

## TAPE CASTING - A VERSATILE METHOD OF MAKING FUEL CELL COMPONENTS AND THEIR CHARACTERISATION

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Among the various methods for making the electrodes and electrolyte structures of fuel cells, the tape casting method is a very attractive technique. The materials employed with regard to the fabrication of components by this method for molten carbonate fuel cells are discussed. The physical characteristics of the green tapes are thickness, density, weight loss and porosity. The heating rate is determined by the TGA analysis of the green tapes.

**Keywords:** Tape casting, fuel cell, characterization, porosity.

### INTRODUCTION

Fuel cell is an electrochemical energy conversion device which converts the free energy of the fuel into electricity. To date, two types of fuel cells, namely, molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) are under development for electric utility power generation [1,2]. The planar design is very attractive because of high efficiency, more simple structure and potential scaling up. In this design the anode, cathode and electrolyte structures are assembled as shown in Fig. 1. The materials employed in these two types of fuel cells are entirely different [3]. Both devices can be made by assembling the individual plates into stacks, just like a voltaic pile.

The MCFC uses molten carbonates immobilized in a porous ceramic matrix, whereas the SOFC employs all ceramic materials. Different techniques have been described in literature to make thin and flat structures of SOFC components [4,5]. Among the various methods available, the tape casting method is a very attractive technique for forming large area, thin and flat ceramic layers [6]. Recently there is a growing interest to adopt this technique to produce the electrolyte [7-12], cathode [13] and interconnector [14-16] structures of SOFC. But MCFC employs metals (nickel powder) as electrodes. Only the fabrication of  $\text{LiAlO}_2$  matrix is reported to be by tape casting method [17-20]. Still many

of the technical details of these processes remain secret and proprietary.

In this paper, the materials employed for the production of electrode and matrix structures by tape casting method and their characterisation techniques are presented.

### EXPERIMENTAL

The matrix material powder was  $\text{LiAlO}_2$  powder, prepared by combustion synthesis as described elsewhere [21]. INCO 255 nickel powder was used to make the electrodes. Commercially available materials were used as solvents, binders and plasticizers.

#### The tape casting procedure

The tape casting process essentially consists of three key steps milling, casting and drying [22-23]. The tape casting involves the preparation of a slurry of the ceramic material with binder and plasticizer in suitable proportions in a solvent system. Both aqueous and nonaqueous solvent systems have been tried. Poly vinyl alcohol (PVA) is used as the binder in aqueous systems and poly vinyl butyral (PVB) in non aqueous systems. The compositions and nature of other additives employed by us are covered by a proprietary technique. The ingredients are mixed either in a single stage or in two stages each time for 2 to 6 hours. In the latter case, the two mix are combined together into a single mix and milled for another 2 h. The particles are broken uniformly and a low viscosity slurry is produced during the first stage. During the second stage, the binder dissolves in the solvent and binds the ceramic particles. The plasticizer is used to

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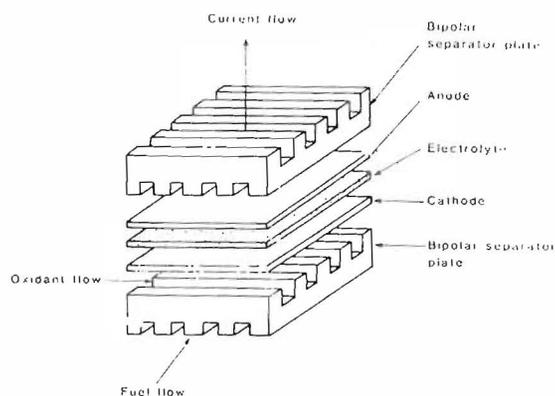


Fig. 1: Expanded view of repeating unit in a plate-type molten carbonate fuel cell stack

modify the properties of the binder. Usually the other additives like dispersants to keep the powder in the suspension, are also added [24]. The optimal amount of these are based mainly on trial and error methods.

After milling, the slurry is deaired to evaporate the excess solvent before casting. The viscosity of the slurry is modified such that it can be handled to produce good quality tapes. A doctor blade assembly as shown in Fig. 2 was used for making green tapes of desired thickness.

