LOW-COST FABRICATION OF THIN-WALLED
SOLID ELECTROLYTE TUBES
FROM DOCTOR-BLADED CERAMIC TAPE

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I. ABSTRACT

Sodium β "- Al_2O_3 tubes having wall thicknesses of typically 0.4 mm were fabricated from doctor-bladed (cast) ceramic tape using proprietary organic slip compositions and zeta processed, lithia stabilized alumina powder. The ceramic tubes fabricated from cast tape had low porosity, low resistivity (~ 4 ohm-cm at 300°C) and good mechanical strength.

Alternative fabrication techniques for manufacture of tubes from tape were evaluated and the primary processing requirements/obstacles were identified. Closed end tubes, nominally 10 mm outer diameter, 60 mm in length, and with a wall thickness of 0.3 mm were supplied to the Department of Energy.

II. INTRODUCTION

This report describes research activities for the period September 1, 1978 to October 31, 1979 on the project entitled "Low-Cost Fabrication of Thin-Walled Solid Electrolyte Tubes From Doctor-Bladed Ceramic Tape".

During the past 10-15 years considerable research has been conducted by personnel at Ford Motor Company⁽¹⁻¹²⁾, the University of Utah⁽¹³⁻²¹⁾, the General Electric Company⁽²²⁻³⁴⁾, Dow Chemical^(35,36), the Lincoln Laboratory at M.I.T.⁽³⁷⁻⁴⁰⁾, and numerous other public and private organizations on the development of ceramic or glass sodium ion conductors for use in a Na-S battery^(15,41). At present the bulk of the research efforts are directed towards four Na^+ -ion conductors 1) Na- β -alumina 2) Na- β "-alumina 3) $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NASICON), and 4) Na^+ - conducting glass. These materials are generally fabricated in the shape of a tube for separation of the Na and Na-S compartments. Ceramic tubes have been fabricated by isostatic pressing, electrophoresis, and extrusion. Although thin wall tubes have been fabricated by the latter technique⁽¹²⁾, tubes with uniform wall thicknesses less than ~ 1 mm are not routinely fabricated by these processes.

In this project, an experimental study to produce Na- β'' -alumina electrolyte of tubular geometry using doctor-bladed (cast) ceramic tape was conducted. The technique of doctor-blading of ceramic tapes is a well established production method used by Globe-Union Inc. and others⁽⁴²⁻⁴⁴⁾ in the manufacture of dielectrics for disc and multilayer (monolithic) ceramic capacitors or for substrates for thick or thin film electronic circuits. The cast tapes produced in this way are flexible, thin (.01 to 0.1 mm), and quite uniform in thickness. Previous results⁽⁴⁵⁾ in our laboratory have demonstrated the applicability of the ceramic tape for tubular construction.

Considerable effort has previously been directed towards preparing ceramic materials which could be sintered into tubes with the desired sodium ion conductivity and strength. In this project one of the more promising compositions and powder preparation procedures^(13-15,17) was selected for use in the fabrication of tubes from tape. Most of the research was conducted on Li_2O stabilized β'' -alumina powder (90.4 Wt. % Al_2O_3 , 0.75 Wt. % Li_2O , 8.85 Wt. % Na_2O) prepared by the "beta"⁽¹⁷⁾ process. It should be noted, however, that the fabrication of tubes from cast tape containing alternative Na^+ -ion conductive solid electrolytes would be expected to be directly applicable.

As a result of the proposal Globe-Union entered into contract with the Department of Energy and agreed, under contract EM-78-C-01-5161 to perform the following tasks:

Task 1. Tapes will be prepared of the $\beta''\text{-Al}_2\text{O}_3$ composition (0.75 w/o Li_2O , 8.85 w/o Na_2O , 90.4 w/o Al_2O_3) starting with dry vibratory-milled zeta powder. Tape quality factors to be maximized will be homogeneity, absence of aggregates in the precast slip, absence of pinholes in the dry tape, and the ease of stripping the tape from the casting surface.

Task 2. The method of tube formation will be refined so that consistently uniform lap joints are produced in rolled and/or wound specimens.

Task 3. Fired tubular specimens will be evaluated according to the following criteria: fired density, porosity, sodium ion conductivity, mechanical strength, chemical composition, and leak-tightness (helium leak rate).

Task 4. Technology from the paper or tobacco products industries will be studied for possible application to the mass production of ceramic tubes and recommendations will be made as to the economic and technical feasibility of these processes for this application.

Task 5. Green and sintered specimens will be made available to state-of-the-art DOE contractors for evaluation. Numbers and dimensions to be agreed upon during the course of the project.

This contract was later amended to include as fulfillment of Task 5 the following items:

- Item 1: Twenty ceramic tubes formed by a lap joint process, nominally 60 mm long, 10 mm diameter (outer), and 0.3 mm wall thickness. The tubes will be closed at one end with a disc insert and will be predominantly of the $\beta''\text{-Al}_2\text{O}_3$ structure.
- Item 2: One unfired, "green", tube formed by a lap joint process as in Item 1.
- Item 3: One ceramic tube formed by a spiral winding process; end closure and dimensions as in Item 1.
- Item 4: One unfired, "green", tube formed by a spiral winding process as in Item 3.
- Item 5: One ceramic tube formed by a lap joint process as in Item 1 with a pinch end closure.
- Item 6: One unfired "green", tube formed with a pinch end closure as in Item 5.
- Item 7: Twenty sheets of ceramic tape nominally 3.8 cm (1.5 in.) x 10.1 cm (4 in.) x 0.11 mm (0.0045 in.).

III. EXPERIMENTAL

A. Fabrication of Ceramic Powders

Meller $\alpha\text{-Al}_2\text{O}_3$, 0.3 micron average particle diameter, LiNO_3 , and Na_2CO_3 were used in powder fabrication. In Table I is contained representative spectrographic analysis of the starting components and analysis of the $\beta\text{-Al}_2\text{O}_3$ (Alcoa XB-2) powder used as setter sand for embedding the ceramic tubes during firing. The primary contaminants, when detected, were silicon and to a lesser extent iron and magnesium. Specific surface areas (Nitrogen BET) and the structures as determined by X-ray diffraction are shown in Table II.

All powders were dried in vacuum at 110°C and stored in sealed glass containers prior to use. Unless otherwise noted the powders used for tape casting were prepared by the "zeta" process⁽¹⁷⁾ and contained 8.85 wt. % Na_2O , 0.75 wt. % Li_2O , and 90.4 wt. % Al_2O_3 . In the zeta process, the Li_2O is prereacted with the $\alpha\text{-Al}_2\text{O}_3$ to form a zeta lithium aluminate spinel ($\text{Li}_2\text{O}:\text{5Al}_2\text{O}_3$) which is ultimately mixed with a prereacted sodium aluminate ($\text{Na}_2\text{O}:\text{5.3Al}_2\text{O}_3$) for use in tape casting. By prereacting the lithia with the alumina a more uniform distribution of lithia can be achieved in the final composition.

In Figure 1 is the processing steps for the powders. Two hundred gram batches of the zeta lithium aluminate were prepared by wet vibratory milling* in hexane** the predried Meller $\alpha\text{-Al}_2\text{O}_3$ and LiNO_3 in 500 ml. polypropylene mill jars filled with ~1.5 kg. of ~2 cm diameter "Saphrox"*** alumina mill media. After vibratory milling for 1/2 hour the slurry was vacuum filtered and dried in a forced air oven at 60°C for 16 hours. The dried powder was calcined at 1250°C for 2 hours in closed zirconia**** crucibles, crushed and stored in sealed glass containers. Two

* Pilemec, Clearwell, England. Megapot Vibratory Mill.

** Fisher Scientific Co., Chicago, Ill., Hexane, H-291.

*** Alumina Ceramics, Inc., Benton, Ark.

**** Zircoa Products, Corning Glass Works, Solon, Ohio.

Table I

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Spectrographic Report of Starting Materials

Element	Detectability Limit (Wt. %)	(1) Al ₂ O ₃ (Wt. %)		Al ₂ O ₃ ⁽²⁾ (Wt. %)	LiNO ₃ ⁽³⁾ (Wt. %)	Na ₂ CO ₃ ⁽³⁾ (Wt. %)
		1081	1062			
Ag	.003	N.D.	N.D.	N.D.	N.D.	N.D.
Al	.0066	>1.0	>1.0	>1.0	N.D.	N.D.
As	.100	N.D.	N.D.	N.D.	N.D.	N.D.
Ba	.100	N.D.	N.D.	N.D.	N.D.	N.D.
Bi	.010	N.D.	N.D.	N.D.	N.D.	N.D.
Ca	.030	N.D.	N.D.	N.D.	N.D.	N.D.
Cd	.030	N.D.	N.D.	N.D.	N.D.	N.D.
Co	.005	N.D.	N.D.	N.D.	N.D.	N.D.
Cu	.002	N.D.	N.D.	N.D.	N.D.	N.D.
Cr	.003	N.D.	N.D.	N.D.	N.D.	N.D.
Hg	.100	N.D.	N.D.	N.D.	N.D.	N.D.
Fe	.003	N.D.	.0065	.15	N.D.	N.D.
Mg	.001	.0034	N.D.	.043	.009	.055
Mn	.003	N.D.	N.D.	N.D.	N.D.	N.D.
Ni	.003	N.D.	N.D.	N.D.	N.D.	N.D.
Pt	.033	N.D.	N.D.	N.D.	N.D.	N.D.
Na	.050	N.D.	N.D.	>1.0	N.D.	>2.0
Si	.003	N.D.	.0143	.45	N.D.	N.D.
Sn	.003	N.D.	N.D.	N.D.	N.D.	N.D.
V	.003	N.D.	N.D.	N.D.	N.D.	N.D.
Zn	.050	N.D.	N.D.	N.D.	N.D.	N.D.
Zr	.010	N.D.	N.D.	N.D.	N.D.	N.D.
Sb	.010	N.D.	N.D.	N.D.	N.D.	N.D.
Ti	.010	N.A.	N.D.	N.A.	N.A.	N.A.

N.D. - Not Detected

N.A. - Not Analyzed

- (1) A. C. Meller Co., P.O. Box 6001, Providence, R.I.
0.3 micron, Deagglomerated Al₂O₃, Lot 1081 and 1062
- (2) Aluminum Company of America, 2900 Missouri Ave., East St. Louis, Illinois
62205. Calcined, XB-2, B-Al₂O₃ (Unground). Lot D10031-3-60
- (3) Research Organic/Inorganic Chemical Corp., 11686 Sheldon St., Sun Valley,
California 91352. Anhydrous LiNO₃ (LI-30), Anhydrous Na₂CO₃ (NA-52).

Table II
Surface Area and Structure
of Starting Materials

	<u>Specific Surface</u> <u>(m²/g)</u>	<u>X-ray Structure</u>
Meller; α -Al ₂ O ₃	27.7	β -Al ₂ O ₃ , corundum, (ASTM 10-173)
Alcoa XB-2, β -Al ₂ O ₃	0.96	β -Al ₂ O ₃ , Na ₂ O:11Al ₂ O ₃
LiNO ₃	0.11	Poor Pattern, LiNO ₃
Na ₂ CO ₃	0.57	Na ₂ CO ₃ + Extra Peaks (ASTM-1208)

hundred gram batches of the sodium aluminate powder were similarly prepared using the Meller α -Al₂O₃ and Na₂CO₃. For brevity, the calcined sodium and lithium aluminates were designated ZNA-X and ZLA-X, where X corresponds to the batch number.

One hundred grams of the appropriate amounts of ZNA and ZLA powders were premixed by hand in polyethylene bags with a dry milling aid (1 pph naphthenic acid as 10 wt. % in 2-propanol). The powder was then transferred to a 1000 ml. polypropylene mill jar and the propanol was dried from the powder in a forced draft oven at 60°C for 1/2 hr. The powder was dry vibratory milled for 4 hours with ~2 kg of the alumina mill media then passed through a 60 mesh polypropylene sieve. Previous results in our laboratory have shown that the surface area of similar powders increases with milling time up to ~4 hours and then begins to level off with no marked increase for milling times up to 7 hours. The vibratory milled mixtures of ZNA and ZLA powders were designated BA-X for β -Al₂O₃ where again X represents the batch numbers.

Surface areas of ZLA, ZNA, and BA powders were routinely determined to evaluate the uniformity of the milling processes. Spectrographic analysis was also made to monitor the contamination by the mill media.

90.4 w/o Al_2O_3 - 9.85 w/o Na_2O - 0.75 w/o Li_2O

$\text{LiNO}_3 + \text{Al}_2\text{O}_3$

$\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3$

VIBRATORY MILL IN HEXANE FOR 1/2 HOURS

VACUUM FILTER

OVEN DRY 60°C FOR 4 HOURS

CALCINE 1250°C FOR 2 HOURS

CRUSH POWDER

ADD MILLING AID
1 pph NAPHTHENIC ACID
IN A 10% SOLUTION 2-PROPANOL

REMOVE 2-PROPANOL

DRY VIBRATORY MILL 4 HOURS

Figure 1. Zeta Powder Fabrication Process

B. Casting of Ceramic Tape

The ceramic tapes were prepared using a casting technique whereby a ceramic slip is uniformly deposited onto a flat surface as a thin sheet using a doctor blade. The ceramic slips were prepared using a proprietary composition used in the fabrication of barium titanate based monolithic capacitors. In a 1.1 liter Roalox* polygonal grinding jar one-quarter filled with a 0.95 cm end radius zirconia mill media** the BA powder is mixed with a thermoplastic organic resin, a compatible plasticizer, solvents, a wetting agent, and a weak acid. In Table III is shown the proportions of the various additives used. Typically 200 g of BA powder is used for each tape casting although batches containing as much as 600 g of powder were successfully cast. In order to have sufficient powder for tape casting, two or more BA powder batches were blended and used for each tape.

