

Tape casting of alternate electrolyte components for solid oxide fuel cells

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The solid oxide fuel cell (SOFC) consists of four electrochemically active solid components, viz., a porous cathode, a porous anode, a dense electrolyte and a dense interconnect to form stacks. Tape casting technology involves the dispersion of inorganic ceramic particles (electrolyte) in a liquid (solvent) medium followed by the addition of organic binders, plasticizers and deflocculating or defoaming agents to fabricate a thin ceramic sheet. In this research work, the selection and loading level of additives have been optimized to fabricate alternate electrolyte components of SOFC viz. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$, $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta}$ and $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-\delta}$ by tape casting technique. In order to remove the organic substances from green electrolyte components and sintering, the heat treatment of green tapes has been optimized by thermogravimetry differential thermal analysis (TG-DTA). The surface morphology of both green and pre-sintered components has been studied by Scanning Electron Microscopy (SEM).

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The solid oxide fuel cell (SOFC) derives its name from its solid electrolyte, yttria stabilized zirconia (YSZ). It is based upon the ability of oxide ions to be conducted through a solid at elevated temperatures. Erwin Baur and H. Preis in 1937 constructed the first SOFC using solid electrolyte, the oxide ion conductivity of which was $\sim 0.1 \text{ Scm}^{-1}$ at 1273 K^1 . In recent years, development of SOFC has gained enormous interest as a potentially economical, clean and efficient means of producing electricity. Solid oxide fuel cell consists of four electrochemically active solid components. (i) a porous cathode, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ to which the oxidant is supplied, (ii) a porous anode, Ni-YSZ to which the fuel is supplied, (iii) a dense electrolyte, YSZ which permits the flow of ions (but not electrons or reactants) between the anode and the cathode and (iv) a dense interconnect, $\text{La}_{1-x}(\text{Mg}/\text{Sr})_x\text{CrO}_3$ to form stacks. The material requirements of the SOFC components are: (i) Each component must have the proper stability (chemical, phase, morphological and dimensional) in oxidizing and/or reducing environments; (ii) Each component should have chemical compatibility with other components, i.e., there should not be any reaction between the components; (iii) The components should have proper conductivity. The cathode, anode and interconnect should have high electronic conductivity

values and the electrolyte should have high ionic conductivity; (iv) The ceramic components should have similar coefficients of thermal expansion to avoid separation or cracking during fabrication and operation; (v) They should have proper microstructure. The electrolyte and interconnect must be dense to prevent gas-mixing, whereas the anode and cathode must be porous to allow gas transport to the reaction sites; and (vi) In addition to the above requirements, other desirable properties for the cell components are high strength and toughness, ease of fabrication and low cost.

The high operating temperature promotes rapid reaction kinetics, allows reforming of hydrocarbon fuels (natural gas, coal gas, bio-gas) within the fuel cell and produces high-quality by-product heat suitable for use in bottoming cycle. Furthermore, because all the components are solid, SOFCs can be fabricated in very thin layers and cell components can be configured into unique shapes that are unachievable in fuel cell systems having a liquid electrolyte.

Principle of operation of solid oxide fuel cell (SOFC)

The electrode on the air side is 'cathode' on which oxygen molecules are reduced to oxide ions and incorporated into the electrolyte. The other electrode is 'anode' where the reactant gas/hydrogen is oxidized by oxygen, which comes through the electrolyte. The electron is extracted to the external circuit from

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cathode to the anode. The combination of cathode/electrolyte/anode is called a 'single cell'. Another important component of SOFC is the interconnect. Since the voltage generated by a single cell is not higher than 1 V, several single cells should be connected in series to obtain a useful voltage. The interconnect is the material which connects the anode of one cell and the cathode of the next cell. The interconnect must separate the fuel and the oxidant of the neighbour cells. Thus, this component is called 'separator' from its function of the gas separation.

Intermediate temperature solid oxide fuel cell (ITSOFC)

The major problems associated with high temperature SOFC are (i) severe restrictions on the choice of materials, (ii) electrodes sintering, (iii) interfacial diffusion between electrode and electrolyte and (iv) mechanical stress due to different thermal expansion coefficients. Another major problem reported in this device is the thermal mismatch of the components at the operation temperature². The primary advantages for lowering the operating temperature of SOFC below 1073 K are (i) to arrive at an optimum between performance and life-time of the stack and (ii) to reduce the overall system cost³.

Two approaches are considered to operate the SOFCs at reduced temperature. One is to make very thin (10–20 μm) layer of YSZ electrolyte, supported on thick electrode, either the anode or cathode. Another is the use of alternate electrolytes with high conductivity. Recently, oxygen ion conductor based on LaGaO_3 (ABO_3) partially substituted with 2+ ions (on A and B sites with Sr^{2+} and Mg^{2+} ions respectively) and rare earth partially substituted CeO_2 have been shown to be the promising candidates for ITSOFC working below 1073 K^{4–7}. In this study, alternate electrolytes such as doped LaGaO_3 ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ -LSGMO) and CeO_2 ($\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta}$ -CGO and $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-\delta}$ -CSO) were synthesized by self-propagation combustion technique^{8,9}. The above compounds were utilized for the preparation of thin components by tape casting technique.

