development of alternate materials and components for operating SOFC systems at intermediate temperature range, namely, 973 – 1073 K [4]. To develop a practical reduced temperature SOFC, two approaches are under active consideration. The first one is, to use an extremely thin YSZ membrane to make the ohmic loss due to electrolyte as minimum as possible [5] and the second one is to use a new electrolyte material from ceramics that shows excellent oxide ion conductivity at the temperature below 1073 K, comparable to that of YSZ at 1273 K. A replacement of YSZ by an alternate intermediate temperature oxide ion conductor might reduce the material and fabrication problems and improve the reliability of the cell over prolonged operation [6-9]. In this paper, the fundamental aspects, problems in the component fabrication in the form of thin and dense membranes and prospects of a few alternative oxide ion conducting solid electrolytes for application in ITSOFC system and their systematic evolution are comprehensively reviewed keeping in view the overall strategies adapted globally.

$LaGaO_3$ based electrolyte materials
Preparation and characterization of $LaGaO_3$ based electrolyte materials

It is reported that partially substituted lanthanum gallate based perovskite oxides exhibit high oxide ion conductivity at relatively lower temperature (<1073 K), which is comparable with that of YSZ at 1273 K over a

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broad range of oxygen partial pressure values in SOFC [10]. These $LaGaO_3$ based powders prepared by glycine nitrate combustion synthesis in different compositions partially substituted with $10-20$ mol% Sr or Ba in the 'A' site and $15-20$ mol % Mg in the 'B' site of the perovskite structure exhibited higher conductivity than YSZ. Table 1 lists the oxide ion conductivity data obtained on $LaGaO_3$ based perovskite oxides [11]. The increased conductivity in the gallates was attributed to both the higher oxygen ion mobility and a higher concentration of oxygen ion vacancies relative to YSZ [12-13]. This $LaGaO_3$ based oxide partially substituted with Sr for La and Mg for Ga sites (LSGM) exhibits the high oxide ion conductivity stable over wide oxygen partial pressure range.

(LCFC) perovskite and $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) perovskite cathodes. The LCFC performance was slightly inferior to the LSC cathode. Nevertheless, it performed well and can be considered a viable cathode material for LSGM based fuel cells [16]. Thangadurai et.al. have shown that isovalent substitution of Mn(II) for Mg (II) in the most promising oxide ion conductor $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) yielded a new oxide ion conductor $(La_{0.9}Sr_{0.1}Ga_{0.8}Mn_{0.2}O_{2.85})$ exhibiting a conductivity (s=4.6×10^{-2} S/cm at 1073 K) that is comparable to the conductivity of Mg (II) analogue. The Mn(II) oxide has a lower activation energy for conduction ($E\alpha = 0.47$ eV) than the Mg (II) oxide [17].

Table: 1 Conductivity data obtained on $LaGaO_3$ based perovskite oxides (prepared by solid state reaction) at 1073 K[12].

La/Sr ratio in LSGM	Oxide ion conductance (Scm^{-1}) at various compositions						
	Ga/Mg ratio in LSGM						
	95:5	90:10	85:15	83:17	80:20	75:25	70:30
95:5	--	--	0.114	--	0.113	--	--
90:10	--	0.116	0.127	--	0.132	0.132	--
85:15	0.126	0.132	0.141	0.151	0.150	0.139	0.113
80:20	--	0.133	0.149	0.166	0.140	0.140	0.116
75:25	--	0.100	0.125	--	0.142	0.128	0.107
70:30	--	--	--	--	0.109	0.122	0.103

Drennan et.al have prepared the $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{3-\delta}$(LSGM1020) perovskite oxide by solid state reaction and they have measured the conductivity at 1073K as 0.12 S/cm [14]. At 1273K, the ionic conductivity of $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{3-\delta}$ (LSGM1020) was higher by a factor of two compared to ZrO_2 doped with 8 mol% Y_2O_3. However, it was similar to that of ZrO_2 doped with 9 mol% of Sc_2O_3. Huang et. al synthesized Sr- and Mg- doped $LaGaO_3$ powders from a salt acetate solution (sol gel synthesis) [15]. The impedance spectroscopy on a 93% dense sample exhibited no grain – boundary contribution and an ac conductivity of 0.11 S/cm at 1073 K. The powder X-ray diffraction data showed that the crystallization of a perovskite phase was initiated at a calcining temperature of 873 K. The formation of single phase LSGM phase cubic form was completed only at 1573 K, with internal sintering occurring at 1623 K.