Table III

Ceramic Slip Composition

	<u>Wt. %</u>
BA Powder	26.6
Organic Solvent	46.1
Thermoplastic Resin	24.9
Plasticizer	1.6
Wetting Agent	0.3
Acid	0.5

The preparation of the ceramic slip involved a two step process as shown in Figure 2. Initially the powder was ball milled for two hours with the solvent, weak acid, and wetting agent to thoroughly wet the powder. After the initial mixing step the thermoplastic resin (binder) and plasticizer were added and the slip ball milled for three hours. After milling, the slip was transferred to a 1000 ml. disposable plastic beaker and placed in a vacuum desiccator for approximately five minutes to remove entrapped air bubbles formed during milling. In addition to

* Morton Company, Akron, Ohio

** Zircoa Products, Corning Glass Works, Solon, Ohio

removing the entrapped air approximately 10% of the solvent is removed due to volatilization.

Approximately 0.1 mm thick sheets, 15 cm X 2 m were formed in the laboratory by doctor blading* the slip onto polyethylene coated paper fixed to glass sheets as shown in Figure 3. The casting rate was typically 150 cm/min. The paper is attached to the glass by spraying a thin layer of rubber cement onto the glass, allowing it to dry to a tacky state, and applying the paper. Typically in capacitor manufacture the doctor blade is fixed above a moving substrate rather than vice versa as here. The tape was stripped from the paper by drawing the paper over the edge of a sheet of glass as shown in Figure 4. The tape is then coiled and stored under dry air in polyethylene bags. For spirally winding tubes, stripping was omitted and the ceramic coated paper was sliced into 2 cm wide strips and stored in polyethylene bags.

Figure 2. Process for Fabrication Cast Tape.

* Gardner Lab. Inc., Bethesda, Md.

Figure 3. Doctor Blading (Casting) of Slip onto Polyethylene Coated Paper.

Samples of tape 3.8 cm X 10.1 cm were blanked from the tape for use in determining the tape density and thickness uniformity. Multiple layers of these tape samples were also pressed in a heated die at 50°C at 2000 psi to form 2 cm X 2 cm square samples, ~2 mm thick, for some of the initial firing studies.

C. Fabrication of Ceramic Tubes

Closed end tubes were fabricated from the cast tape by two techniques: wrapping multiple layers of tape by a spiral winding technique or by wrapping rectangular sheets such that a lap joint extended the length of the tube parallel to the tube axis. Most experimental work was conducted on tubes formed by the latter process since they were considerably easier to form by hand laboratory techniques.

Figure 4. Removal of Ceramic Tape from Polyethylene Coated Paper.

For the tubes formed with a lap joint, rectangular sheets 8.8 cm X 17 cm were cut from the cast tape and wrapped around a 1.27 cm diameter Teflon[®] coated rod such that the tubes were 8.8 cm long and there were four layers of tape in the wall. During rolling, a solvent, either toluene or the solvent used in the tape casting, was applied to the mating surfaces of the tape to partially dissolve and bond together the layers. The tube ends were sealed either by applying a solvent to the internal surface and pinching closed one end or by solvent cementing a disc insert into the end of the tube. The disc inserts were made by pressing multiple layers (typically 4) of the tape in a heated die to form a solid sheet and then by punching out the discs using a small laboratory punch and die set.

Spirally wound tubes were formed using the apparatus shown in Figure 5. A bi-directional, variable speed motor* (0-7 rpm) was connected via a flexible

* Bodine Electric Co., Chicago, Ill.

Figure 5. Laboratory Apparatus for Spirally Winding Tubes.

coupling to a 1.27 cm diameter shaft. A 5 cm diameter Teflon[®] backing roll aided in guiding the tape onto the surface during spirally winding. Attempts were made to wrap tubes from tape with and without the plastic coated paper backing and by either spirally winding a continuous strip of tape, with overlapping edges (Figure 6) or by abutting the strips of tape in each layer and wrapping multiple displaced layers (Figure 7).

D. Firing of Ceramic Tubes

Attempts were made to fire tubes in both vertical and horizontal positions in platinum or alumina crucibles while embedded in Alcoa XB-2 beta alumina setter sand. In general, the tube walls tended to collapse when firing in the horizontal position, hence the vertical position shown in Figure 8 was used for most firings. Up to four tubes were fired, concentrically positioned within a 7.6 cm diameter by 10.2 cm high platinum crucible. Caps, fabricated from platinum foil, covered the ends of the tubes to prevent the sand from entering during firing.

Figure 6. Two layer, spiral wound tube with overlapping, continuous strip of tape.

Figure 7. Spiral wound tube with two layers formed by abutting strips of tape in each layer and wrapping multiple layers.

The organic components were removed in a box furnace by slow heating, typically 10-15°C per hour, to 500°C. The crucibles were usually transferred directly to the high temperature furnace for firing. A furnace* with a movable platform bottom was used for the high temperature firing and annealing. The firing cycles involved heating at ~50°C/min to 1550-1600°C, holding at that temperature for 1 to 10 minutes, followed by a high temperature anneal for one hour at temperatures of 1450-1500°C. During firing the furnace and sample temperatures were monitored with thermocouples located above and at the center of the crucible using a dual pen strip chart recorder. A typical firing cycle is shown in Figure 9. The time at the sintering temperature was taken as the time span from heating to cooling that the samples were at or above the desired temperature. The heating excursion above the desired temperature typically was only 1-3°C. The annealing time was taken as the lapse from when the furnace temperature controller was turned down to the annealing

* Deltech Inc., Denver, Colorado

temperature, to the end of the anneal. For example, one hour annealing at 1500°C in actuality corresponds to ~ 10 min. cool down from the sintering temperature and 50 min. at the annealing temperature. After the post sintering anneal at the lower temperature, the furnace was rapidly cooled to 1000°C and the crucible removed. After cooling to room temperature the tubes were stored either in evacuated desiccators or heat sealed in polyethylene bags in dry air.

Figure 8. Firing Position for Ceramic Tubes

Figure 9. Typical Firing Cycle for Tubes Fired for Approximately 2 Minutes at 1600°C Followed by 1500°C Anneal.

E. Characterization of Fired Tubes

The hermeticity of fired tubes was determined using a Veeco MS-9AB Leak Detector. The relative amounts of β and β'' - Al_2O_3 were determined by an X-ray diffraction technique using the normalized $f(\beta)$ which is approximately equivalent to the fraction of β - Al_2O_3 phase present in a $\beta+\beta''$ - Al_2O_3 mixture⁽¹⁵⁾. The normalized index was calculated by taking the ratio of the integrated intensity of the (110) β - Al_2O_3 peak to the sum of the integrated intensities of that peak and of the (01,11) β'' - Al_2O_3 peak.

Axial resistance measurements were made on fired tubes using platinum wires attached to four platinum band electrodes circumferentially positioned along the axis of sections of tubes ~4 cm long. The platinum was applied with a small paint brush as an unfluxed, platinum resinate*. After drying, the resinate was decomposed to the metal by slow heating on a belt furnace to 500°C. Application was repeated until uniform bands, 2-3 mm wide, were formed. The electrical circuit used to obtain the measurements is shown in Figure 10. Connected in series with the sample was an Eico Model 1171 decade resistance box. The resistance was varied so the voltage across the sample, observed on the oscilloscope, and standard resistance were equal. Measurements were made with 8 and 80 mv (peak-to-peak) across the inner leads of the sample over the frequency range 20 Hz to 200 kHz.

Porosity measurements were obtained by a point-count technique⁽⁴⁶⁾ whereby a grid was superimposed on a metallographic projection of the polished ceramic and the number of superpositions of the grid intersections with pores in the ceramic was determined. These measurements were made on sections of the tube wall, mounted in epoxy such that the polished surface was perpendicular to the axis of the tube. All samples were ground with 120, 240, 400, and 600 grit silicon carbide paper coated with a kerosene-paraffin solution and polished with 15, 9, 6, 3, and 1 micron diamond

* Pt A-1121, Englehard, Inc., East Newark, NJ

polish. Between processing steps the samples were ultrasonically cleaned in hexane. For microstructural examination the polished samples were etched for 1-1½ minutes in hot ($\sim 230^{\circ}\text{C}$), fresh, phosphoric acid.

Figure 10. Electrical Circuit for Resistance Measurements on Tubes.

The modulus of rupture (M.O.R.) was determined for rings tested in diametral compression on a metric Instron Universal Testing machine with a cross-head speed of 5×10^{-3} cm/min, an average calculated stress-rate of 2.7 ± 1.5 MPa/sec. The rings were cut from the fired tubes and were approximately 2.5 mm in axial length. Heavy construction paper was placed between the ring and the tensile tester's upper and lower platens. The M.O.R. was calculated⁽⁴⁷⁾ from

$$\sigma \propto \frac{2P}{\pi (OD) \cdot (L)}$$

where P is the load at fracture, (OD) the outer diameter of the tube, and (L) is the length of the tube section or ring being tested. The proportionality constant, K , in

$$\sigma = \frac{K 2P}{\pi (OD) \cdot (L)}$$

is a complex function of the geometry of the tube, involving the ratio of the tube's inner diameter to outer diameter. Nelson⁽⁴⁸⁾ calculated the value of K for a number of diameter ratios between 0.1 and 0.9, and intermediate values have been determined graphically⁽¹¹⁾ or by Lagrangian interpolation⁽⁴⁵⁾. The tubes in this study have a diameter ratio greater than 0.9. The K values used for computing the M.O.R. were calculated using the equations of Nelson⁽⁴⁸⁾. In Appendix E are the computed values of K for diameter ratios of 0.1 to 0.999.

IV. RESULTS AND OBSERVATIONS

A. Powder Preparation

Typical spectrographic analyses of the vibratory milled and calcined ZLA and ZNA powders and dry milled BA powders are in Table IV. Essentially no difference in impurity content was observed from the starting components for those elements analyzed indicating no noticeable contamination occurred during powder preparation.

In Figures 11-13 are the surface areas of the calcined ZLA and ZNA powders and dry milled BA powder. The BA powder contains approximately 86 wt. % ZNA and 14 wt. % ZLA powder. The average and standard deviation in surface area for the ZNA and BA powders are 5.45 ± 0.78 and 9.22 ± 1.49 m²/g. The number of vibrations per minute (v.p.m.) of the vibratory mill was measured at the start, middle, and end of milling for many of the BA powder millings. The vibration rate varied from approximately 2800 to 3100 v.p.m. The deviation in the surface area for similarly milled powder did not appear to be due to the change in the vibration rate, but may be due to the change in amplitude of the vibrational frequency. After the milling of BA-50 powder batch, since the mill was becoming increasingly noisy, the bearings in the mill were replaced. It is apparent from Figure 13 the variation in surface area for powders BA-50 to BA-80 is considerably less than for powders BA-15 to BA-50.

Table IV

Globe Union Inc.
Materials Test Laboratory

Spectrographic Report for ZLA, ZNA, BA, and Cast Tape

Element	Detectability Limit (Wt. %)	(1) ZLA (Wt. %)	(2) ZNA (Wt. %)	(3) BA (Wt. %)	(4) Cast Tape (Wt. %)
Ag	.003	N.D.	N.D.	N.D.	N.D.
Al	.0066	>1.0	>1.0	>1.0	>1.0
As	.100	N.D.	N.D.	N.D.	N.D.
Ba	.100	N.D.	N.D.	N.D.	N.D.
Bi	.010	N.D.	N.D.	N.D.	N.D.
Ca	.030	N.D.	N.D.	N.D.	N.D.
Cd	.030	N.D.	N.D.	N.D.	N.D.
Co	.005	N.D.	N.D.	N.D.	N.D.
Cu	.002	N.D.	N.D.	N.D.	N.D.
Hg	.100	N.D.	N.D.	N.D.	N.D.
Fe	.003	N.D.	N.D.	N.D.	N.D.
Mg	.001	N.D. -.0014	N.D. -.006	.0035-.0152	.009-.044
Mn	.001	N.D.	N.D.	N.D.	N.D.
Ni	.003	N.D.	N.D.	N.D.	N.D.
Pt	N.D.	N.D.	N.D.	N.D.	N.D.
Na	.050	N.D.	>1.0	>1.0	>1.0
Si	.003	N.D.	N.D.	N.D.	N.D. -.075
Sn	.003	N.D.	N.D.	N.D.	N.D.
V	.003	N.D.	N.D.	N.D.	N.D.
Zn	.050	N.D.	N.D.	N.D.	N.D.
Zr	.010	N.D.	N.D.	N.D.	.063-.20
Sb	.010	N.D.	N.D.	N.D.	N.D.
Ti	.010	N.D.	N.D.	N.D.	N.D.

N.D. - Not Detected

- (1) Range based on 2 analyses each for ZLA powders 4 and 5.
- (2) Range based on 2 analyses each for ZNA powder 20, and blended mixtures of 20-22 and 23-25.
- (3) Range based on 2 analyses each for blended mixtures of BA powders 40-45, 46-51, and 60-61.
- (4) Range based on 2 analyses each for Tape Batch 17, 20 and 24, which was prepared as powders by removing organics by heating to 500°C.

Figure 11. Surface Area of ZNA Powder Batches.

Figure 12. Surface Area of ZLA Powder Batches.

Figure 13. Surface Area of BA Powder Batches.

