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DISCLAIMER

CURRENT STATUS OF SOLID-STATE LITHIUM BATTERIES EMPLOYING SOLID REDOX POLYMERIZATION CATHODES

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1. Introduction.

The rapidly growing demand for secondary batteries having high specific energy and power has naturally led to increased efforts in lithium battery technology. Still, the increased safety risks associated with high energy density systems has tempered the enthusiasm of proponents of such systems for use in the consumer marketplace. The inherent advantages of all-solid-state batteries in regards to safety and reliability are strong factors in advocating their introduction to the marketplace. However, the low ionic conductivity of solid electrolytes relative to non-aqueous liquid electrolytes implies low power densities for solid-state systems operating at ambient temperatures. Recent advances in polymer electrolytes have led to the introduction of solid electrolytes having conductivities in the range of 10^{-4} (ohm cm)$^{-1}$ at room temperature[1]; this is still two orders of magnitude lower than liquid electrolytes. Although these improved ambient conductivities put solid-state batteries in the realm of practical devices, it is clear that solid-state batteries using such polymeric separators will be thin-film devices. Fortunately, thin-film fabrication techniques are well established in the plastics and paper industry, and present the possibility of continuous web-form manufacturing. This style of battery manufacture should make solid polymer batteries very cost-competitive with conventional secondary cells. In addition, the greater geometric flexibility of thin-film solid-state cells should provide benefits in terms of the end-use form factor in device design.

2. Solid Redox Polymerization Electrodes and Redox Resins

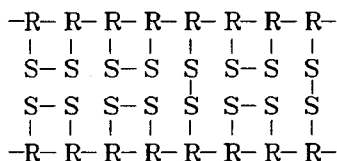Although the majority of research on solid polymer batteries has been performed using intercalation compounds in the positive electrode, research in this laboratory has centered on a new class of materials termed solid redox polymerization electrodes (SRPE's). SRPE's are essentially the oxidation product of dithiols, or polyorganodisulfides,

$$HSRSH + LiOH = Li_2SRS + H_2O$$
$$n\,Li_2SRS + n\,I_2 = (SRS)_n + 2n\,LiI$$
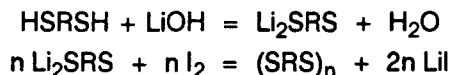
where R is an organic moiety such as CH_2CH_2, phenyl, etc. However, SRPE's are not limited to 2 sulfur groups per organic R group. In fact, the oxidation product of trithiocyanuric acid (three SH groups/R) has been successfully cycled in solid-state lithium cells[2][3]. Polymerization electrodes are unique in that on cell charge the materials are electro-polymerized, and on discharge they are electro-depolymerized,
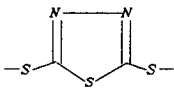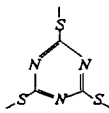
$$n \ Li_2SRS \ = \ (SRS)_n \ + \ 2n \ Li.$$

Further, in contrast to intercalation materials, SRPE's are reversible to many metal ions, and accordingly have been tested in solid-state sodium batteries as well as in lithium cells. Polyorganodisulfides also have the advantage of tremendous flexibility in terms of chemical and macromolecular formulation of the electrodes. The chemical, electrochemical, physical, and thermodynamic properties of these materials are a strong function of the organic group, R, adjacent to the disulfide linkages[4][5][6]. The related polymeric disulfides, the polythiols, are also of potential value as positive electrodes. These materials, also known as redox resins, undergo reversible electro-crosslinking upon oxidation and reduction. Cross-linking in the polythiols can be either inter or intramolecular dependent on the distance between sulfur sites on the poly-mer backbone and on nearest neighbor polythiols as shown below,

```
-R- R- R- R- R- R- R- R-
 |  |  |  |  |  |  |  |
 S- S  S- S  S  S- S  S
             |        |
 S- S  S- S  S  S- S  S
 |  |  |  |  |  |  |  |
-R- R- R- R- R- R- R- R-
```