The slurry is poured into the cavity of the doctor blade assembly. As it moves over the glass plate at a uniform speed, the slurry is spread uniformly on the flat substrate in the form of a thin sheet, to a controlled thickness with the knife edge of the doctor blade. The thickness of the cast

\* Average values

TABLE I: Additives employed in the Tape Casting process

Component	Matrix		Electrodes Aqueous
	Aqueous	Non aqueous	
Substrate	LiAlO <sub>2</sub>	LiAlO <sub>2</sub>	Ni INCO 255
Solvent	Water	MEK+Toluene	Water
Binder	PVA	PVB	PVA
Plasticizer(1)	PEG	PEG	PEG
Plasticizer(2)		DOP/DBP/BBP	
Dispersant/ Defloculant	Oleic acid	Oleic acid	Oleic acid
Defoamer	Silicone Emulsion	Silicone oil	Silicone oil

ware depends upon the blade gap. The casting parameters of this process are described in Ref.25. The tape is dried slowly and then the cured tape is removed from the substrate and stored. The cured tape is flexible in nature.

The characterisation of tapes include thickness and density measurements of green tapes, shrinkage factor during curing and storing. The TGA and DTA curves were obtained in air using PL Thermal Sciences, Model STA 1500, Thermal Analysis System to determine the weight loss during heat treatment and to determine the binder removal conditions.

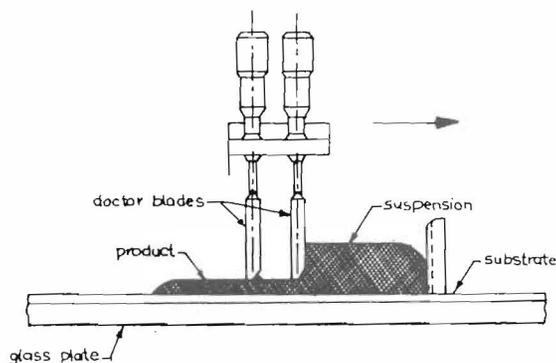
## RESULTS AND DISCUSSIONS

### The casting process

The various additives employed in the tape casting process is indicated in Table I. Several different organic systems as described in Ref.26 have been tried in the tape casting process. The properties of the slurry are reported to be determined by the composition and powder characteristics like particle size and surface area of the ceramic powders [9].

The role of various additives employed are: The solvent dissolves the binder and other components and evaporates slowly after the tape is cast. The binder is used to form an adhering film around the powder particles and to impart strength and handability to the green tape. Maintaining particles of the ceramic in suspension, and avoiding flocculation which would accelerate settling is of prime importance and is achieved by adding dispersants which modify the electrical double layer surrounding each particles [27,28]. The plasticizers modify the strength, flexibility and viscosity of the slip.

The above systems are all based on organic compounds. Water soluble binders, such as acrylics have obvious advantages in terms of nontoxicity associated with the



Details of the tape casting process.

Fig. 2: Doctor blade assembly

**TABLE II: Weight ratios for the Tape Casting slip formulation**

Ratios	Matrix		Electrodes Aqueous
	Aqueous	Non aqueous	
Solid/Total liquid	0.31	0.52	1.04
Binder/Solid	0.09	0.07	0.11
Binder/Plasticizer	0.33	0.80	0.28
Binder/(Binder+Plasticizer)	0.25	0.50	0.13
Binder/Liquid	0.09	0.04	0.10
Plasticizer/Solid	0.16	0.20	0.17
Plasticizer/Liquid	0.26	0.10	0.21
Dispersant/Solid	0.06	0.05	0.05
(Binder+Plasticizer)/Solid	1.14	0.30	0.78

organics and lower cost. The tape casting process based on aqueous systems has also been described in literature [29-31]. Aqueous slurries are very sensitive to the multiphase components particularly organic additives, which try to segregate the ceramics. Wetting agents (Triton X-100) and defoamers like silicones are also added.