Experimental Procedure

Tape casting process technology

The tape casting process involves three steps namely, milling, casting and drying^{10–13}. Milling involves preparation of castable slurry of the ceramic material with binder, plasticizer and other functional ingredients in suitable proportion in a solvent system.

Known quantity of ceramic powder (LSGMO/CGO/CSO) was mixed with poly vinyl butyral (PVB)/poly methyl methacrylate (PMMA) as binder, benzyl butyl phthalate (BBP)/poly ethylene glycol (PEG)/tri-cresyl phosphate (TCP) as plasticizer, silicone oil as defoamer, glyceryl trioleate (GTO) as dispersing agent and cyclohexanone as homogenizing agent. Toluene + methyl ethyl ketone (1:1 v/v), toluene + xylene (1:1 v/v), propanol + methyl ethyl ketone (1:1 v/v) and methyl ethyl ketone + trichloro ethylene (2:1/3:1 v/v) solvent systems were employed. Milling was carried out in a ball mill for 8 h.

After milling the viscosity of the slurry was modified by slow evaporation of the excess solvent in air with uniform stirring before casting in order to produce a good quality tape. A doctor blade assembly was used to obtain the green tapes with controlled thickness. The slurry was poured into the cavity of the doctor's blade assembly¹⁴. As it moved over the glass plate at a controlled speed, the slurry was cast uniformly on the glass plate in the form of a thin sheet of controlled thickness by using the knife-edge of the doctor's blade. The tape was dried slowly and the cured tape was flexible in nature. The cured ceramic tapes were used for further characterization.

Results and Discussion

The fabrication of electrolytes based on LSGMO/CGO/CSO materials with desired functional properties cannot be achieved easily in a single tape casting experiment, since the amounts of functional ingredients such as solvent, binder, plasticizer, etc. are to be optimized in a series of experiments. Further, the parameters such as, ease of handling, strength, flexibility, etc. are also to be adjusted with suitable addition of organic additives in order to bring out a good quality tape.

Role of ingredients

The solvents dissolve the organic materials and distribute them uniformly in the slurry. They are the vehicles that carry the ceramic particles in dispersion until they evaporate and leave a dense tape on the substrate. The binder (PVB/PMMA) provides strength to the green tapes after the evaporation of the solvent by bridging the ceramic particles together. When there was not enough binder, the resulting green tape had minute cracks on the surface and when the amount of binder was too high; on the other hand, the tapes contained many voids. However, the mechanical strength of the green tapes increased with increase in

the binder content. Generally, the green density values increase with increase in binder content.

The plasticizers modify the strength, flexibility and viscosity of the slip. These are the additives that soften the binder in the drying stage. In this work, PEG/BBP was used as plasticizer. These plasticizers were used to increase the flexibility and workability of the tapes. The dispersant gave a kind of coating on the ceramic particles and kept them in a stable suspension in the slurry due to electrostatic repulsion. GTO was used as dispersant in this work. Silicone oil was added to the ceramic slurry in order to improve the wetting characteristics. Cyclohexanone was added to the slurry before casting in order to improve the homogeneity of the slurry. The experimental compositions used for tape casting of alternate electrolyte materials indicated in Table 1.

Tape casting of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte

The tape prepared from LSGMO-1 composition (as like in the tape casting of ZrO_2 ¹⁰) is uniform without cracks, but has pinholes. Also, some portions of the tape stuck to the glass substrate. This sticking

behaviour originated because of the higher binder content. In the next experiments (LSGMO-2 and LSGMO-3), instead of 11.19% PVB binder 9.5% was taken and kept the other constituents same as LSGMO-1. This composition (LSGMO-2) yielded a good quality tape without any sticking problem whereas more pinholes appeared when compared to the previous one. It was reported that the ceramic powder surface was completely covered with a suitable quantity of dispersant during tape casting process⁸. It was thought that highly viscous slurry yielded tapes with pinholes. In order to substantiate this, an experiment (LSGMO-3) was carried out with 0.625% of GTO, 0.625% of cyclohexanone and keeping the other components as such. The tape fabricated with the above composition exhibited smooth surface appearance and had no pinholes. This combination yielded tape with the thickness of 1.0 mm. It was also reported that in the planar electrolyte-supported ITSOFC design, thickness of electrolyte ranges between 100 and 200 μm ¹⁵. Hence, the reduction of electrolyte tape thickness is more important especially for ITSOFC application.

Table 1 – The experimental compositions used for tape casting of alternate electrolyte materials