The calcined powders were examined by X-ray diffraction. The ZNA powders were mixtures of β - NaAlO_2 (ASTM 19-1177) and β - Al_2O_3 (ASTM 10-173). Only lines for LiAl_5O_8 (ASTM 17-573) were noted in the ZLA powder.

B. Casting of Ceramic Tape

Initially a proprietary organic slip composition similar to that used in production of ceramic tape for monolithic capacitors was selected for use in casting the BA powder precursor to β'' - Al_2O_3 . Due to the difference in density of the alumina versus barium titanate based, dielectric materials (3.26 g/cm^3 vs $6-7 \text{ g/cm}^3$) the organic components were increased by approximately 85%. The slips prepared using these compositions were extremely viscous, almost gels, and contained considerable nonuniformity in distribution of the powder. Attempts to increase the fluidity of the slip by adding extra solvent were only marginally successful. Although tape was cast, Figure 14(A), there were numerous defects present due to agglomerated particles. It was assumed the agglomeration was due to the high basicity due to the soda. In order to compensate for the basic nature of the slip a weak acid (acetic acid) was added to complex the sodium ions in solution in the slurry. A similar technique has been successfully used in the preparation of slurry dispersions for spray drying⁽⁴⁹⁾. The acid was successful in breaking up the agglomerates (Figure 14). The slip composition in Table III contained the optimum amount of plastic resin to plasticizer, and acid content, to reproducibly yield a uniform, flexible tape without pinholes.

With few exceptions, only minor perturbations were made in the optimum slip formation process. The slips for Tapes #7-9 were cast from BA powder that was prepared by wet vibratory milling in hexane for one hour rather than dry vibratory milling with the milling aid. The results were unsatisfactory. The tape densities were considerably lower than those shown in Figure 15 and varied between 1.40 and 1.60 g/cm^3 . The reason for the lower tape density is believed to be particle agglomeration and not an increase in particle surface area since the surface area of the BA powders were similar to those in Figure 13.

(A) Tape Batch No. 1

(B) Tape Batch No. 17

Figure 14. Samples of Tapes Cast Without (A) and With (B) Acetic Acid Addition.

Tape was cast with thickness from ~0.05 to 0.2 mm. The thicker tape exhibited "mud cracking" during drying, and was less flexible while the thinner tapes were difficult to form into tubes by hand. (When the solvent was applied to the mating surfaces of the thinner tapes during forming of tubes, the bulk of the tape dissolved eliminating any mechanical integrity of the tape.) An intermediate tape thickness was selected. With a doctor blade setting of 0.5 mm the green tape thickness was 0.117 ± 0.006 mm for the nineteen similarly prepared batches of tape shown in Figure 16. The reproducibility of the process is also evidenced by the uniformity in tape density (Figure 15), 1.994 ± 0.102 g/cm³.

Gravimetric measurements were made on three tape batches to determine green ceramic density. The tapes contained 77.9 wt. % ceramic or had a green density of 49.9% of theoretical based on 3.26 g/cm³ as the theoretical density.

Photomicrographs of the surface of the cast tape which contacted the polyethylene coated paper and the side exposed to air are shown in Figure 17. The surface which contacted the polyethylene paper was quite smooth and reflective when examined with the unaided eye while the surface exposed to the air while drying was dull due to the surface relief. When examined at high magnification, however, both surfaces showed fine shrinkage cracks and approximately the same amount of surface porosity.

In production it may be desirable to recycle the tape scraps back into the process. One batch of tape was cast using powder that was salvaged from prior tape batches. The tape scraps were heated to 500°C in alumina crucibles to remove the organics, sieved through a 60 mesh sieve, and used in casting new tape. The results were encouraging; the tape exhibited properties similar to those prepared from the starting BA powders. It was, however, necessary to add additional solvent to the slip during milling. In production, addition of 5-10% of the recycled powder to new BA powder would not be expected to seriously degrade the tape characteristics.

Figure 15. Tape Density for Similarly Cast Tapes with Optimum Slip Composition.

Figure 16. Tape Thickness for Similarly Cast Tapes with Optimum Slip Composition.

A. Surface which Contacted Polyethylene Coated Paper

B. Surface Exposed to Air.

Figure 17. Surfaces of Cast Tape.

As noted in Table IV, during milling, there is some contamination of the slip by Zr, Mg, and Si. No attempt was made in the present study to determine the effect of each of these contaminants on the physical properties of the fired ceramic. Previous studies⁽⁵⁰⁻⁵²⁾ on beta alumina have shown that depending on the type and concentration of impurity, sintering may be inhibited, grain growth promoted, and intergranular phases may form, blocking conduction. For example, results by De Jonghe^(51,52) indicate that SiO_2 should suppress formation of $\beta''\text{-Al}_2\text{O}_3$ since it reacts with the soda to form sodium aluminosilicate. The reacted sodium aluminosilicate was observed in $\beta\text{-Al}_2\text{O}_3$ to collect at grain boundary triple points and also a silicate phase was observed to wet some grain boundaries. In this study the effect of the Zr, Mg, and Si would not be expected to be large since the concentrations are relatively low.

C. Fabrication of Ceramic Tubes

One of the major obstacles to manually forming tubes from tape was the need for uniform application of the solvent to the mating surfaces of the tape and subsequent rolling of the tape to form a solid body. This step was critical in the tube construction in that if too much solvent was applied and/or too much time elapsed between application of the solvent and rolling of the tube, the tape would lose its mechanical integrity, undergoing nearly complete dissolution or distortion. If too little solvent was applied, or if the excess solvent was not allowed to evaporate leaving a tacky surface, during rolling planar defects would form between the mating surfaces of tape. Occurrence of these defects was most prevalent in the tubes with the lap joint extending the length of the tube since it was difficult to uniformly apply a thin coating of the solvent over such a wide piece of tape.

Spirally winding tubes from the tape without the support of the backing paper required considerable effort and was usually unsuccessful. It was determined, however, that by spirally winding the tubes with the attached polypropylene coated paper, it was relatively easy to form tubes. Since the tape was fed by hand onto the turning mandrel and the solvent was applied manually the process was time consuming.

since the paper backed the tape during wrapping, forming the tubes by the technique illustrated in Figure 6 could not be utilized. Rather, tubes with four layers of tape in the wall were formed such that the layers were wrapped as in Figure 7. Initially one layer of tape with the backing paper was wrapped such that the paper was on the inside of the tube. The paper on the inside of the tube served a dual purpose in that it acted as a release paper for the easy removal of the wound tube from the supporting mandrel and added also to the green strength of the tube. The second layer was coated with the solvent as it was fed onto the mandrel. After wrapping the second layer the paper was removed by reversing the direction of the winding mandrel. A third and fourth layer were applied in a similar process. The outer and inner paper layer were left on the tubes until the end sealing operation.

In Figure 18 are shown "green" tubes formed by the lap joint and spiral winding processes. Included is a tube with a pinch seal and a disc used in forming the tubes with a flat end. After forming, the tubes were considerably stiffer. This is believed to be due to an aging (or degradation) process associated with the solvent used in mating the tape surfaces together. Tapes stored in desiccators were not observed to degrade over extended periods (in some cases months). In order to form tubes with the pinch seal, the end closure had to be made within ~24 hours after fabricating the tube. However, cracking at the point of maximum deformation during pinching, as noted in Figure 18, was a recurring problem. Even when the seal appeared visually to be without defects, after firing it was observed in nearly all tubes with the pinch seal that the tubes leaked under vacuum at the corners.

It was determined that a convenient technique for sealing the disc inserts into the tube ends was to position a flat end rod in the tube leaving ~1 mm of tube extending over the rod end. The inside of the tube was then coated with the solvent used in tube rolling and the disc was inserted and bonded to the tube wall. Some of the slip used in tape casting, diluted with additional solvent, was used to smooth the outer and inner mating seam of the disc and tube wall. When using disc inserts

A. Spiral Wound

B. Lap Joint, Disc Closure

C. Lap Joint, Pinch Closure

D. Pinch Closure

Figure 18. "Green" Ceramic Tubes Formed From Cast Ceramic Tape. In (A), the Upper Tube is Shown with Paper Backing. In (D), Cracks Which Formed in Pinch Closure During Sealing of "Aged" Tubes are visible.

of similar thickness as the tube wall, it was sometimes observed that the disc would deform usually in a concave inward position after firing such as shown in Figure 19. By using thicker inserts or caution in the amount of solvent applied this problem could be eliminated.

An attempt was made on one tube sealed with a disc insert to deform the flat end into a hemispherically shaped end. This was done by first inserting a round bottom test tube of similar outer diameter to the inside diameter of the green tube into the green tube. The tube was then inserted into a short, larger diameter test tube which acted as a die and pressure was applied to the inner tube (punch) to deform the ceramic into a round bottom. Although there were some cracks in the tube end after deformation, the results were encouraging and demonstrated that by using suitable heated dies, it may be possible to deform the green tube end into an alternative shape. This may be desirable for a specific cell design or enhancing the mechanical integrity of the tube end.

Figure 19. Cross Section of Ceramic Tube Showing Disc Closure.

D. Characterization of Fired Specimens

Sintering of Samples:

Porosity measurements were made on polished specimens as a means of evaluating the degree to which the samples had sintered. In Table V is contained measurements for ten batches of tape that were fired for different sintering times and temperatures. For small perturbations in firing time the average porosity was low, $2.2 \pm 0.6\%$, and relatively insensitive to firing temperature. Density measurements on 13 tube specimens that were fired at 1550-1600°C had an average density of 96.0% of theoretical* and the values ranged from 94.3 to 98.5%. During firing the specimens underwent shrinkage of $\sim 18.2\%$.

In Figures 20, 21, and 22 are examples of fired tubes. The lap joints in Figures 20 and 21 are visible and extend the length of the tubes. In tubes designed with the lap joint a region of higher resistance would be present at the location of the overlap. For tubes with four layers of tape, at the lap joint an area of five layers of tape, with a 25% increase in resistance, would extend the length of the tube. Increasing the number of layers in the wall would decrease, but not eliminate, the discontinuity at the lap joint. In the spirally wound tube, although there is not the large discontinuity in wall thickness it is of importance that during winding the alignment of the tape be controlled to eliminate thin spiral voids within the tube wall or on the surfaces due to poor abutment of the edges of the tape. The surface of a fired tube is shown in Figure 23. The difference in surface relief apparent in the green tape (Figure 14), due to one side of the tape contacting the polyethylene paper, is also observed in the fired specimens. If the nonuniform or "roughened" surface does not seriously degrade the mechanical properties it may be advantageous in increasing the surface area in contact with the molten sodium or sulfur electrode.

* Based on 3.26 g/cm^3 for $\beta''\text{-Al}_2\text{O}_3$.

Table V

Porosity Measurements
for Sintered and Annealed Ceramic

Tape #	Sintering		Annealing		Porosity (%)
	T(°C)	t(min)	T(°C)	t(min)	
3	1600	2	1500	60	2.9 $\pm$.4
"	"	10	"	"	2.8 $\pm$.4
4	"	2	"	"	2.4 $\pm$.4
"	"	10	"	"	2.8 $\pm$.4
10	"	2	"	"	3.7 $\pm$.5
"	"	5	"	"	2.6 $\pm$.4
"	"	10	"	"	3.2 $\pm$.5
"	"	10	"	"	1.8 $\pm$.4
11	"	2	"	"	2.1 $\pm$.4
"	"	2	"	"	2.4 $\pm$.4
"	"	5	"	"	1.7 $\pm$.3
"	"	10	"	"	1.3 $\pm$.3
"	"	10	"	"	2.1 $\pm$.1
12	"	2	"	"	2.0 $\pm$.4
"	"	2	"	"	1.7 $\pm$.4
"	"	5	"	"	2.3 $\pm$.4
"	"	10	"	"	2.1 $\pm$.4
"	"	20	"	"	3.6 $\pm$.5
17	"	2	"	"	1.7 $\pm$.4
19	"	2	"	"	2.3 $\pm$.4
21	"	2	"	"	1.8 $\pm$.5
24	"	2	"	"	1.7 $\pm$.4
33	"	2	"	"	1.6 $\pm$.4
"	1585	"	"	"	1.5 $\pm$.3
"	1575	"	"	"	1.5 $\pm$.3
"	1550	"	"	"	2.0 $\pm$.5

A. Front Illuminated.

B. Back Illuminated.

Figure 20. Ceramic Tube with Lap Joint and Pinch Closure.

A. Front Illuminated.

B. Back Illuminated.

Figure 21. Ceramic Tube with Lap Joint and Disc Closure.

A. Front Illuminated.

B. Back Illuminated.

Figure 22. Ceramic Tube, Spirally Wrapped, with Disc Closure.

A. Surface which Contacted Polyethylene Coated Paper

B. Surface Exposed to Air.

Figure 23. Surfaces of Fired Tube

Table VI
X-ray Measurements
on Fired Ceramic Flat Bar Samples

Tape #	Sintering t (min)	<u>f(β)</u>		
		<u>Fired*</u> <u>Surface</u>	<u>Polished*</u> <u>Surface</u>	<u>Fired**</u> <u>Surface</u>
3	2	0.27	—	0.13
	10	0.13	0.05	—
4	2	0.19	—	0.17
	10	0.26	0.11	—
10	2	0.34	—	—
	5	—	—	0.10
11	10	0.48	0.02	—
	2	0.46	—	—
	5	—	—	0.20
	10	0.46	0.05	—

* Alcoa XB2 Setter

** Alcoa XB2 Setter + Na₂O (9.0 wt. % Na₂O)

All samples sintered at 1600°C and annealed at 1500°C for 60 min.

