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PREPARATION OF ELECTROLYTE MATRIX STRUCTURES BY AQUEOUS AND NON-AQUEOUS TAPE CASTING METHOD FOR MOLTEN CARBONATE FUEL CELLS

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The fabrication of thin structures of electrolyte (Li_2CO_3 and K_2CO_3) and matrix γ–$LiAlO_2$) is an essential pre-requisite for the assembly and testing of molten carbonate fuel cells which operate at 923 K. The process involves making a slurry of the ceramic oxide/carbonate powders in a solvent with suitable binders and plasticizers. Both aqueous and non-aqueous solvents were employed. The resulting slurry was cast over a glass plate making use of a doctor blade assembly. Thin tapes in the thickness range 0.25-1.0 mm were produced. The maximum size that could be obtained was 30 x 36 cm. The parameters affecting their quality are discussed.

Keywords: Lithium aluminate, matrix, tape casting, molten carbonate fuel cells

INTRODUCTION

The key factors in the commercialization of Molten Carbonate Fuel Cells (MCFC) technology are the MCFC cell life and cell performance at 923 K. Among the various active components of MCFC, the development of electrolyte layer sandwiched between two nickel electrodes has received significant research attention [1- 3]. The electrolyte is a mixture of molten Li_2CO_3 + K_2CO_3 (62:38 mole%) embedded in γ-$LiAlO_2$ ceramic support, which serves as the matrix. This matrix layer maintains the ionic conductance within cell, provides structural integrity as a separator for the gaseous reactants and electrodes. Several studies have been reported on the pore structure of the matrix, stability of the matrix material itself in molten carbonate [4-7]. Alternate materials have been reported for use as matrix in MCFC [8,9]. Not withstanding the above, the γ-$LiAlO_2$ is continuously used as matrix material in the present day MCFC. Various additives like sub-micron size ceramic particles of Al_2O_3 or $LiAlO_2$ [10] or ceramic fibres [11,12] have been tried for reinforcement and to avoid matrix cracking.

There are various methods reported in literature regarding the fabrication of matrix structures. Hot pressing of the matrix powder with electrolyte mixtures was the standard method of fabrication of a carbonate fuel cell matrix (tile) in 1980s [13 - 15]. One of the challenges to MCFC technology still remains, is the development of a cost effective (< 1 mm thick) larger area matrix sheets, which should meet the technical requirement of long term stability and durability under MCFC operating conditions at 923 K. Because of the inherent functional and manufacturing problems with the hot pressed tiles, alternate fabrication procedures like hot rolling [16], roll milling [17,18] and electrophoretic deposition [19] were adopted. Alternatively, fabrication of thin sheets of $LiAlO_2$ matrix incorporating Al_2O_3 fibre by a process similar to the paper making method has been adopted to produce larger area plates [20- 22]. Recently, the tape casting process, popularly known as "Doctor Blade Process" or "Knife Coating" technique, which is used widely in the processing of ceramics [23] has been adopted by various developers.

The tape casting process was adopted because it is a simple method and also suitable for low cost fabrication of thin matrix structures with larger area [24-26]. The tape casting process for making a combined electrode + electrolyte layer has also been reported [27]. An in-cell sintering procedure was followed in the latter [28].

Though the technique is familiar, the ingredients employed for the slurry preparation and the casting procedure is covered by proprietary specifications. Hence an attempt has been made to prepare matrix tapes from γ-$LiAlO_2$ powder

TABLE I: Characteristics of the tape casting slurry

Function of the additive	Nonaqueous material		Aqueous material	
Ceramic	γ-LiAlO$_2$		γ-LiAlO$_2$	
Solvent	Ethanol+ethyl methyl ketone		Water	
Binder	Polyvinyl butyral (PVB)		Polyvinyl alcohol emulsion (PVA) (15 wt%)	
Plasticizer	Polyethylene glycol (PEG-3000) + Benzyl butyl phthalate (BBP)		Glycerol, Polyethylene glycol (PEG-400) liquid	
Deflocculant	Glycerol trioleate (GTO), fish oil		Glycerol trioleate (GTO)	
Composition (wt%)	min	max	min	max
Binder/Ceramic	0.05	0.25	0.15	0.30
Plasticizer/Ceramic	0.05	1.00	0.50	1.00
Binder/Plasticizer	0.15	0.30	0.25	0.50
Binder/liquid	0.03	0.10	0.05	0.10
Plasticizer/liquid	0.05	0.20	0.20	0.30
Ceramic/liquid	0.15	0.45	0.25	0.35

using both aqueous and non aqueous materials and the results are discussed in this paper.