Tape code	Electrolyte powder (g)	PVB/PMM A (g)	PEG/liquid (mL)	BBP/TC P (mL)	GTO (mL)	Silicone oil (drops)	Cyclo-hexanone (mL)	Solvent System (mL)	Green tape thickness (cm)	Tape quality
LSGMO-1	20.00*	10.00+	2.2	1.8 [#]	1.00	3.00	1.00	Toluene-22.5 Xylene - 22.5	0.117	Pinholes
LSGMO-2	20.00*	8.00+	2.2	1.8 [#]	1.00	3.00	1.00	Toluene-22.5 Xylene - 22.5	0.089	Moderate
LSGMO-3	20.00*	8.00+	2.2	1.8 [#]	0.50	3.00	0.50	Toluene - 22.0 Xylene - 22.0	0.098	Excellent
LSGMO-4	10.00*	5.00+	2.2	1.8 [#]	0.50	3.00	0.50	Toluene - 15.0 Xylene - 15.0	0.023	Excellent
CGO-1	10.00**	10.00+	2.2	1.8 [#]	0.50	3.00	0.50	Toluene - 15.0 Ethyl Methyl Ketone - 15.0	0.031	Sticky. Rough surface appearance
CGO-2	11.00**	7.00+	2.2	1.8 [#]	0.50	3.00	0.50	PrOH - 15.0 MEK - 15.0	0.023	Sticky
CGO-3	10.00**	7.00+	2.2	1.8 [#]	0.50	3.00	0.50	Toluene - 15.0 Xylene - 15.0	0.037	Very good. No Pinholes
CGO-4	10.00**	2.00++	0.7	0.8 ^{##}	0.50	--	0.50	MEK - 20.0 TCE - 10.0	0.039	Sticky
CGO-5	10.00**	3.00++	2.0	0.8 ^{##}	0.50	--	0.50	MEK - 15.0 TCE - 7.5	0.047	Excellent
CSO-1	11.00***	7.00+	2.2	1.8 [#]	0.50	3.00	0.50	Toluene - 15.0 Xylene - 15.0	0.055	Very good. No Pinholes
CSO-2	10.00***	1.50++	0.7	0.8 ^{##}	0.50	--	0.50	MEK - 20.0 TCE - 10.0	0.032	Less binder
CSO-3	10.00***	2.00++	1.5	0.8 ^{##}	0.50	--	0.50	MEK - 15.0 TCE - 5.0	0.020	Excellent

*LSGMO - $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$; **CGO - $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta}$; ***CSO - $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-\delta}$; +PVB; ++PMMA; #BBP; ##TCP

Therefore, in the next composition (LSGMO-4), 9.4% of PVB binder was mixed with 18.86% of LSGMO powder and then with toluene + xylene (1:1 v/v) solvent system to form a slurry, keeping the other ingredients same as LSGMO-3. The tape obtained from this combination exhibited improved functional characteristics viz. flexibility and strength with smooth surface appearance. Thin LSGMO electrolyte tape prepared by this composition (LSGMO-4) is shown in the Fig. 1. From the result, it is found that the use of a toluene + xylene (1:1 v/v) solvents system is suitable to prepare thin LSGMO electrolyte tapes. Also, it is found out that the amount of solvent system must be fixed at the minimum to ensure good dissolution of organic components and good homogenization of the slurry. The optimization of tape casting slurries require the close control of numerous parameters with the aim to avoid cracks during drying. The crucial parameters controlling the quality of the LSGMO slurry and the LSGMO tape were the following ratios: binder/ceramic, plasticizer/ceramic, binder/plasticizer, binder/total liquid, plasticizer/total liquid and ceramic/total liquid. These ratios were found to influence the microstructure of the cast wares. The typical values employed for the tape casting of LSGMO electrolyte powder is presented in Table 2. From Table 2 and it is understood that the binder/ceramic ratio should be between 0.4 to 0.5 in order to produce high quality LSGMO tapes. And also, it is found out that the ratio of the binder or plasticizer or ceramic to total liquid also must be adjusted to get a green tape with desired

properties. It is also noted that the ratio between organic components (binder and plasticizers) and ceramic powder must be as low as possible to get homogeneous green LSGMO tapes.

Characteristics of green $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ tapes

The weight loss observed when the LSGMO green tapes were subjected to annealing for 2 h each at different temperatures are shown in Table 3. The volume and the density values obtained on LSGMO electrolyte tapes as a function of annealing temperature for 2 h duration are presented in Table 4. From Table 3, it is noted that the weights of the specimens ($1.5 \times 1.5 \text{ cm}^2$ area) were found to decrease gradually as the annealing temperature was raised from room temperature to 873 K. These experiments were carried out to understand the escape trend of all the organic functional ingredients from the tapes leaving a crack free surface. From the weight loss measurements, it is noted that the % weight loss for the LSGMO tapes varied between 40 and 50%. All (four LSGMO composition) the tapes exhibited voids/holes due to binder burn out from the tape after annealing at 873 K for 2 h. Also, from Table 3, it is

Table 2 – The typical ratio values used for the tape casting of LaGaO_3 based alternate electrolyte materials

Tape code/ Composition	Ratio			
	LSGMO-1	LSGMO-2	LSGMO-3	LSGMO-4
Binder/ Ceramic	0.500	0.400	0.400	0.500
Plasticizer/ Ceramic	0.200	0.200	0.200	0.400
Binder/ Plasticizer	2.500	2.000	2.000	1.250
Binder/ Total liquid	0.196	0.157	0.163	0.143
Plasticizer/ Total liquid	0.085	0.085	0.089	0.129
Ceramic/ Total liquid	0.392	0.392	0.408	0.286

Table 3 – The weight loss observed on LSGMO electrolyte tapes (area $1.5 \times 1.5 \text{ cm}^2$) at different annealing temperatures