X-ray Measurements:

Bar samples were initially used to determine the relative amount of unconverted β -Al₂O₃ in fired samples since the flat specimens could conveniently be positioned in the X-ray diffractometer. It was observed (Table VI) that when firing in the Alcoa XB-2 alumina setter sand the calculated f(β) values for the surfaces were typically in the range of 0.20-0.40. Complete conversion to the β'' -Al₂O₃ structure appeared to be inhibited by loss of soda and/or lithia from the surface. When approximately one-third of the thickness of the 1 mm thick specimens was removed by grinding and re-examined the f(β) values were below 0.10 tending to support this conclusion.

In order to inhibit soda loss the setter sand was doped with additional soda* to 9.0 wt. % and the surface of similar bar samples analyzed after firing. As noted in Table VI some improvement was observed; the f(β) values ranged from 0.13 to 0.20.

* Chemical analysis of the Alcoa XB-2, β -Al₂O₃ indicated it contained 6.3 wt. % Na₂O.

Table VII

X-ray Measurements on Powder
Samples Ground from Fired Tubes

<u>Sintering</u>		<u>Annealing</u>		<u>Tape #</u>	<u>Setter Composition</u>	<u>f(β)</u>
<u>T(°C)</u>	<u>t(min)</u>	<u>T(°C)</u>	<u>t(min)</u>			
1600	2	1500	60	12	*	0.92
"	4	"	"	"	*	0.98
"	10	"	"	"	*	0.94
"	20	"	"	"	*	0.81
"	30	"	"	"	*	1.00
"	2	"	"	14	*	0.99
"	2	"	"	"	**	0.57
"	10	"	"	"	*	0.95
"	2	"	"	15	*	0.96
"	2	"	120	"	*	0.65
"	10	"	60	"	*	0.98
"	10	"	120	"	*	1.00
"	2	"	60	16	*	0.50
"	10	"	"	"	*	0.60
"	10	"	120	"	*	0.98
"	2	"	60	"	**	0.21
"	2	"	"	17	**	0.17
"	5	"	"	"	**	0.16
"	15	"	"	"	**	0.20
"	2	"	"	"	***	0.04
"	2	"	"	19	**	0.17
"	2	"	"	"	***	0.14
"	2	"	"	21	***	0.13
"	2	"	"	24	**	0.22
"	2	"	"	"	***	0.08
"	2	"	"	31	**	0.20
"	2	"	"	"	***	0.07
1600	2	"	"	33	***	0.06
1585	2	"	"	"	"	0.04
1575	2	"	"	"	"	0.04
1550	2	"	"	"	"	0.05
1575	2	1465	"	"	"	0.05
1550	2	1447	"	"	"	0.07

* Alcoa XB-2 Setter Sand

** Alcoa XB-2 Setter Sand + Na₂O (9 wt. % Na₂O)

*** Alcoa XB-2 Setter Sand + Na₂O + Li₂O (9 wt. % Na₂O, 0.8 wt. % Li₂O)

Measurements were subsequently made on powders ground from tube specimens (Table VII). When firing in the undoped Alcoa XB-2 sinter sand the $f(\beta)$ values were again high, typically >0.50 . The values exceeded those of the bar samples, probably because the samples were thinner. As in the bar specimens, by adding additional soda a substantial improvement was noted in $f(\beta)$; the values were reduced to 0.10 to 0.20. In order to further promote conversion, in addition to the soda, the sinter sand was also doped with 0.8 wt. % Li_2O . As shown in Table VII the $f(\beta)$ was <0.10 when fired in the soda and lithia doped sand.

Tubes prepared from Tape #33 were sintered at temperatures in the range 1550 - 1600°C and annealed at temperatures of 1447 - 1500°C in the sinter sand which contained 9.0 wt. % Na_2O and 0.8 wt. % Li_2O . The results indicated the conversion to the β'' - Al_2O_3 structure was essentially independent of these firing conditions and for the temperature range examined $f(\beta)$ varied from 0.04 to 0.07.

In order to further define the importance of the level of concentration of soda and lithia in the sinter sand, tubes from Tape #43 were fired embedded in sand that contained 6.3, 8.0, or 10.0 wt. % Na_2O and 0, 0.4, or 0.8 wt. % Li_2O . The results are contained in Table VIII and indicated, as one may anticipate, that in order to obtain complete conversion the concentration of soda and lithia in the sand should be similar to, or exceed the composition of the tube.

Microstructural Examination:

In Figure 24 are photomicrographs of the tube wall for samples fired at 1585°C for 2 min. and annealed for 60 min. at 1450°C in sinter sand that contained 10 wt. % Na_2O and 0, 0.4, or 0.8 wt. % Li_2O . When firing in sand without lithia a fine grained, dense, sintered ceramic is produced with almost no evidence of exaggerated grain growth. At a lithia concentration of 0.4 wt. % a duplex microstructure with approximately 50% fine grain (~ 5 microns) and 50% coarse grain (~ 50 -100 microns) forms. At the highest lithia content the microstructure is predominantly coarse grained.

Table VIII

X-ray Measurements on Powder Samples Ground From
Fired Tubes From Tape 43 That Were
Fired in Soda and Lithia Doped Setter Sand.

Composition of Setter Sand*		
Na ₂ O (wt. %)	Li ₂ O (wt. %)	f(β)
10.0	0.8	.01
"	0.4	0.16
"	0.0	0.16
8.0	0.8	0.05
"	0.4	0.06
"	0.0	0.12
6.3	0.8	0.05
"	0.4	0.05
"	0.0	0.26

* Alcoa XB-2 alumina doped with additional Na₂O and Li₂O. All samples sintered at 1585°C for 2 min. with 60 min. anneal at 1450°C.

In most samples that exhibited a duplex structure the large and small grains were distributed uniformly across the sample suggesting little or no compositional inhomogeneity in the ceramic. In those instances where a grain size difference was observed across the tube wall the firing was generally conducted in a low soda content setter sand. In these samples a fine grain structure was observed at the periphery of the tube wall and the inside region exhibited either a duplex or coarse grain structure. Previous investigations^(53,54) have shown that low temperature eutectic liquids form in the Al₂O₃-NaAlO₂-LiAlO₂ ternary system and in the NaAlO₂-Al₂O₃ system. By firing in a setter sand of lower soda and lithia content diffusion of soda and lithia out of the tube should limit liquid phase formation and grain growth. Apparently the inside of the tube was sufficiently sealed to maintain the alkali atmosphere at a sufficiently high level to prevent excessive loss from the inner surface of the tube.

A. 10 wt. % Na_2O + 0.8 wt. % Li_2O

B. 10 wt. % Na_2O + 0.4 wt. % Li_2O

C. 10 wt. % Na_2O + 0.0 wt. % Li_2O

Figure 24. Typical Microstructure of 6''- Al_2O_3 Tubes Sintered at 1585°C for 2 min. and Annealed for 1 h at 1450°C in Various Setter Sand Compositions Shown.

In Figure 25 are shown the microstructures for two tubes sintered at 1550°C for 2 min. and annealed at 1500°C or 1447°C for 1 h. in a setter sand that contains 9 wt. % Na₂O and 0.8 wt. % Li₂O. These results agree with previous studies⁽¹⁵⁾ and demonstrate that by controlling the annealing temperature the grain size of the ceramic may be controlled to yield a preferred grain size distribution. Both samples had nearly complete conversion to the β'' -Al₂O₃ structure (Table VII). By conducting long time anneals at even lower temperatures, such as 1400°C, a fine grained microstructure should be achievable⁽¹⁵⁾ with similar conversion to the β'' -Al₂O₃ structure.

Conductivity Measurements:

In Figure 26 is shown σT (conductivity X absolute temperature) versus $1/T$ for three tube specimens prepared from cast tape. Samples 1600-2-T17-A-11 and 1600-2-T31-A-30 were fired at 1600°C for 2 min. and annealed for 1 h. at 1500°C while embedded in setter sand that contained 9.0 wt. % Na₂O. Both exhibited a fine grain size similar to that in Figure 24C and $f(\beta)$'s of 0.17 and 0.20. Sample 1600-2-T31-A-33 was fired at similar temperatures in setter sand that contained 9.0 wt. % Na₂O and 0.8 wt. % Li₂O. The grain size was large (similar to that shown in Figure 24A) and $f(\beta) = 0.07$. For comparison a commercially available β'' -Al₂O₃ tube was purchased from CERAMATEC INC.* The grain size of the CERAMATEC tube was similar to that of the fine grained tubes fabricated from cast tape.

Over most of the temperature range the data were linear and obeyed the relationship $\sigma T = \sigma_0 e^{-E/kt}$ where E is an activation energy for conduction. The agreement was reasonably good between the values obtained on the tubes prepared from the cast ceramic tape and the isostatically pressed CERAMATEC tube. The lower conductivity for the two fine grained, tape cast tubes is expected since they contain more of the lower conductivity, β -Al₂O₃. These results also suggest that the batch to batch fabrication and firing processes were similar. The higher conductivity for tube 1600-2-T31-A-33 is most likely due to both the decreased amount of β -Al₂O₃ present and the larger grain size.

* Isostatically Pressed β'' -Alumina Tube, Grade A, CERAMATEC INC., Salt Lake City, Utah

A. Annealed 1 h, 1500°C

B. Annealed 1 h, 1447°C

Figure 25. Microstructure of β - Al_2O_3 Tubes Sintered at 1550°C for 2 min. in Setter Sand that Contains 9.0 wt. % Na_2O + 0.8 wt. % Li_2O for Annealing Temperature Shown.

Figure 26. Conductivity-Temperature Curves for Tape Specimens.

In Table IX are summarized the activation energies for conduction based on a least squares fit to the conductivity equation for the linear, lower temperature range of the data. Included is the conductivity at 300°C calculated from the experimental data. Virkar et al.⁽¹⁴⁾ reported activation energies of 0.22 and 0.24 eV for fine grained (1-2 micron) β' - Al_2O_3 and 0.16 and 0.20 eV for coarse grained material. The lower activation energies for each grain size represented a lower contribution of the grain boundary resistance at the higher temperature. No attempt was made in the present study to separate the contributions of the grain boundary versus bulk grain resistance, as other investigations⁽⁵²⁻⁵⁵⁾ have done. However, we feel that the change in slope for both the CERAMATEC and tape cast sample (1600-2-T31-A-33) at 250°C may be due to a decreased contribution of the grain boundary resistance at higher temperatures. Since no similar change in slope was observed for the fine grained tape cast tubes the grain boundary resistance contribution may still be present at the highest temperature investigated (~350°C). Although the activation energies in this study were consistently higher than those reported by Virkar et al.⁽¹⁴⁾ there was good agreement with those reported by Jakubowski and Whitmore⁽⁵⁵⁾ for the low temperature activation energy associated with the grain boundary resistance.

Table IX

Conductivity Data for β'' - Al_2O_3 Tubes

Sample	σ	E (eV)	σ^*	ρ^*
	(ohm ⁻¹ cm ⁻¹ °K)		(ohm ⁻¹ cm ⁻¹)	(ohm-cm)
1600-2-T17-A-11	1.59×10^4	.26	0.126	7.92
1600-2-T31-A-30	2.0×10^4	.28	0.116	8.64
1600-2-T31-A-33	1.26×10^5	.32	0.234	4.27
CERAMATEC GRADE A	4.21×10^4	.29	0.196	5.10

* 300°C

Mechanical Measurements:

The results of diametral compression strength measurements on tubes fabricated from Tapes #15 and #33 are contained in Table X. Included are the firing and annealing temperatures, times, and $f(\beta)$ for the samples. The specimens from Tape #15 were fired in Alcoa XB-2 alumina setter sand without additional soda or lithia. As a result these samples were predominantly of the β - Al_2O_3 structure. The samples from Tape #33 were fired in setter sand that was doped to contain 9.0 wt. % Na_2O and 0.8 wt. % Li_2O and were primarily of the β'' - Al_2O_3 structure. For the β'' - Al_2O_3 tubes (Tape #33) the fracture stress decreased with an increase in the amount of the larger grain size fraction consistent with results of other investigations^(16,56). Although the mode of fracture was not determined in this study, previous investigators⁽¹⁶⁾ have shown that for coarse grained ceramic the mode of crack propagation is transgranular while for fine grain it is a mixed mode of trans- and intergranular. Unlike the β'' - Al_2O_3 tubes, measurements on the two sets of β - Al_2O_3 tubes showed no dependence on grain size for the fairly wide range of grain sizes tested (~ 5 and $\sim 50 \mu\text{m}$).

Table X
Diametral Compression Fracture
Strength Measurements on Tubes.

Tape No.	Firing		Annealing		$f(\beta)$	Strength (MPa)	Grain Size
	T(°C)	t(min)	T(°C)	t(min)			
33	1550	2	1450	60	.07	218±22	~25%, ~20 μm ~75%, <5 μm
33	1550	2	1500	60	.05	132±47	~50%, ~50 μm ~50%, <5 μm
33	1600	2	1500	60	.06	142±14	~100%, ~75 μm
15	1600	2	1500	60	~.90	228±54	~100%, <5 μm
15	1600	15	1500	60	~.90	223±54	~100%, ~50 μm

A complete analysis of the interrelationship of grain size, structure, and fracture stress was beyond the scope of the present investigation. The results indicated, however, that the fracture strength of tape cast β "- Al_2O_3 tubes appears to be comparable to that of tubes formed by alternative techniques such as isostatic pressing.

V. CONCLUSIONS

In this project, a method for casting "zeta"-processed beta alumina powder into ceramic tape for use in fabricating solid electrolyte tubes was developed. Optimization of the tape casting slip and powder preparation processes were carried out to yield a ceramic tape suitable for tube fabrication.