Maffei et.al have reported a simple nitrate synthesis route for $LaGaO_3$ based electrolyte. This new nitrate process yielded material that is phase pure without the need of any complicated or elaborate processing steps and can thus be easily scaled up. A $NiO - CeO_2$ anode performed well with both $La_{0.6}Ca_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$

Similarly, Litty Sebastian et.al have reported the preparation of $LaGaO_3$ based perovskite oxide of the general formula $La_{0.9}Sr_{0.1}Ga_{0.8}M_{0.2}O_{3-\delta}$ (for M= Mn, Co, Ni, Ca and Zn) [18]. All these oxides exhibited high electrical conductivities (s~10^{-2} S/cm at 1073 K) comparable to that of the best perovskite oxide ion conductor $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) (s ~ 8×10^{-2} S/cm at 1073 K). While M= Mn, Co, Ni, Cu members appeared to be mixed conductors with a variable electronic contribution to the conductivity, especially at high oxygen partial pressure ($P(O_2) \geq 1$ atm) arising from mixed– valency of the transition metals, the M= Zn (II) phase was a pure oxide ion conductor exhibiting conductivity (s ~ 1.5×10^{-2} S/cm at 1073 K) that is slightly lower than that of LSGM. The lower conductivity of the M= Zn (II) derivative could be due to the preference of Zn (II) for tertrahedral oxygen co-ordination .

Audinot et.al synthesized $LaGa_{1-x}Ni_xO_{3-\delta}$ ($x \leq 0.50$). The chemical analysis of these materials have shown that both the oxygen non-stoichiometry(δ) and the electron carrier concentration increased with the substitution of nickel for gallium [19]. While $LaGaO_3$ is an insulator, the Ni-doped phases were semi-conducting and behave as a metal for the highest nickel contents.

The dilatometric features versus temperatures showed that these materials were mechanically compatible with the electrolyte $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020). In addition, their chemical composition did not change at high temperature. All these characteristics make Ni-doped $LaGaO_3$ based materials as good candidates for cathodes of SOFCs.

Ishihara et.al developed a new solid electrolyte $(La_{0.9}Nd_{0.1})_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ which exhibited pure oxide ion conduction over the oxygen partial pressures from 1 to 10^{-21} atmosphere and the electrical conductivity attained the value of log (conductivity) S/cm = -0.5 at 1223K [20]. The researchers have also prepared other rare earth based doped lanthanum gallates for SOFC applications [21]. Recently, it was reported that $PrGaO_3$ doped with Sr and Mg for the Pr and the Ga sites, respectively, exhibited the high oxide ion conductivity, which was comparable to that of Sr and Mg substituted $LaGaO_3$. The highest oxide ion conductivity at temperatures higher than 1073 K was obtained for the composition of $Pr_{0.93}Sr_{0.07}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ (PSGM) [22].