Clearly, for any of these materials to be viable for practical systems, the gravimetric and volumetric energy densities must be sufficiently attractive, and the actual behavior of batteries based on SRPE's must demon-strate suitable levels of performance. As can be seen from table I, the volumetric and gravimetric energy densities of lithium batteries based on SRPE's are more than adequate for applications ranging from consumer electronics to electric vehicles. More important than the calculated values shown in table 1 are the actual capacities of batteries based on these materials. Since polyorganodisulfides are not electron-ically conductive, functional electrodes are typically composed of dispersed carbon black in a matrix of polymer electrolyte and active material (SRPE). The volumetric and gravimetric capacities of composite electrodes based on poly(2,5-dimercapto-1,3,4-thiadiazole), X1, and the intercalation compound TiS_2 have been reported previously[7]. The energy densities calculated for such films and the performance of batter-ies based on them[2,3,7], clearly puts them in the realm of commercial application.

Table I

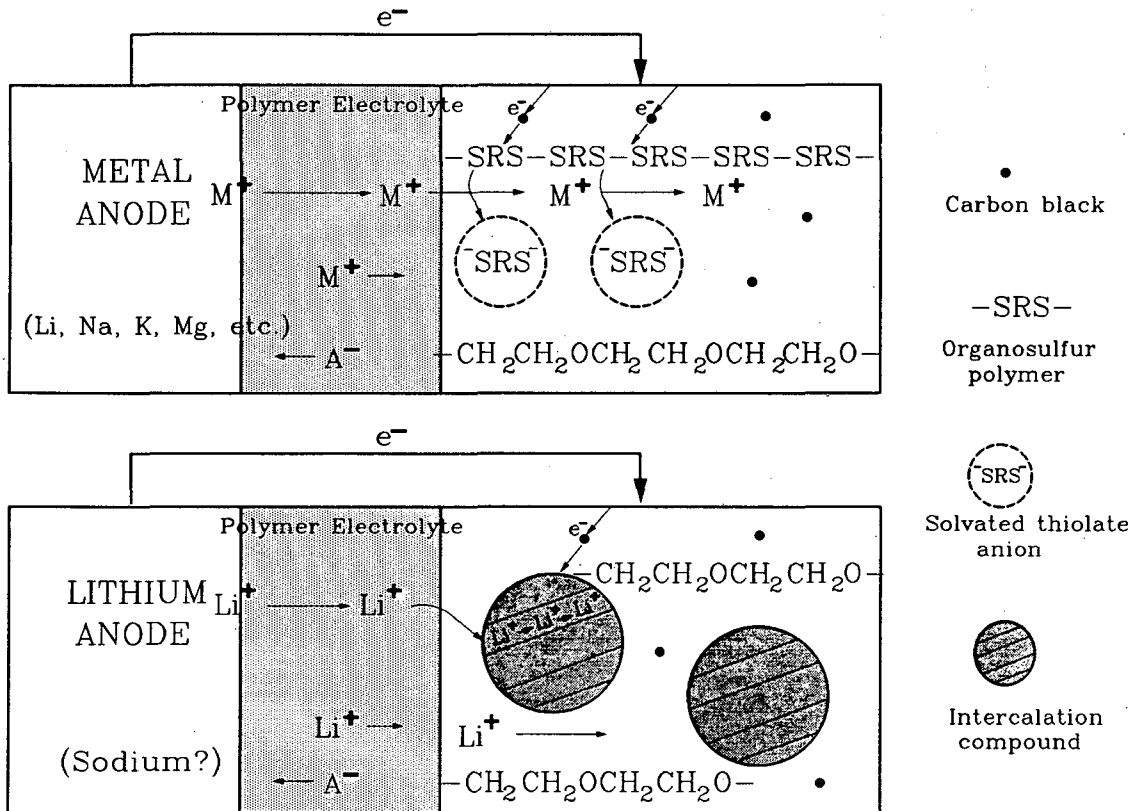| MONOMER	Equivalent Weight	Density	Open Circuit Voltage	Theoretical Volumetric Energy Density Wh/l	Theoretical Gravimetric Energy Density Wh/kg	POLYMER NOMEN-CLATURE
(chemical structure: thiadiazole ring with –S– substituents)	74	1.8	3.0	1480	990	X1
(chemical structure: triazine ring with –S– substituents)	58	1.6	3.0	1630	1240	X5
$O(CH_2CH_2S)_2$-	76	1.6	2.0	880	650	X0
-SCH_2CH_2S-	46	1.6	2.0	1280	1010	X8
TiS_2	112	3.2	2.5	1390	560	————
Li	7	0.534	————	————	————	————

