



**University
of Dayton**

SOLID COMPOSITE ELECTROLYTE MEMBRANE

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ABSTRACT

The performance and scale-up of lithium ion rechargeable batteries and the development and commercialization of lithium air and lithium-water primary batteries are limited by the availability of suitable lithium ion conducting membranes/electrolytes. State-of-the-art lithium ion batteries employ liquid electrolytes which severely limit their performance and scale-up because of flammability and corrosiveness of these liquid electrolytes. These liquid electrolytes are in commercial use because they possess high lithium ion conductivity. Although attempts have been made to search for solids with similar conductivities, these attempts have not been very successful. The progress in the commercialization of lithium-air and lithium-water batteries has also been impeded due to the lack of a suitable membrane/electrolyte.

This invention relates to a development of solid, polymer-ceramic lithium ion conducting electrolyte compositions and a method to process these compositions into useful membrane forms of varying thicknesses. These membranes after processing by the technique explained in this disclosure become water impermeable and mechanically flexible. The membranes also possess ionic conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ at ambient temperature.

The water impermeable and resistant, mechanically flexible membranes have been prepared a number of times in our laboratory and also submitted to potential customers for their evaluation. A flow chart for the processing of a membrane material of this invention is shown in Figure 1. A glass batch comprising of lithium carbonate (Li_2CO_3), alumina (Al_2O_3), titanium dioxide (TiO_2), and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is weighed, mixed and melted in a platinum crucible. The batch is normally melted at around 1400 to 1500°C. The precise melting temperature depends upon the composition of the glass which is illustrated in Table 1. After melting, the glass is poured onto a stainless steel plate and annealed at 550°C for 2 hours. Subsequently, the glass is crushed into chunks, powdered, and screened. The powdered glass with a particle size range of 1 to 75 μm is mixed with fish oil, xylene and alcohol and tumbled for mixing for 24 hours in a glass jar. A binder and a mixture of plasticizers are subsequently introduced in the glass jar and the mixture is tumbled for another 24 hours. A typical batch for tape casting is presented in Table 2. After a total tumbling time of 48 hours, the slurry is cast onto a Mylar[®] sheet and dried for 24 hours. The green tape thus obtained is cut into the desired shape and size and subjected to a binder burnout and sintering process. A typical binder burnout and sintering schedule is illustrated in Figure 2. A slow heating rate from 25 to 400°C ($\approx 0.25^\circ\text{C}/\text{min}$) is practiced to prevent the occurrence of warpage and pin holes. The heating rate is increased to 1.15°C/min from 400 to 950°C. The sintering temperature could be varied from 950 to 1200°C that depends upon the desired characteristics of the sintered tape. For a porous tape, the sintering temperature and time of 950°C and 12 hours, respectively, is adequate. A specimen sintered in such a manner possesses a porosity of 25%. In order to obtain a fully dense tape, a sintering temperature in the 1100 to 1200°C range is required.

The partially sintered tape can be infiltrated with polymers such as polyethylene or poly tetra fluoroethylene (Teflon[®]) to prevent water permeability through the tape. The polymer is normally dissolved in a solvent such as polyethylene in toluene, and the partially sintered tape is submerged and allowed to remain in the polymer solution for a few minutes (≈ 15 min). The infiltrated specimen is subsequently removed and dried before further characterization and use.

The Arrhenius plots of conductivities of a tape which has undergone binder burnout and sintering processes are shown in Figure 3. The figure shows three curves corresponding to sintering temperatures of 950, 1050, and 1100°C for a constant time of 12 hours. The specimen sintered at 950°C shows the lowest conductivity and as the temperature is increased to 1050°C the conductivity increases. The conductivity trend reflects consolidation of the porous structure with increasing sintering temperature. For example, the specimen sintered at 950°C was associated with a porosity of 25%, whereas the specimen sintered at 1100°C exhibited a totally dense structure (zero porosity). The conductivity of the specimen sintered at 1100°C is around $5 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature and increases to $10^{-3} \text{ S cm}^{-1}$ at 50°C. The densities of these specimens were 2.25, 2.57 and 2.71 g/cm³ for sintering temperatures of 900, 1050, and 1100°C, respectively.

The porosity-conductivity relationship for the tape is schematically illustrated in Figure 4. As the porosity increases, the conductivity decreases. For a totally dense tape (zero porosity), conductivity can be as high as $10^{-3} \text{ S cm}^{-1}$. The porosity also allows polymer infiltration which renders other useful properties such as enhanced mechanical properties (strength and flexibility) and superior chemical stability in contact with water. Therefore, the combination of the two phases, i.e., sintered glass and polymer, yield materials which can withstand widely different environmental and application requirements. For some applications where conductivity is the primary consideration, a totally dense tape would be useful. For other applications where chemical stability is required along with good conductivity, the polymer infiltrated tape would be a better choice.