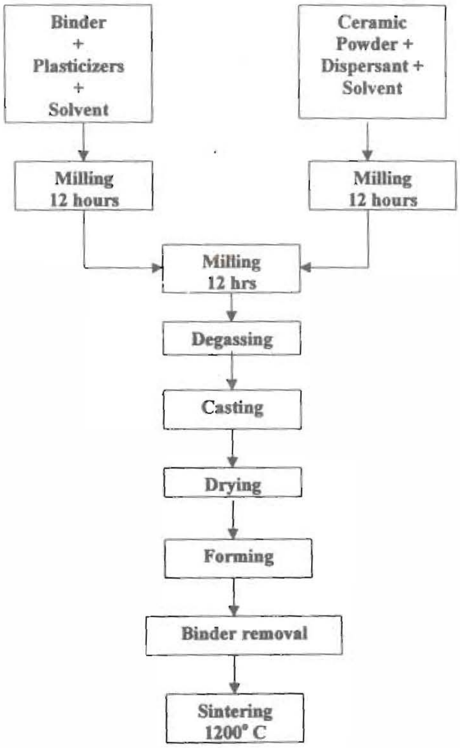

Fig. 1: Flow chart for the matrix fabrication process

EXPERIMENTAL

The γ-LiAlO$_2$ powder prepared by combustion synthesis method was employed for the preparation of the matrix material [29]. The powder had the following characteristics: average particle size 30 microns and BET surface area 12.2 m^2/g. Commercially available solvents, binders and plasticizers were used. The Table I describes the materials employed and their functional characteristics.

A flow chart for the preparation of the matrix by the tape casting process is shown in Fig. 1. The entire process consists of three key stages namely milling, casting and curing. The method involves preparation of slurry of γ-LiAlO$_2$ powder with binder and plasticizer in suitable solvent systems and in different proportions. Both aqueous and non aqueous solvent based systems have been tried. The ingredients are mixed either in a single stage or in two stages for duration exceeding 12 hr each time.

After milling, the slurry was deaired to evaporate the excess solvent. A doctor blade assembly as shown in Fig. 2 was used for making green tapes of desired thickness. It has a width of 15 cm. The slurry was poured into the cavity of the doctor blade assembly. As it moves over the glass plate, which was coated prior with either wax or liquid paraffin at a constant speed (40 cm/min), the slurry was spread uniformly in the form of a thin sheet to a controlled thickness with the knife edge of the doctor blade assembly.

The tape was cured for 24 hr at room temperature and the dried tape was removed from the substrate and stored. The physical observations of the cast surface, the thickness and density measurements were made. The DTA/TGA analysis was also carried out in air at a heating rate of 10 K/min using a PL Thermal Systems DTA/TGA Analyser Model STA 1500 to determine the binder and plasticizer burnt out conditions.

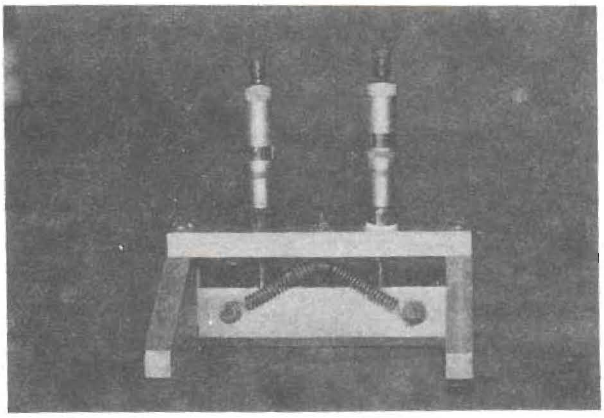

Fig. 2: Photograph of the doctor blade assembly

RESULTS AND DISCUSSIONS

Milling is an essential step for the preparation of the slurry [30]. The role of the additives, the characteristics of the various steps involved in the process and the essential criteria for the selection of suitable combination of materials were described in our previous publication [31]. The Table I summarises the combinations employed for both aqueous and nonaqueous tape casting of the $LiAlO_2$ powder. The amounts of binder and plasticizer materials have been calculated after carrying out a large number of trials and the range is indicated. The ratios are entirely different for aqueous and nonaqueous slurries. The parameters have been optimised for preparing good quality green tapes of length 30 cm and width 15 cm. The photograph (Fig. 3) shows the typical sample.

The physical characteristics of the green tapes such as thickness, shrinkage and green density are all indicated in Table II. The average values are indicated. Generally it is found that the shrinkage factor is high with tapes produced from nonaqueous slurries. The green density values are also higher than tapes prepared by aqueous method. The factors were found to depend upon the nature of the binder material, plasticizer and their ratio [32].

During the trials, it is observed that when solvent is higher (i.e. the ceramic to solid ratio is lower), the shrinkage factor is higher and the resulting tape has lower density values. The range of optimum ratio for the aqueous tape is narrower than the nonaqueous slurry as seen from Table I. This is reflected in the lower shrinkage factor of the aqueous tapes. On the other hand, a nonaqueous suspension dries quickly, produces green sheets having higher density and fine surface appearance. An aqueous suspension has the disadvantage of poor drying characteristics and they have many quality problems to be solved [33].