Tubes with thin walls, ~ 0.3 mm thick, ~ 1 cm diameter, and lengths of ~ 6 cm were prepared and evaluated as a function of firing condition and tube geometry. Closed end β "- Al_2O_3 tubes with mechanical and electrical properties comparable to those formed by alternative techniques, such as isostatic pressing⁽⁵⁶⁾, were produced.

In accordance with contract EM-78-C-01-5161 the tasks as outlined in the "Introduction" to this report were completed. (Task 4 is discussed in Appendix A).

VI. RECOMMENDATIONS FOR FUTURE WORK

In this study, the feasibility for the manufacture of β "- Al_2O_3 tubes was demonstrated on relatively small, laboratory size specimens. Future work on fabrication of larger tubes using commercial tube winding equipment is required to ultimately determine whether the cast tape process is a viable alternative to the more conventional fabrication techniques. With an increase in tube size, not only must the green tube fabrication process be evaluated, but alternative firing processes and equipment and container materials will have to be utilized. The use of large quantities of platinum for crucible liners is not expected to be a preferred manufacturing process. Recent research has been conducted on the firing of β "- Al_2O_3 without platinum encapsulation⁽¹⁹⁾. The applicability of these processes to the firing of thin walled, tape cast tubes will have to be evaluated.

Evaluation of the tape cast tubes in a Na/S cell was not done in this project. Assembly of Na/S cell testing equipment and evaluation of the $\beta''\text{-Al}_2\text{O}_3$ tubes fabricated from tape in cells is required. In addition to Na/S testing, design of prototype cells for assembly of a battery product should be initiated.

Alternative Na^+ -ion conductors should be evaluated when fabricated from cast tape. Initially NASICON tubes should be fabricated from cast tape and the physical properties of the ceramic evaluated for use in the Na/S battery.

A proposal is being prepared for submission to the Department of Energy for contract consideration which incorporates:

- a) The production of larger diameter, spiral wound tubes utilizing commercial tube wrapping equipment,
- b) Development of firing processes for large diameter thin wall tubes;
- c) Na/Na and Na/S cell testing of fired tubes; and
- d) Evaluation of the feasibility for using cast tape to fabricate NASICON tubes for use as a Na^+ -ion conductor.

REFERENCES

1. D. W. Bridges, R. W. Minck, and D. G. Paquette, "Reproducibility and Performance of Large Prototype Na/S Cells", in Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, Aug. 5-10, 1979, Boston, Mass., Paper 799147, American Chemical Society, Washington.
2. Research on Electrodes and Electrolyte for the Ford Sodium-Sulfur Battery, NSF Contract C805, Annual Reports for June 30, 1973-June 29, 1974; June 30, 1974-June 29, 1975; June 30, 1975-June 29, 1976.
3. N. Weber and J. T. Kummer, "A Sodium-Sulfur Secondary Battery", Trans. S.A.E. **76**, 1003-1007 (1968).
4. Method for Preparing a Sodium/Sulfur Cell, S. A. Weiner, U.S. Patent 4,102,042.
5. C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, "Refinement of the Structure of β -Alumina", Acta Cryst. **B27**, 1826-1834 (1971).
6. J. T. Kummer, " β -Alumina Electrolytes" in Progress in Solid State Chemistry, Vol. 7, H. Reiss and J. C. McCaldin ed., Pergamon Press, N.Y.
7. T. J. Whalen, G. J. Tennenhouse, and C. Meyer, "Relation of Properties to Microstructure in a β "-Alumina Ceramic", J. Am. Ceram. Soc., **57**, 497 (1974).
8. 'Energy Conversion Device Comprising a Solid Crystalline Electrolyte and a Solid Reaction Zone Separator, J. T. Kummer and N. Weber, U. S. Patent 3,404,036 (1978).
9. Secondary Battery Employing Molten Alkali Metal Reactant, J. T. Kummer and N. Weber, U. S. Patent 3,404,035.
10. Method of Making a Solid Ionic Conductor, G. J. Tennenhouse, U. S. Patent 3,446,677.
11. Method for Preparing Solid State Ionic Conductor, G. J. Tennenhouse, U. S. Patent 3,475,225.
12. Fabrication of Thin Layer Beta Alumina, NASA Contract 3-19782.
13. M. L. Miller, B. J. McEntire, G. R. Miller, and R. S. Gordon, "A Prepilot Process for the Fabrication of Polycrystalline β "-Alumina Electrolyte Tubing", Bull. Am. Ceram. Soc., **58** [5] 522-526 (1979).
14. A. V. Virkar, G. R. Miller, and R. S. Gordon, "Resistivity-Microstructure Relations in Lithia-Stabilized Polycrystalline β "-Alumina", J. Am. Ceram. Soc., **61** [5-6] 250-252 (1978).
15. G. E. Youngblood, A. V. Virkar, W. R. Cannon, and R. S. Gordon, "Sintering Processes and Heat Treatment Schedules for Conductive, Lithia-Stabilized β "-Al₂O₃, Bull. Am. Ceram. Soc., **56** [2] 206-212 (1977).

16. A. V. Virkar and R. S. Gordon, "Fracture Properties of Polycrystalline Lithia-Stabilized β "-Alumina", J. Am. Ceram. Soc., 60 [1-2] 58-61 (1977).
17. Method for Preparing Dense Beta-Alumina Ceramic Bodies by Liquid Phase Sintering, M. N. Shaikh, I. B. Cutler, A. V. Virkar, R. S. Gordon. U. S. Patent 4,138,455.
18. Method of Preparing Dense, High Strength, and Electrically Conductive Ceramics Containing β "-Alumina, A. V. Virkar, M. L. Miller, I. B. Cutler, R. S. Gordon. U. S. Patent 4,113,928.
19. Fabrication and Characterization of β "-Alumina Electrolytes and Electronic-Ceramic Containers for the Sodium-Sulfur Battery. NSF-C805. Semi-annual Report, June 30, 1976-December 31, 1976.
20. G. R. Miller, G. J. McEntire, T. D. Hadnagy, R. S. Gordon and A. V. Virkar, "Processing and Properties of Sodium β "-Alumina and NASICON Ceramic Electrolytes" presented at the International Conference Fast Ion Transport in Solids, May 21-25, 1979, Lake Geneva, Wisconsin.
21. A. V. Virkar and G. R. Miller, "Degradation of Rapid Ion Conductors Under Electrolytic Conditions", presented at the International Conference Fast Ion Transport in Solids, May 21-25, 1979, Lake Geneva, Wisconsin.
22. R. W. Powers and S. P. Mitoff, "An Effect of Furnace Atmospheres on the Sintering of Beta Alumina", Bull. Am. Ceram. Soc., 57 [4] 456 (1978).
23. W. L. Roth and F. Reidinger, "Studies of Stabilization and Transport Mechanisms in Beta and Beta "Alumina by Neutron Diffraction", in Superionic Conductors, G. D. Mahan and W. L. Roth ed., p. 223-241, Plenum Press, N. Y. (1976).
24. W. L. Roth, I. Chung, H. S. Story, "Characterization of Additive-Modified Beta Alumina Ceramic by Nuclear Magnetic Resonance", J. Am. Ceram. Soc., 60 [7-8] 311-315 (1977).
25. Sulfur Electrode, Sulfur Electrode Container, and Methods of Manufacture, M. W. Breiter and R. N. King, U. S. Patent, 4,140,841.
26. Construction for Solid Electrolyte in Sodium/Sulfur Battery, S. P. Mitoff, U. S. Patent 4,049,885.
27. Method of Producing Lithiated Beta-Alumina Articles, R. W. Powers, U. S. Patent 4,073,711.
28. A Method of Preparing Alkali Metal Beta Aluminates, G. Desplanches, Y. Lazennec, and J. Leboucq, Brit. Patent 1,494,066 and 1,499,308.
29. A Method of Manufacturing an Article Formed of an Alkaline β -Alumina, D. Broussand, Y. Lazennec, Brit. Pat. 1,501,163.
30. Sodium-Sulfur Battery Development for Bulk Power Storage, EPRI Research Project 128-2, Interim Report, May 1, 1974-April 30, 1975.

31. Development of Sodium-Sulfur Batteries for Utility Application, EPRI EM-266 (Research Project 128-3), Annual Report, December 1976.
32. Sodium Sulfur Battery Development, EPRI Project RP 128, Final Report, April 1, 1973-April 30, 1974.
33. Development of Sodium-Sulfur Batteries for Utility Applications, EPRI Project 128-4, Interim Report, May 1, 1976-August 31, 1977.
34. Y. Lazemec, C. Josne, P. Margotin, and J. Fally, "Factors Influencing the Lifetime of Pure Beta-Alumina Electrolyte", *J. Electrochem. Soc.*, **122** [6], 734-737 (1975).
35. J. N. Anand, "Dow Sodium-Sulfur Battery for Energy Storage", in Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, Aug. 5-10, 1979, Boston, Mass., Paper 793146, American Chemical Society, Washington.
36. Research Development in the Glass Fiber Sodium-Sulfur Battery, Contract No. DAHC-15-73-C-0254, Semi-Annual Report, December 31, 1975.
37. J. B. Goodenough, H. Y-P Hong, and J. A. Kafalas, "Fast Na^+ -Ion Transport in Skeleton Structures", *Mat. Res. Bull.*, **11**, 203-220 (1976).
38. H. Y-P Hong, "Crystal Structures and Crystal Chemistry in the System $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ", *Mat. Res. Bull.*, **11**, 173-182 (1976).
39. Solid Electrolytes: Alkali-Ion Transport in Skeleton Structures, NSF/RANN Contract AER 74-02094 and Air Force Contract F19628-76-C-0002. Semi-Annual Technical Summary, January 1, 1976-June 30, 1976.
40. J. A. Kafalas, "Effect of Pressure and Composition on Fast Na^+ -Ion Transport in the System $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ", presented at the International Conference Fast Ion Transport in Solids, May 21-25, 1979, Lake Geneva, Wisconsin.
41. R. Collongues, A. Kahn, and D. Michael, "Superionic Conducting Oxides", *Ann. Rev. Mater. Sci.*, **9**, 123-150 (1979).
42. J. C. Williams, "Doctor-Blade Process", in Treatise on Materials Science and Technology, **9**, ed. by F. A. Wang, Academic, NY.
43. R. E. Mistler, "High Strength Alumina Substrate Produced by a Multilayer Casting Technique", *Bull. Am. Ceram. Soc.*, **52**, 850-854 (1973).
44. R. B. Runk and M. J. Andrejco, "A Precision Tape Casting Machine for Fabricating Thin Ceramic Tapes", *Bull. Am. Ceram. Soc.*, **54** [2] 199-200 (1975).
45. R. T. Dirstine, W. O. Gentry, R. N. Elementhal, and W. Hammetter, "Calcium Doped Ceria Electrolyte Tubes for Low Temperature Oxygen Sensors" presented at Annual Meeting of the American Ceramic Society, May 7-10, 1978, Detroit, Michigan.
46. R. T. DeHoff and E. H. Aigeltinger, "Experimental Quantitative Microscopy with Applications to Sintering", in Perspectives in Powder Metallurgy, Vol. 5, ed. by J. S. Hirschorn, Plenum Press, New York (1970).

47. E. A. Ripperger and N. Davids, "Critical Stresses in a Circular Ring", Trans. Am. Soc. Civil Engineering, 112, 619 (1947).
48. C. W. Nelson, "Stresses and Displacements in a Hollow Circular Cylinder", Ph.D. Thesis, University of Michigan, May, 1939.
49. D. W. Johnson, E. M. Vogel, and M. F. Yan, "Processing and Sintering of β - Al_2O_3 ", presented at the Annual Meeting of the American Ceramic Society, April 29-May 2, 1979, Cincinnati, Ohio.
50. J. H. Kennedy, "Inhibition of Sintering of Beta Alumina by V_2O_5 ", J. Am. Ceram. Soc., 59 [5-6] 297-30 (1976).
51. M. Y. Hsieh and L. C. DeJonghe, "Silicate-Containing Sodium Beta-Alumina Solid Electrolytes", J. Am. Ceram. Soc., 61 [5-6] 185-191 (1978).
52. Substructure and Properties of Sodium Beta Alumina Solid Electrolytes, EPRI FP-1058, Project 252-2, Final Report, May 1979.
53. Research on Electrodes and Electrolyte for the Ford Sodium-Sulfur Battery, NSF (RANN)-C805. Annual Report, June 30, 1974 to June 29, 1975.
54. Research on Electrodes and Electrolyte for the Ford Sodium-Sulfur Battery, NSF (RANN)-C805, Semi-annual Report, June 29, 1975-December 31, 1975.
55. W. Jakubowski and D. H. Whitmore, "Analysis of Electrolyte Polarization in Polycrystalline Sodium β -Alumina by a Complex Admittance Method", J. Am. Ceram. Soc., 62 [7-8] 381-385 (1976).
56. J. N. Lingscheit, G. J. Tennenhouse, and T. J. Whalen, "Compositions and Properties of Conductive Ceramics for the Na-S Battery", Bull. Am. Ceram. Soc., 58 [5], 536-538 (1979).
57. Low-Cost Fabrication of Thin-Walled Solid Electrolyte Tubes from Doctor-Bladed Ceramic, Technical Proposal, D.O.E. contract EM-78-C-01-5161 (Awarded Aug. 31, 1978).