Physico-chemical characterization of $LaGaO_3$ based electrolyte materials

Due to high ionic conductivity values, the $LaGaO_3$ based materials are effectively used as alternative electrolytes for ITSOFC systems. Yamaji et.al have measured the electron and hole conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM1020) by ion blocking method [23]. They found that in a region of $P(O_2) > 10^{-5}$ atm., the hole conduction is dominant and proportional to $P(O_2)^{1/4}$. The transference number of hole is 0.012 at 1273 K at $P(O_2)$ = 0.21 atm. and decreases with decreasing temperature. The optimum thickness was calculated from oxygen permeability and joule loss and was found to decrease with decreasing temperature. It is 10 mm at 873K under current flow of 0.5 Acm^{-1}. Decrease in temperature made the transference number of holes small. Recently, Anderson et.al have reported the ionic and electronic conduction in $La_{0.95}Sr_{0.05}GaO_{3-\delta}$, $La_{0.95}Sr_{0.05}AlO_{3-\delta}$, $Y_{0.95}Sr_{0.05}AlO_{3-\delta}$ as a function of oxygen partial pressure $P(O_2)$ - ranging from air to 10^{-15} Pa) and temperature ranges between 1073 – 1273 K [24]. $La_{0.95}Sr_{0.05}GaO_{3-\delta}$ samples had the highest ionic conductivity with only a minor p-type contribution in air and an ionic domain extending to high $P(O_2)$ levels. They have shown that these materials were stable with large $P(O_2)$ domains and exhibited negligible n-type conductivities even under reducing conditions typical of fuel rich atmospheres. Temperature dependence of electrical conductivity for some oxide ion conductors (high temperature range) is shown in Fig. 1
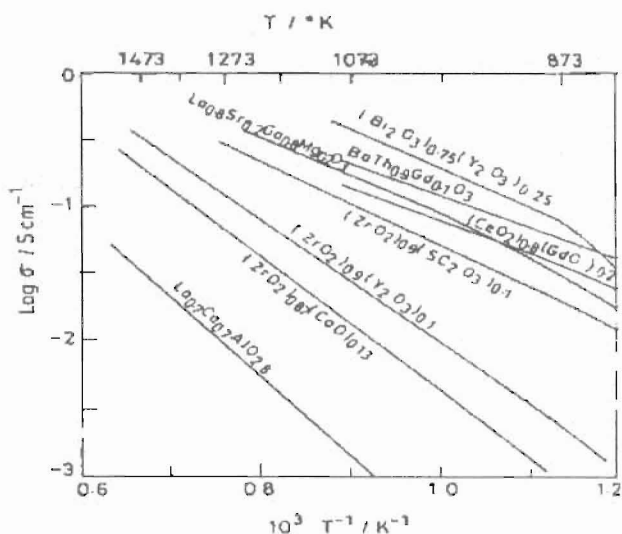

Fig.1 Temperature dependence of electrical conductivity for oxide ion conductors (high temperature range) (Ref: 2)

Huang and Petric have investigated the solid solution range and conductivity of Sr and Mg-doped $LaGaO_3$ perovskites [25]. The solid solution range can be extended by balancing the oxygen vacancies created by doping Sr and Mg ion at A and B sites, respectively. Dopants on both sides enhanced the oxygen ion conductivity, but the oxygen vacancies originating from doping Sr for La had resulted in lower activation energy. They have shown that $La_{0.8}Sr_{0.2}Ga_{0.9}Mg_{0.1}O_{2.85}$ (LSGM2010) was found to have the highest conductivity at temperatures below 973 K (7.14 x 10^{-2} S/cm at 973 K, 2.92 x 10^{-2} S/cm at 873 K), while $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM2015) had the highest value at temperatures above 973 K (0.14 S/cm at 1073K). Gharbage et.al have carried out the high temperature electrochemical permeability measurements with $La_{0.9}Sr_{0.1}Ga_{1-x}Fe_xO_{3-\delta}$ [26]. They confirmed that Fe plays an important role in determining the p-type conductivity of this family of materials. The increase in p-type conductivity with Fe was explained by the formation of Fe^{4+} ions under oxidizing conditions. This would be coherent with a small polaron type conduction mechanism. The activation energy for p-type conductivity was found to be in the range 0.9 – 1.0 eV, lower than usually observed for alternative electrolytes based in zirconia or ceria. Wolfensteine et.al have measured the creep behaviour of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM2015) over the temperature range 1473 to 1573 K in air [27]. A comparison of the activation energies determined by ionic conductivity, oxygen tracer diffusion and theoretical predictions revealed that the creep rate of LSGM2015 was controlled by cation lattice diffusion.

Steady-state creep rate vs. reciprocal absolute temperature for $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ is shown in Fig.2. Similarly, Wolfenstine had experimentally measured and compared the intrinsic resistance of cubic zirconia with LSGM2015 [28]. The results revealed that the intrinsic creep resistance of cubic zirconia was much higher than that of doped lanthanum gallate (LSGM2015) over the entire temperature range. This is most likely a result of the difference in the complexity of crystal structure. Grain size and temperature compensated steady-state creep rate vs. applied stress for $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ (LSGM2015) and cubic zirconia doped with yttria, scandia and calcium oxide are shown in Fig. 3.