Tape code	Initial weight (g)	Weight at 473 K (g)	Weight at 673 K (g)	Weight at 873 K (g)	% weight loss at 873 K
LSGMO-1	0.30	0.22	0.18	0.18	40.00
LSGMO-2	0.25	0.18	0.14	0.15	40.00
LSGMO-3	0.23	0.16	0.14	0.12	47.83
LSGMO-4	0.12	0.08	0.06	0.06	50.00

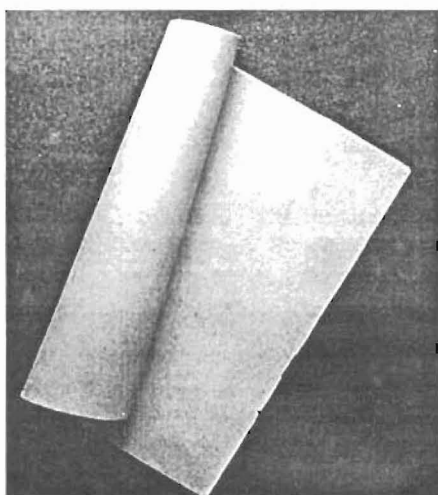


Fig. 1– Thin LSGMO electrolyte tape (LSGMO-4) prepared by tape casting process

Table 4 – Volume and density data obtained on LSGMO electrolyte tapes (area $1.5 \times 1.5 \text{ cm}^2$)

Temperature/ Tape code		LSGMO-1	LSGMO-2	LSGMO-3	LSGMO-4
Green	Thickness (cm)	0.117	0.089	0.098	0.023
	Volume (cc)	0.263	0.200	0.220	0.052
	Density (g/cc)	1.141	1.250	1.045	2.308
473 K	Thickness (cm)	0.114	0.082	0.098	0.020
	Volume (cc)	0.256	0.184	0.220	0.045
	Density (g/cc)	0.859	0.978	0.727	1.778
673 K	Thickness (cm)	0.114	0.082	0.096	0.020
	Volume (cc)	0.256	0.184	0.216	0.045
	Density (g/cc)	0.703	0.761	0.648	1.333
873 K	Thickness (cm)	0.110	0.079	0.088	0.016
	Volume (cc)	0.247	0.178	0.198	0.036
	Density (g/cc)	0.729	0.843	0.606	1.667
873 K	% shrinkage in thickness (%)	5.98	11.23	10.20	30.43
	% shrinkage in volume (%)	6.08	11.00	10.00	30.77
	% reduction in density (%)	36.11	32.56	42.00	27.77

noted that the volume of specimen decreased when the annealing temperature was raised. The reduction in thickness of the tapes was noted due to the gradual escape of organic ingredients from the tapes. The reduction in thickness of the tapes caused reduction in their volumes. Also, the % shrinkage in the volume of the LSGMO tapes is observed between 5 and 30%. Also, the % reduction in density at 873 K for all the tapes is found in the range of 28 to 36%.

TG-DTA measurements and micro-structural studies of LSGMO tape

The LSGMO tape is subjected to TG-DTA measurements at a heating rate of $10^\circ\text{C}/\text{min}$ in air from room temperature to 873 K. The experiment was aimed to obtain information of the binder burn out conditions from the green tape. Fig. 2 shows the TG-DTA pattern obtained on LSGMO tape. In the TGA pattern, the LSGMO tape showed a weight loss of 5% at 523 K. This was due to the removal of solvents from the tape. There was further reduction in weight to an extent of 20% in the range 523-598 K. It is reported that the binder (PVB) decomposes above 500 K. The organic plasticizer materials (PEG and BBP) also decompose above 573 K¹³. The decomposition of the binder, plasticizers and other organic ingredients was completed below 773 K. The total weight loss was 30% in the LSGMO tape at 873 K. The exothermic peaks appeared at 475, 650 and 720 K indicated the liberation of oxides of carbon from the organics employed¹⁶⁻²⁰. Fig. 3 shows the SEM picture

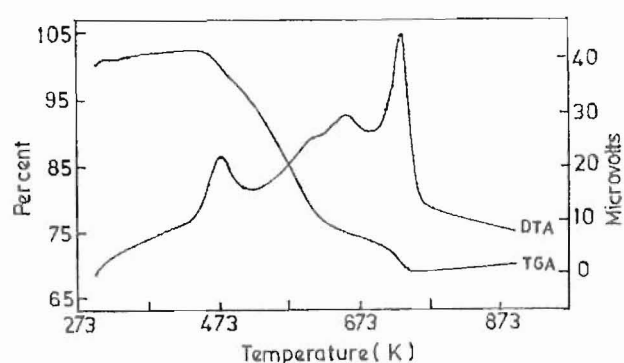


Fig. 2 – TG-DTA curves of green LSGMO tape

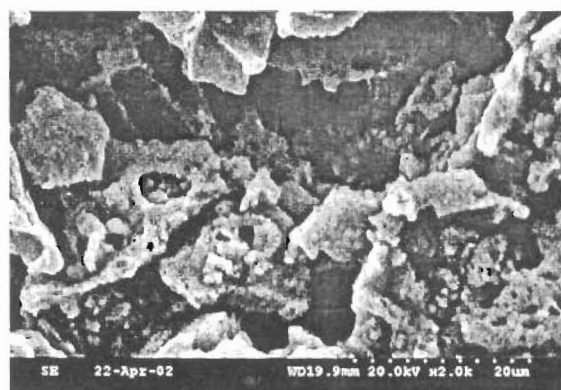


Fig. 3 – SEM photograph of green LSGMO tape

obtained on the green LSGMO-4 tape. SEM revealed the homogeneous particle packing in the tape. It is evident that the packing of ceramic particles depends on the binder content in the green tapes.