Figure 1. Schematic comparison of thin-film polymer batteries using SRPE positive electrodes (top) and intercalation compounds (bottom).

3. Solid-State Li/PEO/SRPE Batteries

The basic components of solid polymer cells are shown in figures 1 and 2. If 5 micron metallized polyethylene terephthalate (PET) current collectors are used to build the basic cell, the dimensions of each component can be calculated as shown in table II. As is evident from table II, if the cell capacity is close to 1 C/cm^2, the total cell thickness including current collectors would be about 50 microns (1/2 mil) which is exceeding thin in relation to conventional battery design. From the basic formulation shown in table II one can easily extrapolate energy and power densities for thin-film cells as a function of surface capacity, electrolyte thickness, and current density. Although the majority of laboratory thin-film cells were tested between thick stainless steel plates, tests using metallized films showed no difference in performance. Energy and power densities were consequently extrapolated from lab cell performance using the dimensions of metallized PET current collectors. Shown in fig. 3 is the dependence of volumetric energy density on cell capacity. As one might expect the energy density improves as the electrode thickness increases, yet the improvement beyond 3 C/cm^2 is not dramatic. This is fortunate since the power density of the cell certainly drops off with increasing electrode thickness; the rate of decrease depending on the current density at which the cell is operated.
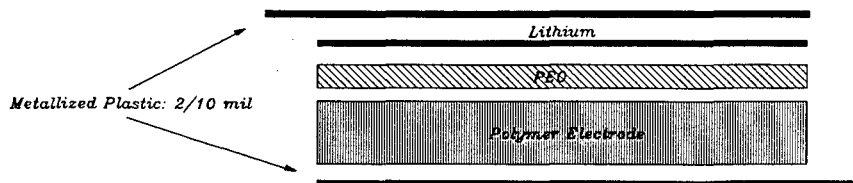
Figure 2. Cross-section of thin-film cell.

Table II

DIMENSIONS FOR BASIC THIN-FILM Li/PEO/SRPE CELL	Thickness (microns)	Weight/cm^2 (grams)
Lithium (4 C/cm^2)	6	0.0003
PEO	10	0.0015
Polymer Electrode (1 C/cm^2)	18	0.0026
Metallized Current Collectors	5 (x2) (commercially available)	0.00092
TOTAL	44	0.00532
ENERGY DENSITY	190 Wh/l	160 Wh/kg