Polymeric additives have been reported to have a great influence on the processing parameters in the production of high performance ceramics. The interaction between the organic addition and the inorganic ceramics are also reported [32]. Usually citric acid is recommended as an additive and dispersant for aqueous suspensions [30,33]. We have adopted a different approach to use other acids as an additive [34]. The deaeration is an essential step to remove the trapped gas bubbles. During the drying stage (curing), the solvents evaporate at a slow rate leaving the tape with ceramics and binders only. Water based systems take 8-12 hours for drying. Slow drying rate is preferred to avoid surface roughness and skin formation. The drying characteristics

depend upon the nature of solvent systems, dispersant and plasticizer employed. It is a common practice to use mixture of solvents to control the drying rate of the tape [26]. The drying conditions depend upon the length of the cast ware, the humidity and air above the cast specimen. These conditions are carefully controlled to minimise curling, cracking etc.

The plasticizer is usually having a lower molecular weight than the binder. This provides higher flexibility to the green tape for easy handling and storage. The plasticizer also acts as a release agent and helps in removing the tape from the glass substrate without tearing. The green tape containing no plasticizer was found to be fragile and stuck to the glass plate, while the presence of plasticizer prevented sticking of the green tape. Poly ethylene glycol (PEG 200) liquid and glycerol have been found to be suitable for aqueous based systems, while PEG with dibutyl phthalate (DBP) or dioctyl phthalate (DOP) were preferred for nonaqueous systems.

The critical parameters controlling the quality of the slurry and the tape are the different ratios of the following ceramic/binder, ceramic/solvent, ceramic/dispersant, plasticizer/binder, effect of total binder, ceramic/(binder + plasticizer), binder/(binder + plasticizer) etc. These ratios may vary depending upon the ceramic or metal powder and ultimately influence the porosity values. The nominal values employed by us are reported in Table II.

A binder/solid ratio higher than 5 wt% was found to be necessary to avoid cracks during drying. The binder/(binder + plasticizer) ratio is important to avoid fissuring, while handling the green tapes. The solid/liquid ratio will give details regarding the shrinkage during curing (after casting) and packing factor. The lower the solid/liquid ratio, lower will be the viscosity of the slip, very thin tapes will be produced and shrinkage will be more. On the other hand (binder + plasticizer)/solid ratio will determine the voids created during sintering and the porosity of the resultant body. This will also impart mechanical strength to the green tape. The lower value will result in poor handling strength. Normally as much plasticizer is required as the binder for optimum results.

**Characteristics of the green tape**

The blade gap, the thickness of the tape, the shrinkage factor during curing are given in Table III. The shrinkage factor is normally 50%. The dried green tape thickness is reported to depend upon the slip viscosity, casting rate, blade gap setting and reservoir height behind the doctor blade [35]. These conditions must be controlled to obtain uniform tapes. The green density values are also indicated in the table.

An important consideration in the tape casting process is the binder content, which decompose slowly on heating. The

**TABLE III: Characteristics of the Tape Cast MCFC components**

	Matrix		Electrodes Aqueous
	Aqueous	Non aqueous	
Blade gap (mm)	2.000	2.000	2.030
* Thickness (mm)	1.318	0.806	1.076
* Shrinkage (%)	34.08	59.70	47.09
* Density (g/cc)	1.135	1.297	1.177

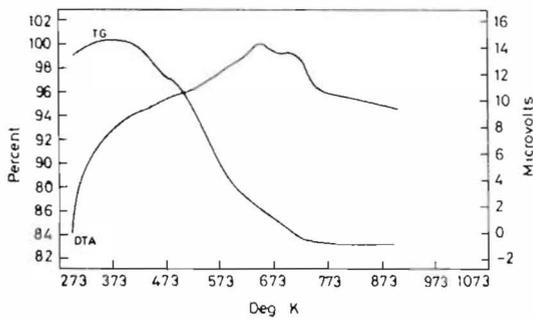


Fig. 3: TGA/DTA curve of the aqueous Ni tape

heating rate is usually less than 1 K/min. The result is that the shape and strength of the tape are not disturbed much in the pre-sintering stage. The binder migration is an important parameter and depends upon the binder/solid ratio [36,37]. TGA and DTA are used to characterise the green tapes.