From TG-DTA studies, the heat treatment of LSGMO green tapes has been optimized as given as (i) heating from room temperature to 873 K at a rate of 2 K/min; (ii) soaking at 873 K for 1 h and cooling to room temperature; (iii) heating from room temperature to the sintering temperature of 1473 K at 2 K/min; (iv) soaking at 1473 K for 2 h for sintering and (v) cooling down to 773 K at 2 K/min and then to room temperature by natural cooling.

The fabricated LSGMO green tape was pre-sintered in between two alumina plates as per the first two steps. Pre-sintering was carried out in between alumina plates in order to avoid bending of tapes during the decomposition of organic ingredients. The pre-sintering was performed until 873 K (soaking time 1 h) and then cooling procedure was performed until room temperature in order to remove the top alumina plate. Then, final sintering was performed from room temperature to 1473 K as per the schedule. The photograph of the green and sintered LSGMO tape (1473 K) is shown in Fig. 4. Fig. 5 shows the SEM photograph of LSGMO tape sintered at 1473 K for 2 h. It was seen that the grains in LSGMO tape are between 50-100 μm size and were connected with each other leaving pores. The surface of the sintered tape was uniform. It is evident that sintering beyond 1473 K is necessary to fabricate dense LSGMO electrolyte.

Tape casting of $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2.5}$ electrolyte

In the case of CGO electrolyte tape casting process, solvent systems other than toluene + xylene had also been tried. Initially (CGO-1), 17.2% of PVB binder was mixed with 17.2% of CGO electrolyte powder for the preparation of slurry with toluene + methyl ethyl ketone (1:1 v/v) solvent system keeping the other ingredients similar to that of the optimized LSGMO tape casting process. The resulting tape with this composition stuck onto the glass substrate. In the second experiment (CGO-2), instead of 17.2% of PVB binder 12.5% was taken and instead of toluene + methyl ethyl ketone solvent system, propanol + methyl ethyl ketone (1:1 v/v) solvent system was taken keeping the other ingredients as such. This compositional tape also stuck onto the glass substrate and exhibited a rough surface appearance. So, in the third experiment (CGO-3), the solvent system was changed. Instead of propanol + methyl ethyl ketone solvent system, toluene + xylene solvent system had been tried while keeping the other ingredients as such. The tape prepared from the above combination

showed good characteristics with improved surface appearance and without pinholes. It is reported that the PMMA is the best binder for the fabrication of interconnector materials for SOFC by tapecasting procedure²¹. In the fourth composition (CGO-4), 4.49% of PMMA binder, 1.573% of PEG, 1.797% of TCP plasticizers, 1.12% of GTO dispersant and 1.12% of cyclohexanone homogenizer were mixed with 22.7% of CGO powder for the preparation of slurry with trichloro ethylene + methyl ethyl ketone solvent system. This combination yielded a good tape while some portions cracked while removing the green tape from the glass substrate. This problem was due to the low binder content on the slurry. In the fifth experiment (CGO-5), instead of 4.49% of PMMA binder 7.63% was added and kept the other constituents same. This composition yielded a good CGO electrolyte tape in terms of strength, flexibility, etc. Also, the surface of the tape prepared by the above composition was smooth with no pinholes.

Tape casting of $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2.5}$ electrolyte

The optimized compositions for CGO tapecasting (CGO-3 and CGO-5) have been tried for the tape casting of CSO electrolyte. In the first experiment