APPENDIX A

Evaluation of Equipment and Cost Estimate for Tube Fabrication

In order to evaluate the technical feasibility of adapting commercial tube rolling equipment to the fabrication of ceramic tubes from cast tape, the Rockport Machine and Tool Co., Cleveland, Ohio was visited. Rockport manufactures electronically controlled spiral tube winders, adhesive stands, cut off machines, and curl and disc end closure machines primarily for the manufacture of paper tubes. Mr. Molnar, owner, discussed the types of products that have been fabricated with their machines and arranged for a visit to a tube producer.

In addition to supplying numerous "jobbers", one of the major contractors for Rockport equipment is Union Carbide who manufactures tubular cases for dry cell batteries. Some of the products that have been formed into tubes with Rockport machines were mylar, paper, fiber glass, wet asbestos, coated papers (such as zinc coated, for battery cases), filter materials, and convoluted tubes. Typical production speeds for the easiest materials were ~100,000 in/hr (~1 inch diameter tube) and ~20,000 in/hr (~4 inch diameter tube). Up to 12 plies of material have been simultaneously wound.

With regard to the specific requirements for forming tubes from cast tape, Mr. Molnar noted that the mechanical strength of the tape was not important since it could be supported as it is fed onto the winding machine. In one application, the spiral winding of wet asbestos, the material had almost no strength prior to tube forming. He also noted that the tape could be heated during the forming process to promote bonding or solvent removal. The stationary mandrel that the tape is wrapped around may be heated internally, by steam or electrically. A backing paper or release paper is often used and no major problem was foreseen with the use of ceramic tape backed with or without paper.

The primary modification to existing tube forming equipment would involve changes in the disc insert machine to solvent seal rather than curl seal the disc into the tube end.

A cost analysis⁽⁵⁷⁾ for 44 cm long tubes, 2.9 cm diameter, with 1.5 mm thick walls was made in August 1977. On a production rate of 268,800 tubes per year with a 95% product yield the cost per tube was estimated to be \$2.772/tube. In the initial cost analysis a dry tape thickness of 30 mil was used. The present study indicated a tape thickness of ~5 mil could be successfully used for tube fabrication. Revision of the initial cost estimate to include the increase in tape casting equipment and labor indicates a more realistic estimate of the cost/tube would be \$3.837 (based on the August 1977 figures).

APPENDIX B

Bibliography of Papers and Presentations

R. T. Dirstine, "Fabrication of β "- Al_2O_3 Tubes from Cast Ceramic Tape", presented at the International Conference on Fast Ion Transport in Solids, Lake Geneva, Wisconsin, May 21-25, 1978.

W. O. Gentry and G. E. Stapleton, "The Diametral Compression Test", submitted to the Am. Ceram. Soc. (1979).

A Note Prepared for Submission to the Journal of the
American Ceramic Society

THE DIAMETRAL COMPRESSION TEST

by
W. O. Gentry and G. E. Stapleton

The mechanical strength of a ceramic material which has been formed into a tube and fired can be conveniently measured in the diametral compression test ⁽¹⁾. In this test a ring of some length is cut from the tube, placed between the platens of a testing machine such that it will be loaded on the bottom and top of the ring's diameter, and loaded to fracture. The material's strength, or the tube's Modulus of Rupture, is given by

$$\sigma_{\text{mor}} = K \cdot \frac{2 \cdot (\text{load at fracture})}{\pi \cdot (\text{OD}) \cdot (\text{length})}$$

The proportionality constant, K , is a complex function of the ratio, α , of the tube's inner diameter to outer diameter. This constant was evaluated by Nelson ⁽²⁾ for the nine equispaced values of α between 0.1 to 0.9. These allowed the K 's for intermediate ratios to be estimated graphically or by an arithmetical interpolation technique, 9-point Lagrangian interpolation being more accurate than linear interpolation when α is larger than 0.35. For the very thin wall tubes now being made of ceramic electrolytes such as cerium dioxide ⁽³⁾ for use as atmosphere sensors or beta alumina ^(4, 5) for battery electrolytes, a very useful approximation is

$$K \approx \frac{(1 + \alpha)(1 + 3\alpha)}{\alpha(1 - \alpha)^2}$$

This approximation gives a value of K only 1.6% larger than the true value at $\alpha = 0.9$ and the error decreases as α increases.

For greater accuracy (and to confirm the utility of the approximation) a computer technique was used to solve Nelson's analytical expression; a table of these calculated values is appended.

-
1. S. A. Bortz and H. H. Lund, "The Brittle Ring Test," Mechanical Properties of Engineering Ceramics, W. Wurth Kriegel and H. Palmour III, eds., Interscience, (New York, 1961).
 2. C. W. Nelson, "Stresses and Displacements in a Hollow Circular Cylinder," Ph.D. Thesis, University of Wisconsin, May 1939.
 3. R. T. Dirstine, W. O. Gentry, R. N. Blumenthal, and W. Hammetter, "Calcium Doped Ceria Ceramic Tubes for Low Temperature Oxygen Sensors," Bull. Am. Ceram. Soc. 58 (8), 778 (1979).
 4. R. T. Dirstine, "Fabrication of β - Al_2O_3 Tubes from Cast Ceramic Tape," Proceedings of the International Conference on Fast Ion Transport in Solids, Lake Geneva, Wisconsin, May 1979.
 5. R. W. Davidge, et al., "Strength and Delayed Fracture Behavior of Beta Alumina," Bull. Am. Ceram. Soc. 58, 771 (1979).

Table J
Interpolated Values of K

<u>ID/OD</u>	<u>Nelson's Calculations</u>	<u>New Calculations</u>	<u>9 Point Lagrangian</u>	<u>Δ (%)</u>	<u>Linear Interpolation</u>	<u>Δ (%)</u>
0.9	581.59	-	-	-	-	-
0.85	-	254.337	269.46	6	361.15	42
0.80	140.72	-	-	-	-	-
0.75	-	88.5497	86.88	2	100.58	14
0.70	60.45	-	-	-	-	-
0.65	-	43.6444	44.090	1	46.64	7
0.60	32.838	-	-	-	-	-
0.55	-	25.5012	25.286	1	26.57	4
0.50	20.311	-	-	-	-	-
0.45	-	16.5196	16.694	1	16.997	3
0.40	13.682	-	-	-	-	-
0.35	-	11.5204	11.291	2	11.719	2
0.30	9.856	-	-	-	-	-
0.25	-	8.5744	9.086	6	8.727	2
0.20	7.598	-	-	-	-	-
0.15	-	6.8791	4.632	49	6.992	2
0.10	6.385	-	-	-	-	-

MAXIMUM TENSILE STRESS DURING DIAMETRAL COMPRESSION OF TUBE.

STRESS = $K \cdot (2 \cdot \text{LOAD}) / (\pi \cdot \text{ID} \cdot \text{LENGTH})$
 K'S CALCULATED BY V.O. GENTRY AND G.E. STAPLETON,
 JOHNSON CONTROLS, INC., GLOBE-UNION, INC., MILWAUKEE, WI.

ID/OD	C	1	2	3	4	5	6	7	8	9										
0.99	0.598176E	05	0.738713E	05	0.933221E	05	0.122189E	06	0.146363E	06	0.239635E	06	0.374544E	06	0.666058E	06	0.549908E	07	0.599814E	07
0.98	0.149087E	05	0.145244E	05	0.184171E	05	0.206539E	05	0.233235E	05	0.245450E	05	0.304819E	05	0.353626E	05	0.415147E	05	0.494210E	05
0.97	0.460575E	04	0.707136E	04	0.758781E	04	0.816279E	04	0.880548E	04	0.952494E	04	0.103406E	05	0.112628E	05	0.123137E	05	0.135135E	05
0.96	0.370426E	04	0.389787E	04	0.410699E	04	0.433333E	04	0.457883E	04	0.484572E	04	0.513654E	04	0.543425E	04	0.580226E	04	0.613454E	04
0.95	0.236377E	04	0.246159E	04	0.256602E	04	0.267721E	04	0.279574E	04	0.292229E	04	0.305738E	04	0.320244E	04	0.335779E	04	0.352458E	04
0.94	0.163611E	04	0.169257E	04	0.175199E	04	0.181437E	04	0.188054E	04	0.195016E	04	0.202368E	04	0.210143E	04	0.218371E	04	0.227039E	04
0.93	0.119827E	04	0.123364E	04	0.127059E	04	0.130922E	04	0.134961E	04	0.139190E	04	0.143619E	04	0.148261E	04	0.153130E	04	0.158241E	04
0.92	0.914535E	03	0.938131E	03	0.962644E	03	0.988123E	03	0.101462E	04	0.104218E	04	0.107088E	04	0.110077E	04	0.113191E	04	0.116439E	04
0.91	0.720307E	03	0.736818E	03	0.753899E	03	0.771575E	03	0.789873E	03	0.808825E	03	0.828460E	03	0.848812E	03	0.869916E	03	0.891811E	03
0.90	0.581591E	03	0.593599E	03	0.605959E	03	0.618715E	03	0.631873E	03	0.645452E	03	0.659468E	03	0.673941E	03	0.688891E	03	0.704335E	03
0.89	0.479116E	03	0.488104E	03	0.497345E	03	0.506847E	03	0.516621E	03	0.526677E	03	0.537026E	03	0.547679E	03	0.558650E	03	0.569949E	03
0.88	0.401296E	03	0.403201E	03	0.415283E	03	0.422548E	03	0.430003E	03	0.437655E	03	0.445510E	03	0.453576E	03	0.461860E	03	0.470371E	03
0.87	0.340827E	03	0.346245E	03	0.351790E	03	0.357468E	03	0.363282E	03	0.369237E	03	0.375338E	03	0.381589E	03	0.387996E	03	0.394563E	03
0.86	0.292924E	03	0.297250E	03	0.301672E	03	0.306192E	03	0.310812E	03	0.315536E	03	0.320368E	03	0.325309E	03	0.330364E	03	0.335536E	03
0.85	0.254337E	03	0.257247E	03	0.261428E	03	0.265084E	03	0.268815E	03	0.272625E	03	0.276515E	03	0.280487E	03	0.284545E	03	0.288689E	03
0.84	0.222808E	03	0.225692E	03	0.228633E	03	0.231630E	03	0.234687E	03	0.237803E	03	0.240980E	03	0.244220E	03	0.247526E	03	0.250897E	03
0.83	0.196715E	03	0.199116E	03	0.201560E	03	0.204048E	03	0.206582E	03	0.209163E	03	0.211791E	03	0.214468E	03	0.217196E	03	0.219974E	03
0.82	0.176885E	03	0.176903E	03	0.178956E	03	0.181043E	03	0.183167E	03	0.185328E	03	0.187526E	03	0.189763E	03	0.192040E	03	0.194357E	03
0.81	0.156439E	03	0.158157E	03	0.159892E	03	0.161660E	03	0.163458E	03	0.165285E	03	0.167142E	03	0.169030E	03	0.170949E	03	0.172900E	03
0.80	0.140716E	03	0.142181E	03	0.143669E	03	0.145180E	03	0.146714E	03	0.148272E	03	0.149855E	03	0.151462E	03	0.153095E	03	0.154754E	03
0.79	0.127206E	03	0.128470E	03	0.129751E	03	0.131052E	03	0.132372E	03	0.133711E	03	0.135071E	03	0.136450E	03	0.137851E	03	0.139273E	03
0.78	0.115515E	03	0.116612E	03	0.117724E	03	0.118852E	03	0.119995E	03	0.121155E	03	0.122331E	03	0.123524E	03	0.124734E	03	0.125951E	03
0.77	0.105332E	03	0.106290E	03	0.107261E	03	0.108245E	03	0.109242E	03	0.110252E	03	0.111276E	03	0.112315E	03	0.113367E	03	0.114434E	03
0.76	0.964101E	02	0.972516E	02	0.981039E	02	0.989671E	02	0.998414E	02	0.100727E	03	0.101626E	03	0.102533E	03	0.103454E	03	0.104387E	03
0.75	0.885497E	02	0.892928E	02	0.900450E	02	0.908065E	02	0.915775E	02	0.923580E	02	0.931483E	02	0.939484E	02	0.947587E	02	0.955792E	02
0.74	0.815901E	02	0.822495E	02	0.829166E	02	0.835917E	02	0.842748E	02	0.849661E	02	0.856657E	02	0.863737E	02	0.870903E	02	0.878156E	02
0.73	0.753998E	02	0.759873E	02	0.765817E	02	0.771828E	02	0.777909E	02	0.784060E	02	0.790281E	02	0.796575E	02	0.802942E	02	0.809384E	02
0.72	0.698696E	02	0.703956E	02	0.709273E	02	0.714649E	02	0.720085E	02	0.725580E	02	0.731137E	02	0.736756E	02	0.742439E	02	0.748185E	02
0.71	0.649101E	02	0.653826E	02	0.658602E	02	0.663428E	02	0.668306E	02	0.673236E	02	0.678219E	02	0.683255E	02	0.688347E	02	0.693493E	02
0.70	0.604457E	02	0.608718E	02	0.613022E	02	0.617370E	02	0.621763E	02	0.626202E	02	0.630687E	02	0.635219E	02	0.639798E	02	0.644425E	02
0.69	0.564133E	02	0.567957E	02	0.571879E	02	0.575810E	02	0.579781E	02	0.583791E	02	0.587841E	02	0.591933E	02	0.596065E	02	0.600240E	02