Goodenough et.al found out that $La_{0.80}Sr_{0.20}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM2017) exhibited a stable conductivity of 0.166 and 0.079 S/cm at 1073 K and 973 K respectively and concluded that it is purely an oxide ion conducting phase and it is the most promising candidate for thick membrane electrolytes (>100 mm) for ITSOFC [29]. Hrovat et.al have studied the subsolidus equilibria in air in the La_2O_3 - Ga_2O_3 – NiO system at 1573 K with the aim of obtaining information on possible interactions between a $LaGaO_3$ based solid electrolyte and NiO during preparation of the anode in SOFC [30]. The results indicated that NiO had not undergone any reaction with "pure" $LaGaO_3$. Huang et.al have studied the chemical reactions between two cathode materials, $La_{0.84}Sr_{0.16}MnO_{3-\delta}$ (LSM), $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSC), and the electrolyte $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) [31]. Significant interdiffusion of Co into LSGM and Ga into LSC were found at the interface even at relatively low fabrication temperatures. In contrast, only small interdiffusion of Mn into LSGM and Ga into LSM were detected at the LSM/LSGM interface, though it was fired at 1743 K for 36 hours.

Considering both the small interdiffusion reactions between LSM and LSGM and their similar thermal expansion coefficients, LSM could be an appropriate cathode material for LSGM based fuel cells. The comparison of technical data between LSGM, LSM and LSC is shown in Table 2. Slater et.al has studied the actual structure of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) based solid electrolyte by using high resolution powder neutron diffraction technique [32]. It was shown that the room temperature structure of the new fast ion conducting solid electrolyte $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) is monoclinic, rather than orthorhombic, as for the undoped parent phase $LaGaO_3$.
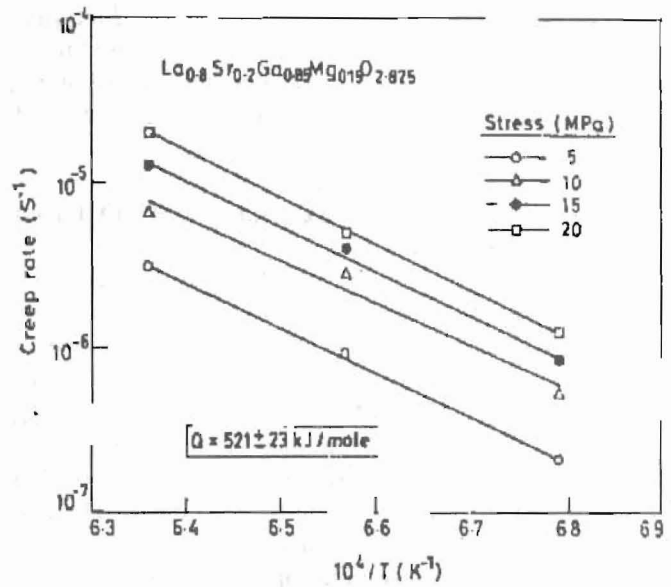

Fig.2 Steady-state creep rate vs. reciprocal absolute temperature for $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ (Ref.27)

Table: 2 Comparison of technical data between LSGM, LSM and LSC [31].

| Compound properties	LSGM	LSM	LSC
Composition	$La_{0.9}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$	$La_{0.84}Sr_{0.16}MnO_3$	$La_{0.5}Sr_{0.5}CoO_3$
Conductivity	≈0.10 S/cm at 1073 K	≈150 S/cm at 1273 K	≈1000 S/cm at 1273 K
Thermal expansion coefficient	12.7 (886 to 1123 K)	≈12.0 (298 to 1273 K)	≈20.0 (298 to 1273 K)
Chemical stability	$1 < pO_2 < 10^{-22}$ atm. at 1073 K	Decomposes at 1273 K if $pO_2 < 10^{-14}$ atm, Sr doping reduces stability	Decomposes at 1273 K if $pO_2 < 10^{-7}$ atm, Sr doping reduces stability
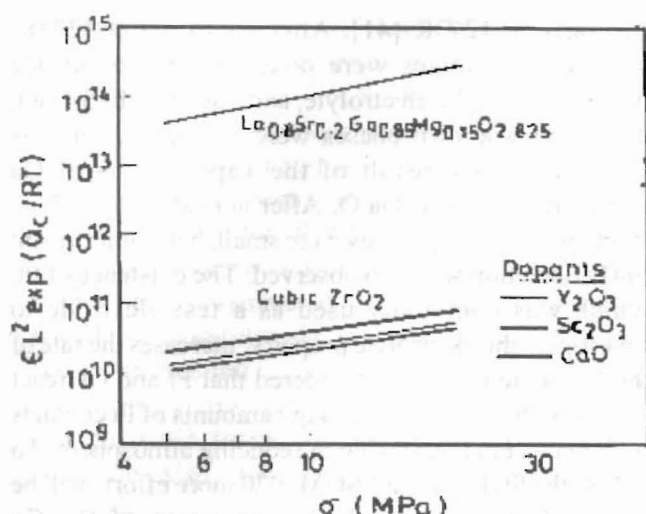
Fig.3 Grain size and temperature compensated steady-state creep rate vs. applied stress for $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_3.d$ and cubic zirconia. The dopants for ZrO_2 are shown (Ref: 28)