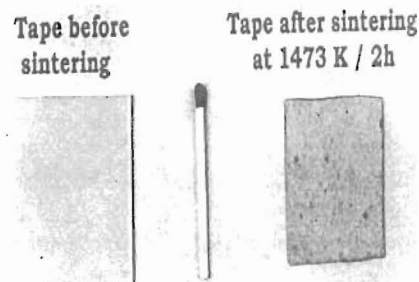


Fig. 4 – The photograph of the green and sintered LSGMO tape

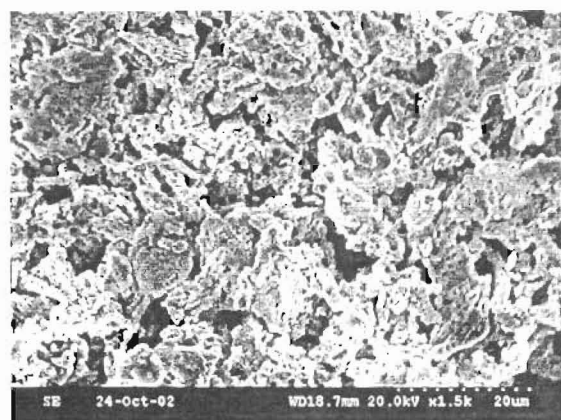


Fig. 5 – The SEM photograph of LSGMO electrolyte tape sintered at 1473 K for 2 h

(CSO-1), 12.5% of PVB binder was mixed with CSO electrolyte powder then made of slurry in toluene + xylene (1:1 v/v) solvent system by keeping the other ingredients same as CGO. This composition yielded a good tape with smooth surface. The higher binder content may influence the component property after sintering. Hence, in the second experiment (CSO-2), PMMA binder was chosen instead of PVB as in the case of CGO tape casting. In the second experiment, 3.4% g of PMMA binder was mixed with CSO powder, 1.81% of TCP and 3.41% of PEG plasticizers, 1.14% of GTO dispersant and 1.14% of cyclohexanone homogenizer for the preparation of slurry with trichloro ethylene + methyl ethyl ketone solvent system. This combination yielded thin sheet with smooth surface appearance. However, the tape cracked while bending. This cracking problem was mainly associated with the low binder content. So, in the third experiment (CSO-3) instead of 3.4%, 5.66% PMMA binder was taken keeping the other ingredients same as above. This combination (CSO-3) yielded tape with surface smoothness. The ceramic to binder ratio for the third (CSO-3) composition was 0.5 while it was 1.4 in the case of first (CSO-1) composition. More ceramic and less binder content in the tape casting composition usually resulted as the best functional component after high temperature sintering process^{22,23}.

From the above results, it is found out that the toluene+xylene and methyl ethyl ketone + trichloro ethylene solvent systems are more preferred for the tape casting of ceria based electrolyte powder. The inhomogeneity and cracks on the surface of the tapes were found to be very sensitive to the ratio of the solvent systems. The optimization experiments on

tapecasting composition was mainly based on the following important ratios: They were binder/ceramic, plasticizer/ceramic, binder/plasticizer, binder/total liquid, plasticizer/total liquid and ceramic/total liquid. These ratios played main roles in producing quality ceria based electrolyte tapes. The typical ratio values employed for the tape casting of ceria based electrolyte powder is presented in Table 5. From Table 5, it is noted that binder/ceramic ratio was 0.6 for the tapes prepared by PVB binder and it was only 0.2 in the case of tape prepared by PMMA binder with suitable solvent proportions. Also, it is observed that plasticizer/ceramic ratio is lesser (0.23) for the tapes prepared by ethyl methyl ketone + trichloro ethylene solvent system than the tapes prepared by toluene + xylene solvent systems (~0.4). It is found out that the ceramic to organic ingredients have to be adjusted by experiments in order to obtain green tapes with desired properties. In general, the ceramic to organic ingredients ratio should be as high as possible to produce ceria based electrolyte components without any holes/cracks and also with sufficient strength.

Characteristics of green ceria based electrolyte tapes

The weight loss observed when the CGO/CSO electrolyte tapes were subjected to annealing for 2 h each at different annealing temperatures is shown in Table 6. The volume and density values obtained on ceria based electrolyte tapes as a function of annealing temperature for 2 h duration are presented in Table 7. From Table 6, it is noted that the weight of the ceria based electrolyte tape decreased with increase in annealing temperature. The weight loss observed in the tapes was due to the burn out of organic ingredients from the tapes. Also, it is found

Table 5 – The typical ratio values used for the tape casting of ceria based electrolyte materials

Tape code/ Composition	Ratio							
	CGO-1	CGO-2	CGO-3	CGO-4	CGO-5	CSO-1	CSO-2	CSO-3
Binder/ Ceramic	1.000	0.636	0.700	0.200	0.300	0.636	0.150	0.200
Plasticizer/ Ceramic	0.400	0.364	0.400	0.150	0.280	0.364	0.150	0.230
Binder/ Plasticizer	2.500	1.750	1.750	1.333	1.071	1.750	1.000	1.150
Binder/ Total liquid	0.286	0.200	0.200	0.060	0.114	0.200	0.045	0.082
Plasticizer/ Total liquid	0.129	0.129	0.129	0.048	0.119	0.129	0.048	0.109
Ceramic/ Total liquid	0.286	0.314	0.286	0.298	0.380	0.314	0.298	0.411

out that the weight of the tapes after annealing at 673 K is close to the weight of the tapes after annealing at 873 K. From this, it is drawn that most of the organic constituents get oxidized at 700 K. The % weight loss after annealing at 873 K for 2 h was 55% for the tapes prepared by PVB binder with toluene/xylene solvent system. But, the % weight loss was in the range of 25-40% for the tapes prepared by PMMA binder with ethyl methyl ketone + trichloro ethylene solvent system. The tapes prepared with PMMA binder showed a uniform surface without any voids after pre-sintering at 873 K. From this, it is noted that the tape with low% of organic constituents showed crack free structures after initial sintering at 873 K for 2 h. From Table 7, it is seen that the volume of the tapes decreased when the annealing temperature was raised. The binder burn out caused reduction in the thickness of the tapes, which reduced the volume of the tapes. The density also got reduced until 673 K. From Table 7, it is evident that the % shrinkage in volume is in the

range of 10-20% and the % reduction in density is in range of 40-50% after annealing at 873 K for 3 h for the tapes prepared with PVB binder and toluene + xylene solvent system respectively. But, the % shrinkage in volume is in the range of 5-25% and the % reduction in density is in the range of 15-40% after annealing at 873 K for 3 h for the tapes prepared with PMMA binder and ethyl methyl ketone + trichloro ethylene solvent system. The weight loss and change in volume/density obtained on ceria based electrolyte tapes have given useful information about the slow escape of the organic functional ingredients from them.