0.68 0.527592E 02 0.531090E 02 0.534621E 02 0.538184E 02 0.541785E 02 0.545420E 02 0.549090E 02 0.552796E 02 0.556538E 02 0.560317E 02
 0.67 0.494381E 02 0.497563E 02 0.500776E 02 0.504019E 02 0.507292E 02 0.510596E 02 0.513931E 02 0.517298E 02 0.520697E 02 0.524128E 02
 0.66 0.466409E 02 0.467014E 02 0.469945E 02 0.472903E 02 0.475887E 02 0.478899E 02 0.481935E 02 0.485007E 02 0.488102E 02 0.491227E 02
 0.65 0.436444E 02 0.439102E 02 0.441783E 02 0.444488E 02 0.447217E 02 0.449970E 02 0.452748E 02 0.455550E 02 0.458372E 02 0.461231E 02
 0.64 0.411099E 02 0.413536E 02 0.415995E 02 0.418474E 02 0.420975E 02 0.423493E 02 0.426043E 02 0.428609E 02 0.431193E 02 0.433810E 02
 0.63 0.387222E 02 0.390063E 02 0.392923E 02 0.394601E 02 0.396899E 02 0.399216E 02 0.401553E 02 0.403909E 02 0.406285E 02 0.408682E 02
 0.62 0.363990E 02 0.368664E 02 0.370545E 02 0.372643E 02 0.374759E 02 0.376892E 02 0.379042E 02 0.381210E 02 0.383396E 02 0.385600E 02
 0.61 0.346640E 02 0.348546E 02 0.350467E 02 0.352403E 02 0.354355E 02 0.356323E 02 0.358306E 02 0.360305E 02 0.362320E 02 0.364351E 02
 0.60 0.328379E 02 0.330142E 02 0.331919E 02 0.333709E 02 0.335513E 02 0.337332E 02 0.339164E 02 0.341011E 02 0.342873E 02 0.344749E 02
 0.59 0.311471E 02 0.313105E 02 0.314751E 02 0.316409E 02 0.318081E 02 0.319764E 02 0.321461E 02 0.323171E 02 0.324894E 02 0.326630E 02
 0.58 0.295789E 02 0.297304E 02 0.298832E 02 0.300371E 02 0.301922E 02 0.303484E 02 0.305057E 02 0.306643E 02 0.308240E 02 0.309850E 02
 0.57 0.281215E 02 0.282625E 02 0.284046E 02 0.285476E 02 0.286915E 02 0.288369E 02 0.289831E 02 0.291304E 02 0.292788E 02 0.294282E 02
 0.56 0.267653E 02 0.268967E 02 0.270289E 02 0.271621E 02 0.272963E 02 0.274314E 02 0.275674E 02 0.277045E 02 0.278425E 02 0.279815E 02
 0.55 0.253012E 02 0.256237E 02 0.257471E 02 0.258713E 02 0.259963E 02 0.261223E 02 0.262491E 02 0.263768E 02 0.265054E 02 0.266349E 02
 0.54 0.243213E 02 0.244357E 02 0.245509E 02 0.246669E 02 0.247836E 02 0.249012E 02 0.250196E 02 0.251388E 02 0.252588E 02 0.253796E 02
 0.53 0.232183E 02 0.233253E 02 0.234331E 02 0.235415E 02 0.236507E 02 0.237606E 02 0.238712E 02 0.239826E 02 0.240947E 02 0.242076E 02
 0.52 0.221860E 02 0.222862E 02 0.223871E 02 0.224886E 02 0.225906E 02 0.226937E 02 0.227972E 02 0.229015E 02 0.230064E 02 0.231120E 02
 0.51 0.212185E 02 0.213125E 02 0.214070E 02 0.215022E 02 0.215980E 02 0.216944E 02 0.217915E 02 0.218892E 02 0.219874E 02 0.220864E 02
 0.50 0.203107E 02 0.203990E 02 0.204877E 02 0.205771E 02 0.206670E 02 0.207574E 02 0.208485E 02 0.209401E 02 0.210323E 02 0.211251E 02
 0.49 0.194580E 02 0.195410E 02 0.196244E 02 0.197083E 02 0.197928E 02 0.198778E 02 0.199633E 02 0.200493E 02 0.201359E 02 0.202231E 02
 0.48 0.186562E 02 0.187342E 02 0.188127E 02 0.188917E 02 0.189711E 02 0.190510E 02 0.191314E 02 0.192123E 02 0.192937E 02 0.193756E 02
 0.47 0.179015E 02 0.179749E 02 0.180488E 02 0.181232E 02 0.181979E 02 0.182732E 02 0.183489E 02 0.184250E 02 0.185016E 02 0.185787E 02
 0.46 0.171903E 02 0.172595E 02 0.173292E 02 0.173993E 02 0.174697E 02 0.175406E 02 0.176119E 02 0.176837E 02 0.177550E 02 0.178264E 02
 0.45 0.165196E 02 0.165849E 02 0.166507E 02 0.167167E 02 0.167832E 02 0.168501E 02 0.169173E 02 0.169850E 02 0.170530E 02 0.171215E 02
 0.44 0.158866E 02 0.159483E 02 0.160103E 02 0.160727E 02 0.161354E 02 0.161986E 02 0.162620E 02 0.163259E 02 0.163901E 02 0.164547E 02
 0.43 0.152846E 02 0.153468E 02 0.154095E 02 0.154644E 02 0.155237E 02 0.155833E 02 0.156433E 02 0.157036E 02 0.157642E 02 0.158252E 02
 0.42 0.147232E 02 0.147783E 02 0.148338E 02 0.148895E 02 0.149456E 02 0.150019E 02 0.150586E 02 0.151156E 02 0.151729E 02 0.152306E 02
 0.41 0.141834E 02 0.142405E 02 0.142930E 02 0.143457E 02 0.143988E 02 0.144521E 02 0.145057E 02 0.145596E 02 0.146139E 02 0.146684E 02

0.40 0.136821E 02 0.137315E 02 0.137811E 02 0.138317E 02 0.138813E 02 0.139318E 02 0.139825E 02 0.140336E 02 0.140849E 02 0.141355E 02
 0.39 0.132025E 02 0.132493E 02 0.132963E 02 0.133437E 02 0.133912E 02 0.134390E 02 0.134871E 02 0.135355E 02 0.135841E 02 0.136329E 02
 0.38 0.127440E 02 0.127924E 02 0.128370E 02 0.128818E 02 0.129269E 02 0.129722E 02 0.130178E 02 0.130636E 02 0.131096E 02 0.131559E 02
 0.37 0.123170E 02 0.123591E 02 0.124014E 02 0.124439E 02 0.124867E 02 0.125297E 02 0.125729E 02 0.126163E 02 0.126600E 02 0.127039E 02
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 0.35 0.115206E 02 0.115582E 02 0.115963E 02 0.116346E 02 0.116731E 02 0.117118E 02 0.117507E 02 0.117897E 02 0.118290E 02 0.118685E 02
 0.34 0.111527E 02 0.111881E 02 0.112243E 02 0.112606E 02 0.112972E 02 0.113339E 02 0.113708E 02 0.114079E 02 0.114452E 02 0.114827E 02
 0.33 0.108027E 02 0.108336E 02 0.108711E 02 0.109056E 02 0.109403E 02 0.109752E 02 0.110102E 02 0.110454E 02 0.110808E 02 0.111164E 02
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 0.30 0.985644E 01 0.988566E 01 0.991504E 01 0.994458E 01 0.997426E 01 0.100041E 02 0.100341E 02 0.100643E 02 0.100946E 02 0.101250E 02
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 0.28 0.930275E 01 0.932908E 01 0.935555E 01 0.938216E 01 0.940891E 01 0.943580E 01 0.946283E 01 0.949000E 01 0.951731E 01 0.954477E 01
 0.27 0.904693E 01 0.907191E 01 0.909702E 01 0.912226E 01 0.914764E 01 0.917315E 01 0.919880E 01 0.922458E 01 0.925050E 01 0.927656E 01
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 0.23 0.815047E 01 0.817057E 01 0.819077E 01 0.821110E 01 0.823153E 01 0.825208E 01 0.827275E 01 0.829353E 01 0.831442E 01 0.833544E 01
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 0.21 0.777174E 01 0.778965E 01 0.780767E 01 0.782579E 01 0.784402E 01 0.786236E 01 0.788080E 01 0.789936E 01 0.791802E 01 0.793678E 01
 0.20 0.759836E 01 0.761521E 01 0.763221E 01 0.764929E 01 0.766647E 01 0.768375E 01 0.770114E 01 0.771863E 01 0.773623E 01 0.775393E 01
 0.19 0.743519E 01 0.745106E 01 0.746702E 01 0.748309E 01 0.749925E 01 0.751552E 01 0.753188E 01 0.754835E 01 0.756492E 01 0.758159E 01
 0.18 0.729194E 01 0.729693E 01 0.731131E 01 0.732689E 01 0.734207E 01 0.735735E 01 0.737272E 01 0.738819E 01 0.740376E 01 0.741943E 01
 0.17 0.713934E 01 0.715227E 01 0.716630E 01 0.718042E 01 0.719464E 01 0.720895E 01 0.722336E 01 0.723786E 01 0.725246E 01 0.726713E 01
 0.16 0.700412E 01 0.701713E 01 0.703023E 01 0.704341E 01 0.705670E 01 0.707007E 01 0.708354E 01 0.709710E 01 0.711075E 01 0.712450E 01
 0.15 0.687904E 01 0.689117E 01 0.690336E 01 0.691564E 01 0.692801E 01 0.694047E 01 0.695302E 01 0.696566E 01 0.697839E 01 0.699121E 01
 0.14 0.676297E 01 0.677420E 01 0.678550E 01 0.679688E 01 0.680836E 01 0.681992E 01 0.683158E 01 0.684332E 01 0.685515E 01 0.686707E 01
 0.13 0.665566E 01 0.666601E 01 0.667644E 01 0.668695E 01 0.669755E 01 0.670824E 01 0.671901E 01 0.672988E 01 0.674083E 01 0.675186E 01
 0.12 0.655694E 01 0.656643E 01 0.657600E 01 0.658564E 01 0.659541E 01 0.660524E 01 0.661515E 01 0.662515E 01 0.663524E 01 0.664541E 01
 0.11 0.646665E 01 0.647530E 01 0.648404E 01 0.649286E 01 0.650174E 01 0.651075E 01 0.651982E 01 0.652897E 01 0.653821E 01 0.654753E 01
 0.10 0.638847E 01 0.639249E 01 0.640040E 01 0.640840E 01 0.641647E 01 0.642463E 01 0.643287E 01 0.644119E 01 0.644959E 01 0.645808E 01

LIST COMPLETION

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50 THIS PROGRAM CALCULATES VALUES OF "F" FOR DI/OD RATIOS (ALPHA)
60 OF 0.100 TO 0.999.
70 THE OUTPUT IS FORMATTED TO GENERATE A TABLE BEING THE 102
80 AVAILABLE COLUMNS ON LINE 14 HALF PAGE. THE FORMAT WILL HAVE TO
90 BE MODIFIED TO FIT ON STANDARD 72 COLUMN PAPER.
10 DOUBLE PRECISION ALPHA
20 DIMENSION XALPHA(10),ANSWER(10),ANSWERC(10)
30 PRINT 110
350 LINE 40 INITIATES ALPHA (DI/OD) TO ITS LARGEST VALUE.
40 ALPHA=.999
50 LINE =0
60 PRINT 101
70 PRINT 120
80 PRINT 130
90 PRINT 100
950 LINE 100 STARTS A LOOP TO CALCULATE AND STORE IN ARRAY "ANSWER"
960 VALUES OF "F" IN SETS OF 10.
970 THE NECESSARY EQUATIONS ARE FOUND IN APPENDIX 1 PAGE 1 IN
980 "STRESSES AND DISPLACEMENTS IN A HOLLOW CIRCULAR CYLINDER," PHD
990 THESIS BY C.W. NELSON, UNIVERSITY OF MICHIGAN, MAY, 1939.
100 1 DD461L=1,10
110 2 X=2.
120 XMM=0.
130 XK=0.
140 XMM1=0.
150 XDIF=0.
160 XMD=2/(1-ALPHA**2)
1650 LINE 170 THROUGH 280 CALCULATE THE SERIES FOR ONE VALUE OF
1660 DI/OD. INCREMENTING "X" BY 2 UNTIL THE DIFFERENCE BETWEEN TWO
1670 CONSECUTIVE VALUES IS LESS THAN OR EQUAL TO 1.0E-6.
170 20 ON=(1-ALPHA**2*X)**2-2*(X**2)*(ALPHA**2*X-2)*(1-ALPHA**2)**2)
180 XMM1=XMM
190 XMM=(4*(1-ALPHA**X-2)*(1-ALPHA**2)*(1-ALPHA**2*X))/ON
200 X=X+MM
210 IF (X-2)/10<10.15
220 15 XDIF=XMM1-XMM
230 IF (XDIF-1.0E-6)/11,11,16
240 16 X=X+2
250 GO TO 20
260 10 X=X+2
270 GO TO 20
280 11 ANSWER(1L)=X-XMD
290 XALPHA(1L)=ALPHA
2950 ALPHA IS NOW DECREMENTED BY 0.001 AND ANOTHER "Y" IS CALCULATED.
300 ALPHA=ALPHA-.001
310 40 CONTINUE
3150 THE REMAINING STATEMENTS ARE FORMAT RELATED.
320 LINE=LINE+1
330 IF (LINE,GE,60)PRINT 98
340 IF (LINE,GE,60-LINE=0
350 ISSUE=1,10
360 ISSUEWO=11-IUE
370 50 ANSWER(IUE)=ANSWER(IUEWO)
380 PRINT 99,ALPHA,ANSWERS
390 100 FORMAT(100,"ID OD",T13,"0",T36,"1",T39,"2",T52,"3",T65,"4",
400 & "178","5",T91,"6",T104,"7",T117,"8",T130,"9")
410 IF (ALPHA-.100)GOTO 1,1
420 98 FORMAT(101,F4.2,1X,10(1X,E12.6))
430 99 FORMAT(100,F4.2,1X,10(1X,F12.6))
440 120 FORMAT(1H,"T43,"F5.0,CALCULATED BY M.D.GENTRY AND G.E.STAPLETON.")
450 101 FORMAT(1H,T49,"STRESS = 1+(2+1.04D)/(PI*OD*LENGTH)")
460 110 FORMAT(1H,T36,"MAXIMUM TENSILE STRESS DURING DIAPYRAL ",
461 & "CONFESSION OF TUBE.")
480 130 FORMAT(1H,T40,"JOHNSON CONTROLS INC., GLOBE-UNION INC. ",
481 & "HILMARNEC,WI.")
490 31 STOP
500 END

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FABRICATION OF β'' - Al_2O_3 TUBES FROM CAST CERAMIC TAPE

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ABSTRACT

Most conceptions of the sodium/sulfur batteries for commercial use in electric vehicles or stationary energy storage applications show in each cell a tube-shaped sodium ion-conducting ceramic electrolyte. Presently such tubes are fabricated by one of several batch ceramic processes based on electrophoresis or isostatic pressing. These methods of production cause the electrolyte component to be inherently costly and are limited to their ability to produce thin-walled tubes, which is reflected in higher internal resistance and reduced performance of the battery.