The typical DTA/TGA curve for the green nickel tape (aqueous) and the matrix tapes (non aqueous) are shown in figures 3 and 4 respectively. The DTA, TGA curves were obtained at 10 K/min. At temperatures below 393 - 443 K, the evaporation of the solvent system is completed. This weight loss is 10% maximum. Further there is second weight loss upto 673 K.

Decomposition of binder and plasticizer is completed below 673 K. The initial shrinkage is due to the organic solvent removal. The secondary shrinkage is higher upto 40%. This is dependent upon the ratio of binder and plasticizer to solid. With Ni tapes the DTA curve shows an increase in weight due to oxidation of Ni above 723 K. But with  $\text{LiAlO}_2$  the reduction is complete at 673 K and remains constant upto 923 K. Increase of temperature beyond 923 upto 1673 K for

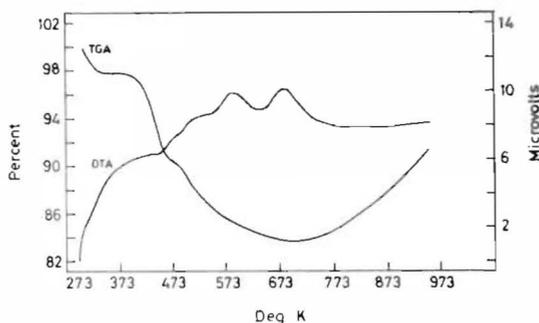


Fig. 4: TGA/DTA curve of the non-aqueous matrix tape

the matrix tapes will show a further shrinkage in size due to sintering of the ceramic ( $\text{LiAlO}_2$ ) particle. This portion is not shown in the figure. This shrinkage due to high temperature sintering is dependant upon the ceramic particle size, surface area and volume loading. This is a very critical parameter for making electrolyte and inter connection structure of SOFC, since they need to be gas light, with zero porosity and 95% of the theoretical density.

The characteristic DTA and TGA patterns reveal the sintering conditions to be employed [38]. Either the component can be sintered outside the cell inside the cell called in situ sintering [39]. The optimum values for presintering and sintering the electrodes and matrix are arrived from the DTA results, in the following steps.

- (i). heating from room temperature to 423 K at 1 K/min under nitrogen.
- (ii). soaking at 423 K for 3 h to remove the solvent.
- (iii). heating from 423 K upto 623 K at 1° K/min in  $\text{N}_2$ .
- (iv). soaking at 623 - 673 K for 3 h. (binder removal).
- (v). heating from 673 K - maximum sintering temperature 1123 K for electrodes at 1 K/min in hydrogen.
- (vi). soaking at maximum temperature 1123 K/hour sintering in  $\text{H}_2$
- (vii) cooling to room temperature at 1 K/min in  $\text{H}_2$

The above has resulted in good quality sintered material for use in molten carbonate fuel cells.

### Multilayer tape casting

Another important aspect of the tape casting process is the multilayer tape casting[39], in which the electrode and electrolyte structures are cast one over the other to produce a laminated structure. This is possible when a common binder and solvent system is employed for both the layers. The composition ratio's for the two different layers may be different particularly depending upon the nature of the material, particle size, and surface area. The common binder and solvent will not pose additional problems to the tape handling and burnt out conditions during presintering. The shrinkage of the two layers will be different and heating rate necessarily must be lower to avoid any thermal stress and mismatch between them. This becomes a stringent requirement for fabrication of monolithic SOFC components with corrugated shape[40,41] mismatch can cause cracks. But this problem has also been overcome by proper control of experimentation.

### CONCLUSION

Tape casting process by itself is an unique material architecture. It offers several potential advantages. Very thin,

flat ceramic substrates are produced with reproducible limits with desired final characteristics. The reliability is more and it is a low cost technique. Very large area samples are produced. The flows associated with this process is very much less compared to other sophisticated deposition techniques. Hence this technique is gaining interest to produce the electrode and electrolyte materials for assembling large scale planar fuel cell components.

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