The Arrhenius plots of a sintered tape before and after the polyethylene infiltration are shown in Figure 5. The tape was sintered at 950°C for 12 hours. After infiltration with polyethylene, there is a slight decrease in conductivity of the composite tape.

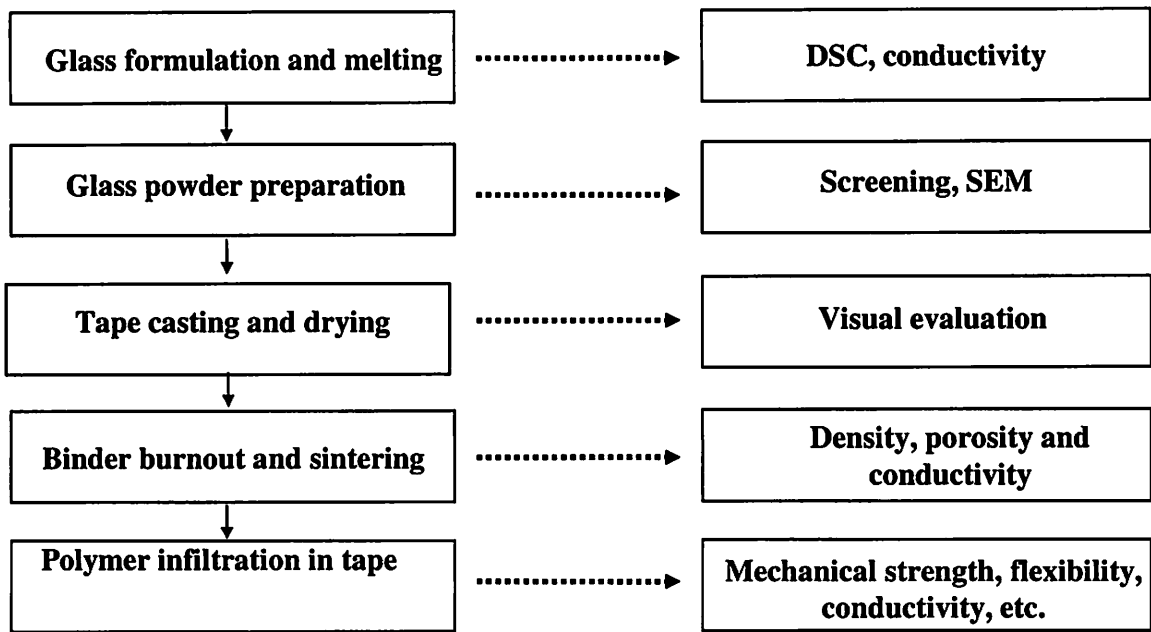


Figure 1. A flow chart for the processing of lithium ion conducting membranes.