An alternative approach is proposed for fabricating thin wall (~ 0.3 mm) β'' - Al_2O_3 tubes from cast ceramic tape. The fabrication process and characteristics of the fired tubes are described.

INTRODUCTION

Doctor-blading to form ceramic tape is a well established production method for manufacturing the disc and multilayer ceramic capacitors and substrates for thick or thin film electronic circuitry [1-5]. The ceramic tapes produced by this process are flexible, self-supporting, and may be made into thin sheets (0.02 to 0.1 mm) of large area with uniform density.

Recent results have shown that ceramic tape may be used for forming cylindrical, closed end, electrolyte tubes [6] by simply wrapping the tape around a mandrel. The wall thickness may be considerably thinner than is the case with extruded tubes [7], as thin as two layers of tape (~ 40 microns), and of variable diameter if desired. By combining continuous tape casting equipment with technology borrowed from the paper industry for manufacturing paper tubes, it may be possible to very cheaply mass produce solid electrolyte tubes. This becomes more apparent when it is realized that in 1976 the paper industry produced an estimated 11.4 billion such tubes [8].

In this paper a new fabrication technique for thin wall tubes is described based on the use of a doctor-bladed ceramic tape. Although the solid electrolyte used in this study is β'' - Al_2O_3 , other materials, such as NASICON [9], should be equally suited for tube fabrication by this technique.

EXPERIMENTAL

β'' - Al_2O_3 bar and tube specimens were fabricated from doctor-bladed tape which contained 8.85 w/o Na_2O , 0.75 w/o Li_2O , and 90.4 w/o Al_2O_3 . The composition was prepared from powder mixtures of α - Al_2O_3 , Na_2CO_3 *, and LiNO_3 ** using the zeta

* Deagglomerated, 0.3 micron, Adolf Meller Co.

** Research Organic/Inorganic Chemical Co.

process [10]. In the zeta process, the dried LiNO_3 is pre reacted with Al_2O_3 to form the zeta lithium aluminate, $\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$. By pre reacting the Li_2O to form the spinel, the lithium distribution in the final composition is improved. In addition to this powder, a soda containing precursor, nominally $\text{Na}_2\text{O} \cdot 5.3\text{Al}_2\text{O}_3$, is prepared. As shown in Figure 1, after calcination of each precursor powder, a mixture of both are dry vibratory milled for 4 hours to form the powder used in tape casting. In the powder milling processes high purity alumina mill media and polyethylene containers are used to reduce contamination. Typical specific surface areas of the calcined $\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 5.3\text{Al}_2\text{O}_3$, and vibratory milled combined powder were 5.6, 8.4, and $8.7 \text{ m}^2/\text{g}$.

About 200 g of powder is mixed with a thermoplastic organic resin, a compatible plasticizer, a solvent, and a wetting agent in a 1.1 liter Rosinex polygonal grinding jar one-half filled with a 0.95 cm end radius zirconia mill media. The organic formulation used in doctor-blading was derived from a proprietary composition used in the fabrication of BaTiO_3 based multilayer capacitors. Approximately 0.1 mm thick sheets, 15 cm x 2 m were formed by doctor-blading the slip onto polyethylene coated paper fixed to glass sheets. The tape, after drying to form a flexible sheet, was stripped from the paper by drawing the paper over the edge of a sheet of glass.

Closed end tubes have been fabricated by wrapping this cast ceramic tape into several configurations. These included spiral lap joints like paper tubes and, by wrapping rectangular sheets around a rod, linear lap joints which extend the length of the tubes. In the present study the latter technique was used. Ceramic tape, 8.8 cm x 17 cm, was wrapped around a 1.27 cm dia Teflon® coated rod such that there were four layers of tape in the wall. Application

Fig. 1 Preparation of Zeta Process Powder.

of an organic solvent during forming partially dissolved the mating surfaces of the tape to form a solid body. After the tube was removed from the rod, one end was sealed by either coating the internal surface with the solvent and pinching closed that end in a heated die or by solvent bonding a flat, 1.27 cm dia disc inside the tube. The disc inserts for the tubes were ~0.5 mm thick and were formed by pressing multiple layers of tape in a heated die at 50°C. Specimens, ~2.0 x 2.0 cm x 1 mm were also cut from these bars for use in determining an optimum firing cycle for the tubes.

Tubes were fired in both vertical and horizontal positions in platinum or alumina crucibles while embedded in beta alumina* setter sand. Since the tube walls tended to collapse when firing in a horizontal position, the vertical position shown in Figure 2 was preferred. Four tubes were concentrically positioned within the 7.6 cm dia x 10.2 cm high platinum crucible. Platinum foil caps covered the open ends of the tubes to prevent entry of the setter sand. The furnace and sample temperature were measured by locating thermocouples immediately above and at the center of the crucible. The firing cycles involved heating at 50°C/min. to 1600°C for 2 to 10 minutes followed by a high temperature anneal at 1500°C for one hour to promote conversion to the $\beta''\text{-Al}_2\text{O}_3$ phase [10]. In order to minimize soda loss from the tubes, additional soda was

added to the setter sand. Prior to the high temperature firing the organic components were removed by slow heating to 500°C.

Porosity measurements and microstructural characterization were made on fired tubes. The relative amounts of β - and $\beta''\text{-Al}_2\text{O}_3$ was determined by an x-ray diffraction technique using the normalized $f(\beta)$ which is approximately proportional to the fraction of β -phase present in a $\beta + \beta''\text{-Al}_2\text{O}_3$ mixture [10]. The normalized index was calculated by taking the ratio of the integrated intensity of the (110) $\beta\text{-Al}_2\text{O}_3$ peak and the sum of the integrated $\beta\text{-Al}_2\text{O}_3$ peak and the (01,11) $\beta''\text{-Al}_2\text{O}_3$ peak.

Fig. 2 Firing Position for Ceramic Tubes.

DISCUSSION AND RESULTS

Ceramic Tape: In modifying the proprietary formula for the slip used in making doctor-bladed barium titanate, it was necessary to adjust the ratio of ceramic powder to organic to compensate for the lower density of the zeta processed powder and to add a weak acid to neutralize the highly basic soda component. Without the acid addition an extremely viscous gel formed that was unsuitable for doctor-blading.

Eleven, ~200 g batches of tape were similarly prepared using a preferred slip composition. The reproducibility of the process is evidenced by the uniformity in the tape thickness ($0.117 \pm .007$ mm) and tape density (2.055 ± 0.084 g/cm³). Gravimetric measurements indicated the tapes contained 77.9 w/o ceramic, or a green density of 49.1% of theoretical based on 3.26 g/cm³ as the theoretical density. No degradation of the ceramic tape was observed during storage in a desiccator. After application of the solvent to mate the tape surfaces and the forming of the tubes, the tape underwent an aging process becoming considerably less flexible with time. For example, the end closure operation had to be accomplished within ~24 hours of forming the tube. Once the closed end tube was formed, this aging process became desirable in that the

*Alcoa XB-2, unground

green tubes were then quite rigid and maintained their form for firing.

Sintering of Samples: Bar samples were fired while embedded in Alcoa XB-2 setter sand to determine a heating cycle which would achieve a ceramic with high density. Porosity measurements are presented in Table I for sintered and annealed specimens. The porosity was in all cases low and insensitive to variation in the time interval, 2-10 minutes, at the sintering temperature. Although the porosity was low, the x-ray measurements on the fired surfaces indicated $f(\beta)$, as noted in Table II, was undesirably high. In order to determine whether the high $f(\beta)$ values were due to the firing cycle or soda loss from the surface approximately one-fourth of the thickness of several of the flat bar samples was removed by polishing and the now exposed interior examined by x-ray diffraction. The $f(\beta)$ values ranged from 0.02 to 0.11, considerably lower than for the measurements on the surface, suggesting soda had been lost during firing. In order to substantiate this the Alcoa XB-2 setter sand, which originally contained 7.3 w/o Na_2O , was enriched with additional Na_2CO_3 to bring the total Na_2O content to 9.0 w/o. Although complete conversion was not observed (Table II) substantial improvement was noted.

Table I
POROSITY MEASUREMENTS

TAPE #	t (min)	POROSITY (%)
3	2	2.9±0.4
	10	2.8±0.4
4	2	2.4±0.4
	10	2.6±0.4
10	2	3.7±0.5
	5	2.6±0.4
	10	3.2±0.5
11	2	2.1±0.4
	5	1.7±0.3
	10	1.3±0.3
17	2	1.7±0.4
	5	1.7±0.4
	10	2.1±0.4

t=sintering time at 1600°C

Table II

XRAY MEASUREMENTS				
TAPE #	t(min)	$f(\beta)$		
		FIRE* SURFACE	POLISHED SURFACE	FIRE** SURFACE
3	2	0.27	--	0.13
	10	0.13	0.05	--
4	2	0.19	--	0.17
	10	0.26	0.11	--
10	2	0.34	--	--
	5	--	--	0.10
	10	0.46	0.02	--
11	2	0.46	--	--
	5	--	--	0.20
	10	0.46	0.05	--

*ALCOA XB2 (7.3 w/o Na_2O)

** " " + Na_2O (9.0 w/o Na_2O)

Examples of fired tubes demonstrating both end closures are shown in Figure 3. The lap joint is also visible extending the length of each tube. Since the area is thicker than the bulk of the tube it represents a strip of higher resistance. Electrical measurements to determine the extent this affects the Na/S cell performance have not yet begun.

A

B

Fig. 3 $\text{B}''\text{-Al}_2\text{O}_3$ Tubes Formed From Doctor-Bladed Tape. (A) Pinch Closure (B) Disc Insert Closure.

Sections of a fired tube are shown in Figure 4. In the polished section planar defects are present at positions in the tube wall corresponding to former mating surfaces of the green tape. These defects are formed during tube fabrication and may be due to air entrapment or inadequate solvent application. By using a forming machine to uniformly apply pressure and solvent the occurrence of these internal defects should be considerably reduced.

Fig. 4 Polished (A) and Polished and Etched (B) Section of β'' - Al_2O_3 Tube.

X-ray diffraction indicated that the tubes consisted of primarily β'' - Al_2O_3 with some β - Al_2O_3 ($f(\beta)$ approximately 0.15). The grain size was typically ≤ 5 microns. However, it was not uncommon to observe few grains in the microstructure which had undergone exaggerated grain growth and exceeded 5 microns (Figure 4).

CONCLUSIONS

The present study has demonstrated the feasibility for fabricating β'' - Al_2O_3 tubes from doctor-bladed ceramic tape. Combining existing powder preparation processes for this ionic conductor with slip formulations similar to those used in the production of multilayer capacitors, thin-walled tubes have been successfully fired.

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REFERENCES

1. J. C. Williams in *Treatise on Materials Science and Technology*, Vol. 9, ed. F.F.A. Wang, p. 173 (Academic Press 1976).
2. R. E. Mistler, *Am. Ceramic Soc. Bulletin*, 52, 850 (1973).
3. R. B. Runk and M. J. Andrejco, *Am. Ceramic Soc. Bull.*, 54, 199 (1975).
4. D. J. Shanefield and R. E. Mistler, *Am. Ceram. Soc. Bull.*, 53, 416 (1974).
5. H. W. Stetson and W. J. Gyork, U.S. Pat. 3, 698,923.
6. R. T. Dirstine, W. O. Gentry, R. N. Blumenthal, and W. Hammett, *Am. Ceram. Soc. Bull.* to be published.
7. G. J. Tennenhouse and R. A. Pett, "Fabrication of Thin Layer Becca Alumina Tubes", Ford Motor Co., NASA-CR-135-308, Contract No. NAS-3-19782.
8. American Paper Inst., N. Y., N. Y. (1977). Based on 1976 U.S. production of tissue (3.12×10^9 lbs) and paper towels (1.50×10^9 lbs) and roll weights of 0.33 lb and 0.77 lb respectively.
9. H. Y. Hong, *Mat. Research Bull.*, 11, 179 (1976).
10. G. E. Youngblood, A. V. Virkar, W. R. Cannon, and R. S. Gordon, *Am. Ceram. Soc. Bull.*, 56 [2], 206 (1977).