Another important observation noticed is the blade gap employed with nonaqueous slurries. When the blade gap is closer to the desired final thickness value, the shrinkage factor is lower and the finally obtained tape has got higher green density values. The binder provides the green strength to the green tapes after the evaporation of the solvent through the organic bridges between ceramic particles. When there is not enough binder, the resulting green tapes tend to develop cracks. The green tape density values are found to decrease as the binder and plasticizer content increases as reported for alumina tapes [34].

TABLE II: Characteristics of the matrix tapes

Characteristics	Aqueous tape	Non-aqueous tape
Blade gap (mm)	2.00	2.00
Average thickness (mm)	1.32	0.85
Shrinkage factor (%)	30-35	60-65
Density (g/cc)	1.135	1.30

The TGA/DTA pattern is used to determine the binder burn out conditions. The typical DTA/TGA patterns for the aqueous tape and the nonaqueous tape are indicated in Figs. 4 and 5 respectively. There is a steady loss in weight of the tapes from 373 K to 473 K in aqueous tapes and from 473 to 573 K in nonaqueous tapes. The initial wt loss is about 28% for aqueous tapes and 5% upto 473 K for nonaqueous tapes. This is mainly due to the removal of water from aqueous tapes and removal of solvents from nonaqueous tapes. There is a further reduction in wt to an extent of 15% in the range 473-573 K in Fig. 5. It is reported that the binder (PVB) starts decomposing above 473 K. The organic plasticizer materials (phthalates) also start decomposing above 573 K. The secondary weight loss of about 15% observed in the case of aqueous tapes is due to the removal of the binder (PVA) and plasticizer (glycerol). The decomposition of the binder and the plasticizers is completed below 863 K. This region is indicated by a shallow decrease

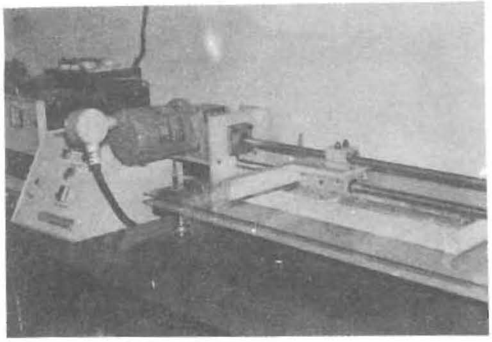

Fig. 3: Photograph of the matrix tape (15 x 50 cm)

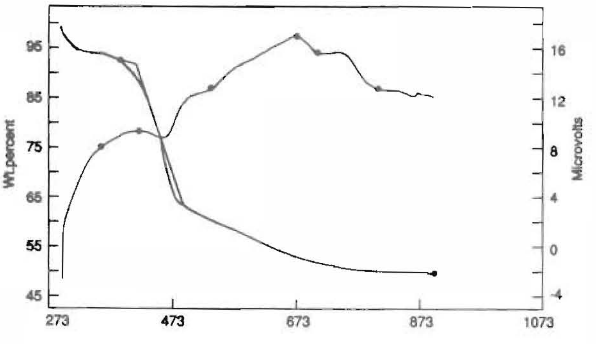

Fig. 4: DTA/TGA curve of an aqueous matrix tape

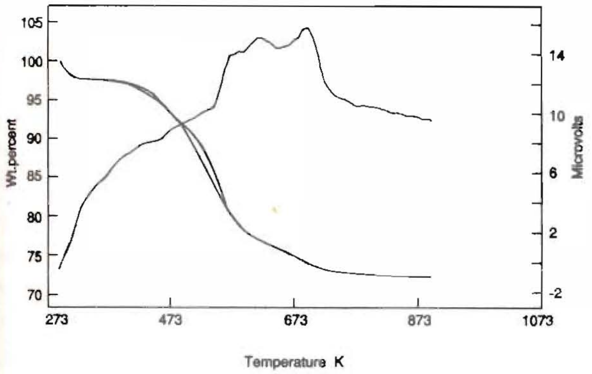

Fig. 5: DTA/TGA curve of an non-aqueous matrix tape

in the curves. The net weight loss is about 51% for aqueous tapes and 27% only for nonaqueous tapes. The peaks at various locations in the DTA curves indicate the removal of various compounds employed for the preparation of the slips. Because of the multiplicity of the plasticizer material employed for the preparation of the nonaqueous tapes, multiple peaks are observed in the temperature range 573-873 K. These values are useful in fixing the heating rates to be employed during the cell start up.

CONCLUSION

The preparation of matrix tapes by both aqueous and nonaqueous tape casting method has been followed. The tapes prepared from nonaqueous slip had better drying characteristics and higher density compared to the ones prepared by aqueous method. However the aqueous method is recommended because of the nontoxic nature of the materials and ease of handling.

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