TG-DTA measurements and micro-structural studies of ceria based electrolyte tapes

The CGO and CSO electrolyte tapes were subjected TG-DTA measurements at heating rate of 10°C/min in air from room temperature to 873 K. Figs 6 and 7 show the TG-DTA patterns of CGO-3 and CSO-1 electrolyte tapes in air respectively. In the

Table 6 – The weight loss observed on ceria based electrolyte tapes (area $1.5 \times 1.5 \text{ cm}^2$) at different annealing temperatures

Tape code	Initial weight (g)	Weight at 473 K (g)	Weight at 673 K (g)	Weight at 873 K (g)	% weight loss at 873 K
CGO-1	0.18	0.16	0.09	0.08	55.55
CGO-2	0.13	0.12	0.06	0.06	53.84
CGO-3	0.18	0.16	0.08	0.08	55.55
CGO-4	0.18	0.16	0.12	0.11	38.88
CGO-5	0.16	0.14	0.09	0.09	43.75
CSO-1	0.27	0.24	0.13	0.13	51.85
CSO-2	0.28	0.26	0.20	0.20	28.57
CSO-3	0.16	0.15	0.11	0.10	37.50

Table 7 – Volume and density data obtained on ceria based electrolyte tapes (area $1.5 \times 1.5 \text{ cm}^2$)

Temperature/Tape code		CGO-1	CGO-2	CGO-3	CGO-4	CGO-5	CSO-1	CSO-2	CSO-3
Green	Thickness (cm)	0.031	0.025	0.037	0.039	0.047	0.055	0.032	0.020
	Volume (cc)	0.070	0.056	0.083	0.088	0.106	0.124	0.072	0.045
	Density (g/cc)	2.571	2.321	2.169	2.045	1.509	2.177	3.889	3.555
473 K	Thickness (cm)	0.047	0.028	0.047	0.037	0.045	0.061	0.030	0.015
	Volume (cc)	0.106	0.063	0.106	0.083	0.101	0.137	0.067	0.034
	Density (g/cc)	1.509	1.905	1.513	1.928	1.386	1.752	3.880	4.412
673 K	Thickness (cm)	0.032	0.020	0.032	0.037	0.044	0.047	0.030	0.015
	Volume (cc)	0.072	0.045	0.072	0.083	0.099	0.106	0.067	0.034
	Density (g/cc)	1.250	1.333	1.111	1.446	0.909	1.226	2.985	3.235
873 K	Thickness (cm)	0.028	0.020	0.032	0.037	0.044	0.045	0.029	0.015
	Volume (cc)	0.063	0.045	0.072	0.083	0.099	0.101	0.065	0.034
	Density (g/cc)	1.270	1.333	1.111	1.325	0.909	1.287	3.077	2.941
873 K	% shrinkage in thickness (%)	9.68	20.00	13.51	5.13	6.38	18.18	9.37	25.00
	% shrinkage in volume (%)	10.00	19.64	13.25	5.68	6.60	18.55	9.72	24.44
	% reduction in density (%)	50.60	42.57	48.77	35.21	39.76	40.88	20.88	17.27

TGA pattern, both CGO and CSO tapes showed a weight loss of 15% at 550 K due to the evaporation of solvent from the tapes. A further weight loss of 30% was observed in the range of 550-650 K. The weight loss above 550 K indicated the removal of binders and plasticizers from the tapes. Decomposition of binders and plasticizers and other ingredients got completed at 850 K. From the TGA traces, it was understood that the net weight loss due to the removal of the organic ingredients was 50% in both CGO and CSO tapes. Fig. 8 shows the microstructure of $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-8}$ (CGO-3) green electrolyte tape prepared by tape casting technique. From Fig. 8, it was noticed that there was no uniform distribution of ceramic particles and binder on the surface. Also, the grains are in the range of 150-200 μm . Fig. 9 shows the microstructure

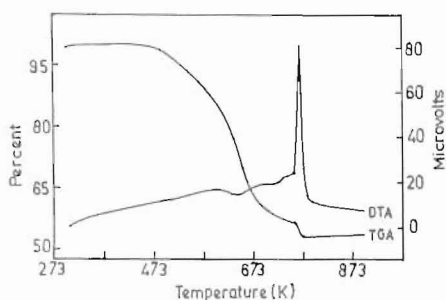


Fig. 6 – TG-DTA curves of green CGO green tape.

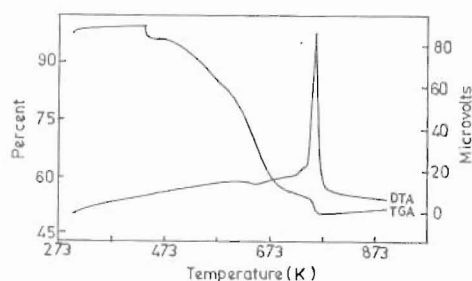


Fig. 7 – TG-DTA curves of green CSO green tape.