Performance characteristics of $LaGaO_3$ based ITSOFCs

The ITSOFCs with new alternate solid electrolytes (having high oxide ion conductivity) were studied for power generation applications with high energy conversion efficiency. Feng et.al have constructed the SOFC with doped lanthanum gallate electrolyte material and tested from 873 to 1073 K [33]. Both ceria and the lanthanum gallate electrolyte material were mixed with NiO powder respectively to form composite anodes. Doped lanthanum cobaltite was used exclusively as the cathode material. Power density realized was 0.336 W/cm^2, which is 70% of theoretical value 0.517 W/cm^2 (thickness - 395 mm, electrolyte conductivity - 0.07S/cm and OCV = 1.08 V) using Ni/LSGM anode. Huang et.al have studied the electrode performance of a single

SOFC using a 500 mm thick $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) electrolyte membrane [34]. Comparison of $La_{0.6}Sr_{0.4}CoO_3.d$(LSC) and $La_{0.9}Sr_{0.1}MnO_{3-\delta}$ (LSM) as cathodes showed LSC has an exchange current density two orders of magnitude higher than that of LSM. Comparison as CeO_2/Ni and LSGM/Ni anodes showed a degradation of the latter with time. The anode – electrolyte interface and the reactivity of NiO and LSGM suggest that better anode performances can be obtained with a buffer layer that prevents formation of $LaNiO_3$. The cell performance showed that, with a proper choice of electrode materials and LSGM as the electrolyte, a SOFC operating at temperatures $973 < T < 1073$ K is a realistic goal.

Ishihara has assembled and tested SOFC consisting of $La_{0.9}Sr_{0.1}Ga_{0.2}Mg_{0.2}O_{3-\delta}$ (LSGM1020), Ni and $La_{0.9}Sr_{0.1}CoO_{3-\delta}$ (LSC) as the electrolyte, anode and cathode respectively [35]. The maximum power density was as high as 1.01 Wcm^{-2} at 1273 K despite the low thickness (0.5mm) of the electrolyte plate. The maximum power density of cells with $LaGaO_3$ based electrolyte was three times larger than that of YSZ at 1273 K, an order of magnitude larger at 973 K. High power density of SOFC at low temperature seems to be due to the high oxide ion conductivity of $LaGaO_3$ based perovskite and the high activity of $La_{0.9}Sr_{0.1}CoO_{3-\delta}$ (LSC) cathode for the dissociation of oxygen molecules to oxide ions. Choi et.al have studied the oxygen ion conductivity and cell performance with $La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LBGM1020) electrolyte [36]. The oxygen ion conductivity of LBGM1020 system was 0.1 S/cm at 1073 K. The single cell of composite Ni/ electrolyte anode exhibited a higher power density than that of the Ni anode. The single cell of Ni/electrolyte

Table: 3 The power generation characteristics of SOFCs with LSGM1020 electrolyte [37].

Sl. No	Anode	Cathode	Temp. of operation (K)	OCV (V)	Max. power density (Wcm^{-2})
1.	Pt	Pt	1273	1.098	0.09
2.	Ni	Pt	1273	1.099	0.15
3.	Ni	$La_{0.54}Sr_{0.36}MnO_{3-\delta}$	1273	1.098	0.31
4.	Ni	$La_{0.60}Sr_{0.40}MnO_{3-\delta}$	1273	1.099	0.71
5.	Ru	$La_{0.60}Sr_{0.40}MnO_{3-\delta}$	1273	1.051	0.01
6.	Co	$La_{0.60}Sr_{0.40}MnO_{3-\delta}$	1273	1.100	0.53
7.	Ni	$La_{0.75}Sr_{0.25}CrO_{3-\delta}$	1000	1.099	0.15
8.	Ni	$La_{0.60}Sr_{0.40}FeO_{3-\delta}$	1000	1.100	0.51
9.	Ni	$Sm_{0.60}Sr_{0.40}CoO_{3-\delta}$	1000	1.100	1.30