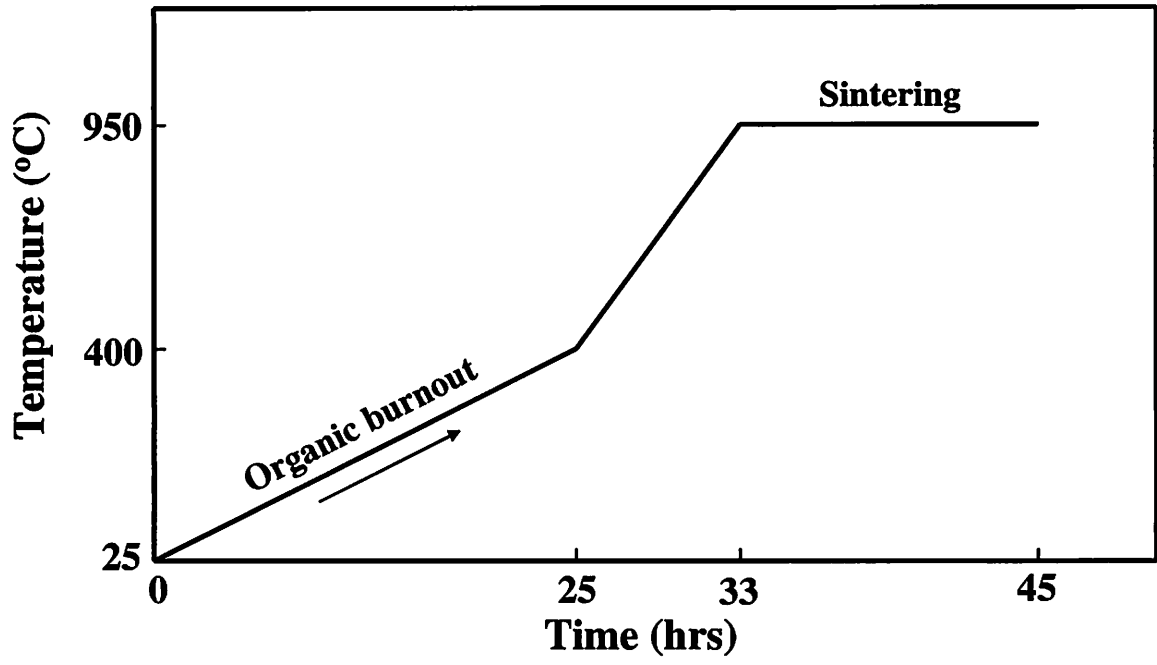


Figure 2. Organics burnout and sintering of schedules of a glass tape.

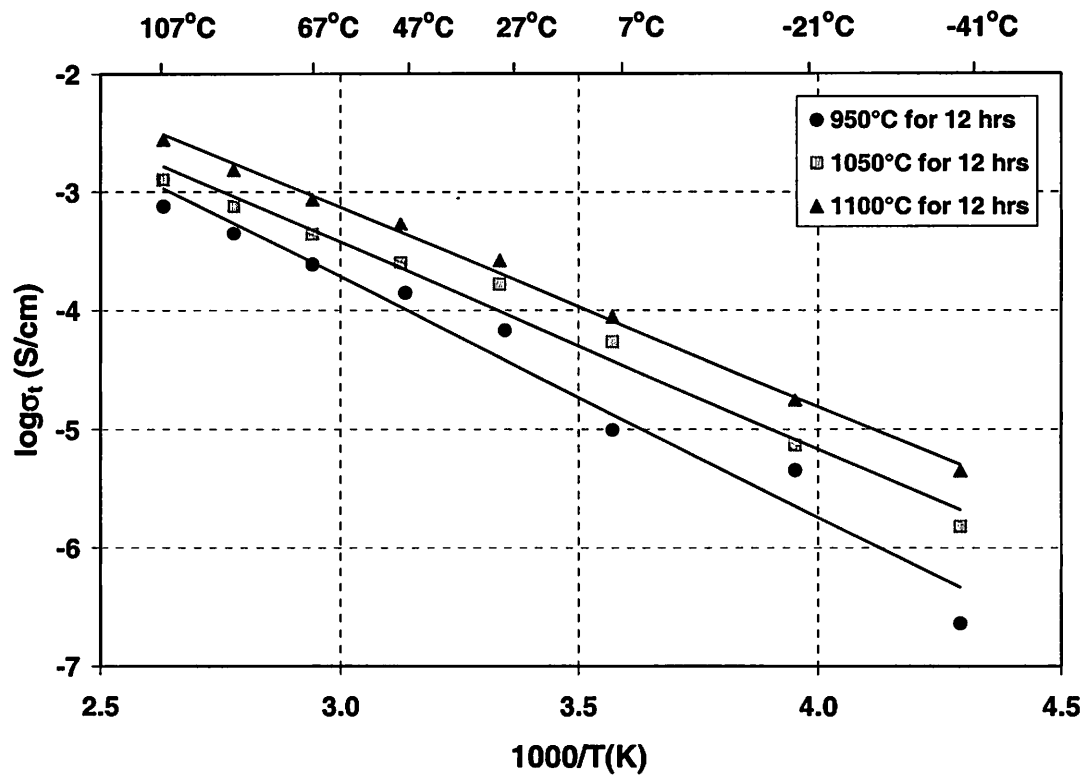


Figure 3. Conductivity of glass tape sintered at 950, 1050, and 1100°C.