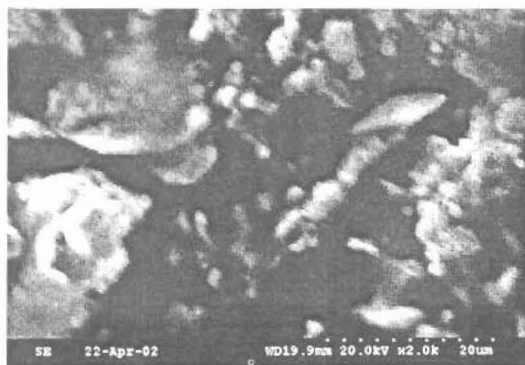


Fig. 8 – SEM photograph of the green CGO tape

of $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-8}$ (CSO-1) green electrolyte tape prepared by tape casting technique. It is seen that the binder is uniformly distributed with the ceramic particles. The grain size was around 250 μm . Also, from Fig. 10, it was evident that all the ceramic particles were completely covered by the organic ingredients.

The TG-DTA patterns reveal the sintering conditions to be adopted for the $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-8}$ and $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-8}$ tapes. The optimum heating conditions were same as in the case of LSGMO green tape.

The fabricated CGO and CSO green electrolyte tapes were heat treated as in the case of LSGMO green tape. The photograph of the green and sintered CSO electrolyte specimen is shown in Fig. 10. Figs 11 and 12 show the microstructure of CGO and CSO tapes sintered at 1473 K for 2 h respectively. The grains were uniform. Some big agglomerates (100 μm) leaving small pores (2-5 μm) in between, were also seen. It is understood that sintering of CGO and CSO electrolytes have to be carried out beyond 1473 K to realize tapes with desirable property.

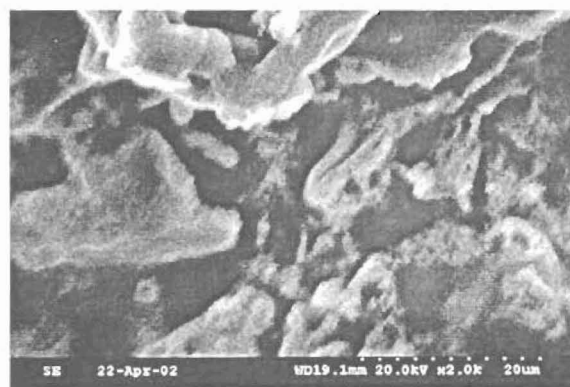


Fig. 9 – SEM photograph of the green CSO tape

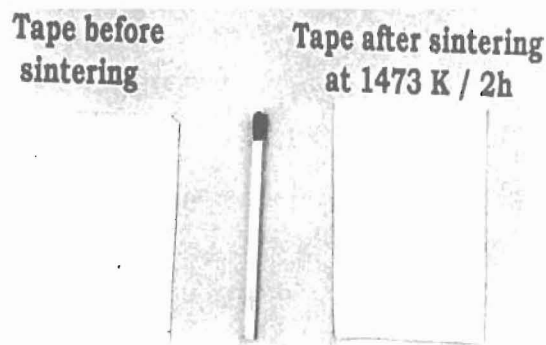


Fig. 10 – The photograph of the green and sintered CSO tape

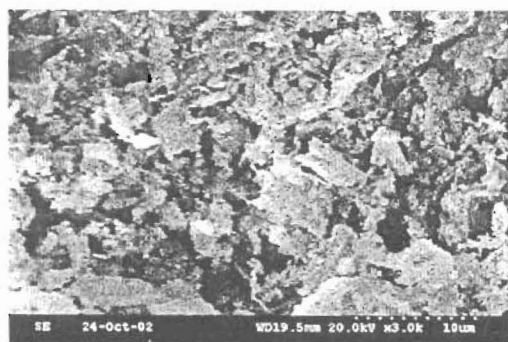


Fig. 11 – The SEM photograph of CGO electrolyte tape sintered at 1473 K for 2 h

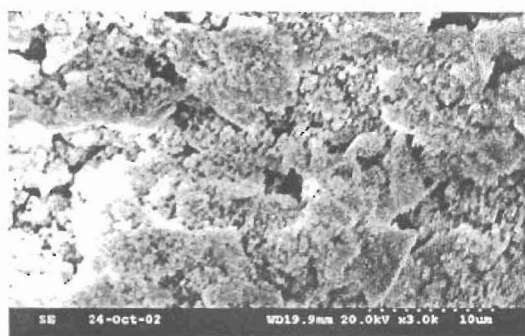


Fig. 12 – The SEM photograph of CSO electrolyte tape sintered at 1473 K for 2 h

Conclusions

Fabrication of thin $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$, $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{2-\delta}$ and $\text{Ce}_{0.80}\text{Sm}_{0.20}\text{O}_{2-\delta}$ electrolyte tapes from fine powders by tape casting technique for ITSOFC is dealt with. LSGMO tapes prepared with PVB binder and toluene + xylene solvent system exhibited desirable microstructures. The CGO and CSO green electrolyte tapes prepared with both PVB binder and toluene + xylene solvent system and PMMA binder with MEK/TCE solvent system exhibited desirable characteristics. The pre-sintered (at 873 K) CGO and CSO specimens prepared with PMMA binder showed better characteristics than the specimens prepared with PVB binder. From the optimized tape casting compositions, LSGMO, CGO and CSO electrolyte tapes in large size components can also be prepared for ITSOFC.

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