composite anode/$La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_3$-d/$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ cathode, with a specimen thickness of 1600 mm and an electrode surface area of 0.5 cm^2 showed a maximum power density of 0.21 W/cm^2 at 1273 K. Ishihara et.al had found that the Ni and doped $SmCoO_3$ ($Sm_{0.6}Sr_{0.4}CoO_3$) were suitable as anode and cathode for SOFC with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM1020) electrolyte [37]. The maximum power density of SOFC, with these materials, attained a value as high as 1.3 W/cm^2 at 1273K, despite 0.5 mm thickness of electrolyte. Moreover, the power density of the cell was still as high as 0.44 W/cm^2 even at 1073 K. This power density is about 9 times higher than that of SOFCs where YSZ is used as electrolyte under the same conditions. The power generation characteristics of SOFC with LSGM electrolytes is compared in Table 3. Yamaji et.al have studied the compatibility of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) [38]. They reported that it reacted with other components such as alumina tubes or pyrex glass sealant in test cell. It was reported that a significant depletion of B-site ions, especially Ga ion, from the surface outside the effective electrode area in $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) occurred and the surface morphology was changed from dense to porous.

The reaction of NiO with LSGM ($La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$) was prevented by using an interlayer Sm – CeO$_2$ in between the anode and the electrolyte [39]. It prevented the formation of LaNiO$_3$. The peak power density of the inter layered cell was 100mW higher than that of the standard cell without the interlayer. This improvement is due to a significant reduction of the anode over-potential; the over potential of the cathode $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) remained unchanged. The power density obtained was 550 mW/cm^2 at 1073 K. Yamada et.al have reported increased power density of SOFC by doping small amount of Co to LaGaO$_3$ electrolyte [40]. Increasing the amount of doped Co monotonically enhanced the hole conduction resulting in a decrease in the OCV and an increase on the amount of leaked oxygen which results in diminished electric power. Consequently, it became clear that the optimized composition for this electrolyte was $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ considering the power density and the amount of oxygen leakage. Although the thickness of electrolyte with the above composition was as thick as 0.5mm, a maximum power density obtained was 242 mW/cm^2 at 1073 K. Yamaji et.al have investigated the chemical stability of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM1020) as an SOFC electrolyte in humidified

hydrogen at 1273K [41]. After annealing at 1273K, significant changes were observed in the surface morphology of the electrolyte, and La(OH)$_3$, LaSrGaO$_4$ and some unknown phases were formed, which was interpreted as a result of the vaporization of Ga components such as Ga$_2$O. After annealing at 1073K, changes in the morphology were small, but slight amount of Ga depletion was also observed. The existence of Pt, which was commonly used as a test electrode to investigate the electrolyte property, increases the rate of the Ga depletion. It is considered that Pt and Ga react and form Pt-Ga alloys if enough amounts of Pt contacts with Ga – contained oxide in reducing atmosphere. To realise the SOFC using LSGM1020 more efforts will be required to decrease the vaporization of the Ga component by adding some other dopants in LSGM, so that one can decrease the operating temperature of SOFC.

Yaremchenko et. al studied the performance of lanthanum gallate based electrolyte materials with the addition of Co content [42]. The $LaGa_{1-x-y}Co_xMg_yO_{3-\delta}$ solid solutions with rhombohedrally distorted perovskite structure were ascertained to form in the concentration range of $0 \leq y \leq 0.10$ at x = 0.60 and $0 \leq y \leq 0.20$ at x = 0.35 – 0.40. Increasing cobalt content has resulted in an increase in electrical conductivity and thermal expansion of the perovskites. The thermal expansion coefficients of the $LaGa_{1-x-y}Co_xMg_yO_{3-\delta}$ ceramics were calculated from the dilatometric data to vary in the range of 12.4 – 19.8 x 10^{-6} K^{-1} at 300 – 1100 K. Doping La(Ga,Co)O$_{3-\delta}$ solid solution with Mg has led to increasing oxygen non stoichiometry, electronic and oxygen ionic conductivity. Oxygen penetration fluxes through $LaGa_{1-x-y}Co_xMg_yO_{3-\delta}$ membranes were found to be limited by the bulk ionic conduction and increase with magnesium concentration, being essentially independent of cobalt content.