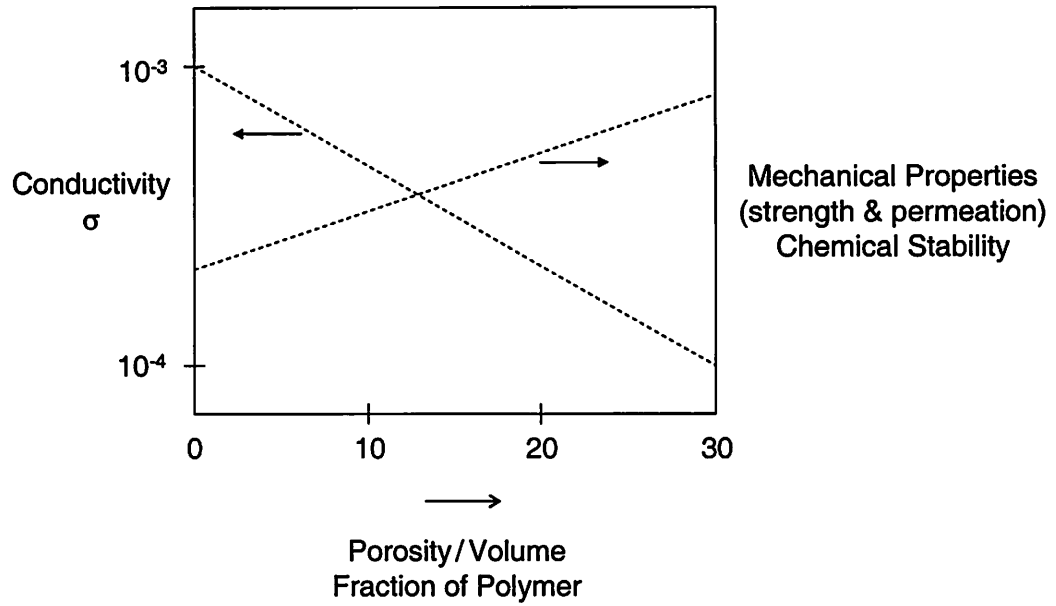


Figure 4. Schematic presentation of conductivity – mechanical properties – chemical stability – porosity relationships.

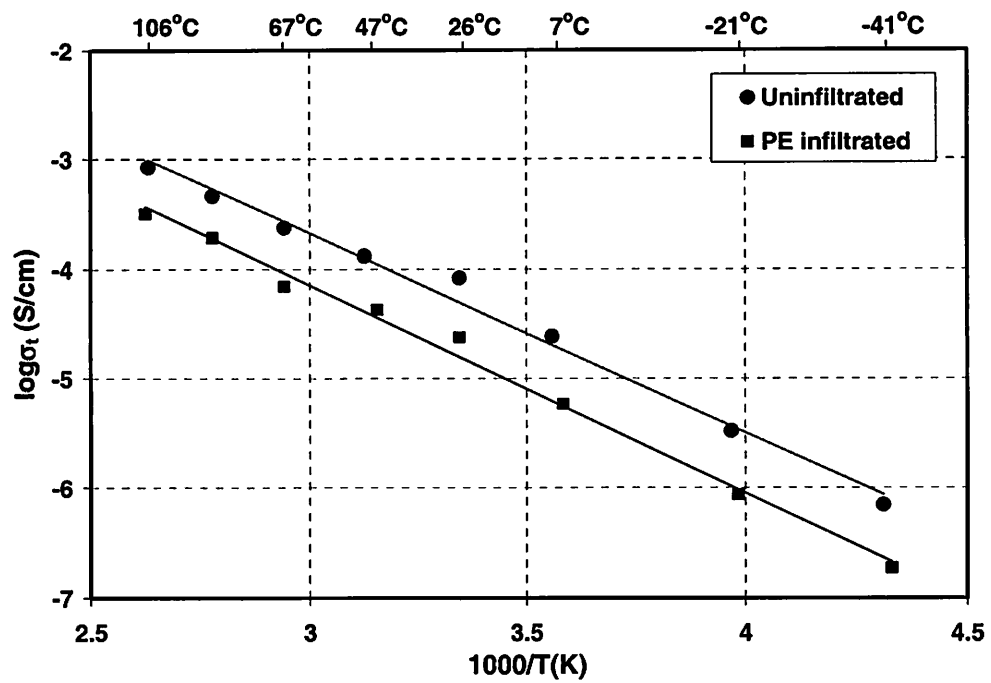


Figure 5. Arrhenius plots of sintered glass tape before and after polymer infiltration.

Table 1. Range of Glass Compositions Evaluated in This Invention

	Mol Percent
Li_2O	10 to 20
Al_2O_3	0 to 10
TiO_2	30 to 60
P_2O_5	30 to 60

Table 2. Tape Cast Batch

Part I				
Chemicals	Purpose	Wt%	Weight (g)	Weight (ml)
Powder glass	Powder (1-75 μm)	69.40	13.88	
Menhaden fish oil blown Z-3	Dispersant	1.19	0.238	
Xylene	Solvent	11.00	2.200	2.520
Alcohol	Solvent	12.50	2.500	3.227
Milling for 24 hrs				
Part II				
Poly(vinyl butyl) B-98	Binder	2.95	0.590	
Butylbenzyl phthalate S-160	Plasticizer I	1.48	0.296	
Poly(alkalene glycol)	Plasticizer II	1.48	0.296	
Milling for 24 hrs				
Total		100	20	