Ishihara et.al have found that doping small amount of Fe is effective for improving the oxide ion conductivity in $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM1020) [43]. Power density of the SOFC was also increased by doping Fe in LSGM electrolyte due to the increased oxide ion conductivity. The maximum power density close to 700 mW/cm^2 was reported at 1073 K on the cell employing 0.5mm thick $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.17}Fe_{0.03}O_3$ (LSGMF) electrolyte and O$_2$ as oxidant. Ishihara et.al have also reported the power generation characteristics of SOFC with $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ electrolyte [44]. The maximum power density obtained was 1.53 and 0.50 W/cm^2 at 1073 and 873 K respectively, when

the thickness of electrolyte was 0.18mm. Maric et.al have studied the electrode performance using $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM1020) electrolyte, $La_{0.6}Sr_{0.4}Co_{3-\delta}$ (LSC) cathode and samaria doped ceria $(CeO_2)(SmO_{1.5})_{0.2}$–Ni cermet anode materials [45]. The maximum power density of the cell of about 425 mW/cm^2 was achieved for SOFC at 1073 K . Ishihara et.al have reported the power generation characteristics of cells employing various materials as anodes and cathodes [46]. They have found that the maximum power density of cells increased in the following order, $Pt<La_{0.75}Sr_{0.25}CrO_3<(La_{0.6}Sr_{0.4})_{0.9}MnO_3<La_{0.6}Sr_{0.4}FeO_3<La_{0.6}Sr_{0.4}CoO_3$ for the cathode, and $Ru<Pt<Co<Ni$ for the anode. Also, they have reported that the maximum power density of the SOFC, which consisted of Ni anode and $Sm_{0.6}Sr_{0.4}CoO_3$(SSC) cathode attained the values as high as 0.44 and 0.14 W/cm^2 at 1073 K and 973 K respectively. Comparison of the power generation characteristics of SOFCs where Yb and Y-stabilized ZrO_2 and $LaGaO_3$ based oxide were used for electrolyte at 1073 K is shown in Fig.4. Due to its very good performance characteristics, the commercialization of $LaGaO_3$ based ITSOFC at intermediate temperature range is a realistic goal. Also, these results indicate the possibility of using ITSOFC for stationary power generation applications in the future.

Conclusion

The technology of intermediate temperature solid oxide fuel cells (ITSOFCs) is attractive towards commercialization with newer alternative $LaGaO_3$ based solid electrolytes for bulk power generation at lower temperatures (<1073 K) with high energy conversion efficiency. The $LaGaO_3$ based electrolyte materials are showing high oxide ion conductivity (>0.1S/cm) at relatively lower temperatures (1073 K). The thermal and chemical compatibility of LSGM electrolyte is good with the adjoining cell components. These materials are also stable over wide oxygen partial pressure range unlike cerium/bismuth-based oxides. It will not undergo any reduction at lower oxygen partial pressure range. In general, the stable $LaGaO_3$ based electrolyte materials may be used as alternative electrolytes in SOFCs for low temperature operation(<1073 K) to overcome the practical problems such as severe restrictions on the choice of materials, electrode sintering, interfacial diffusion between electrode and electrolyte, mechanical stress due to different thermal expansion coefficients, etc. in the high temperature SOFC systems.
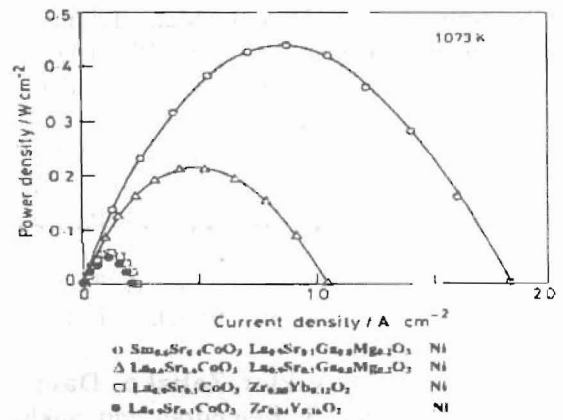

Fig. 4 Comparison of the power generation characteristics of SOFCs where Yb and Y-stabilized ZrO_2 and $LaGaO_3$ based oxide were used for electrolyte at 1073 K (Ref: 46)

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