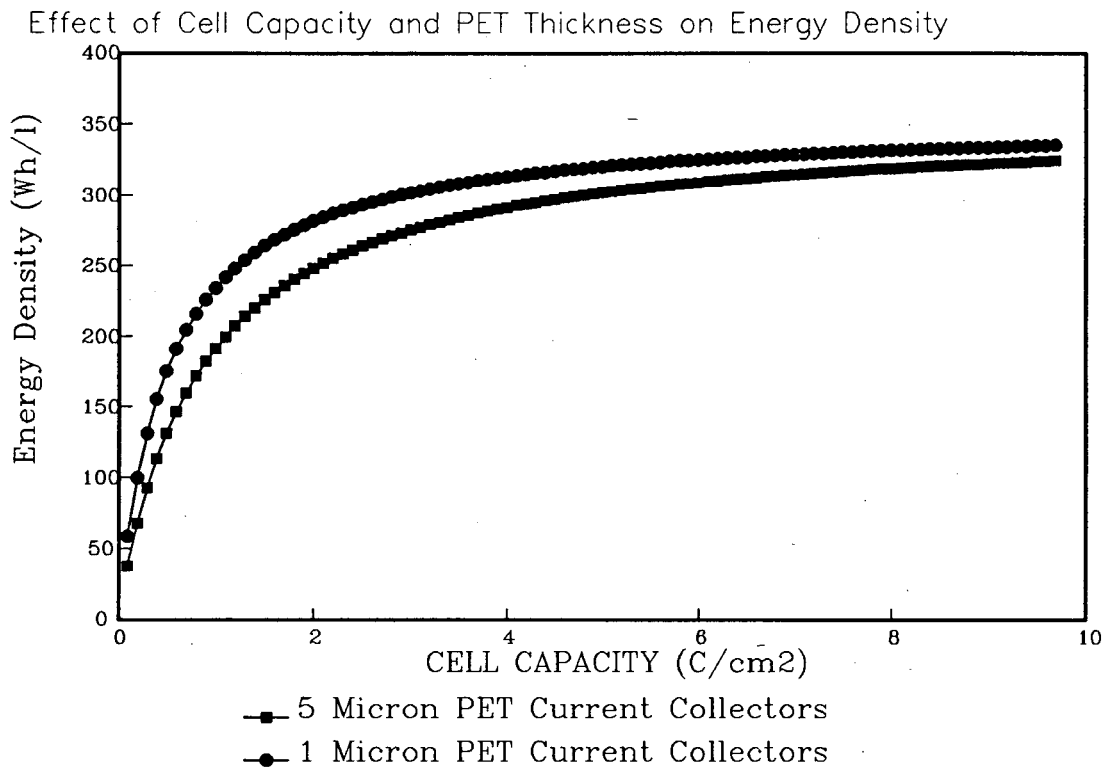## Effect of Cell Capacity and PET Thickness on Energy Density

Figure 3. Dependence of energy density on cell capacity and current collector thickness; electrolyte thickness constant at 10 microns.

Figure 4 shows the 1st 15 cycles of a Li/p(EO)$_8$LiCF$_3$SO$_2$/X1 cell at operating at 20°C. The electrolyte contains modified polyethylene oxide which is amorphous at room temperature with a conductivity of approximately 10^{-4} (ohm cm)$^{-1}$. As is evident from figure 4, the room temperature cells can attain capacities of approximately 1 C/cm^2 at a current density of 50 μm/cm^2 and about half of that (0.5 C/cm^2) at a current density of 100 μmA/cm^2. At these current densities, it is clearly necessary to maximize the total surface area of the cell, or to increase the rate of discharge. Given the current densities shown in figure 4, the power densities of thin-film cells can be extrapolated as a function of surface capacity, electrolyte thickness, and current collector thickness. Shown in figure 5 is the dependence of power density on cell capacity (thickness) at for ambient temperature batteries at current densities of 0.05 or 0.1 mA/cm^2. One can see from these curves, that for these current densities, the power density falls off fairly rapidly beyond a surface capacity of 0.5 to 1 C/cm^2. Consequently, for those applications where power densities in excess of 100 W/l are necessary, one would probably not want to increase the surface capacity of the solid-state cells beyond the levels indicated in figure 4. Conversely, for low to medium rate applications where high energy density is more important, it would be advantageous to use electrodes with greater than 1 C/cm^2. As one would expect, both the energy and power density increase with decreasing thickness of the current collectors. One micron metallized PET films are presently used in the capacitor industry and would be

attractive as current collectors in solid polymer batteries (although the cost of PET films increases with decreasing thickness). Accordingly, the cell dimensions should be scaled with the intended application of the battery.
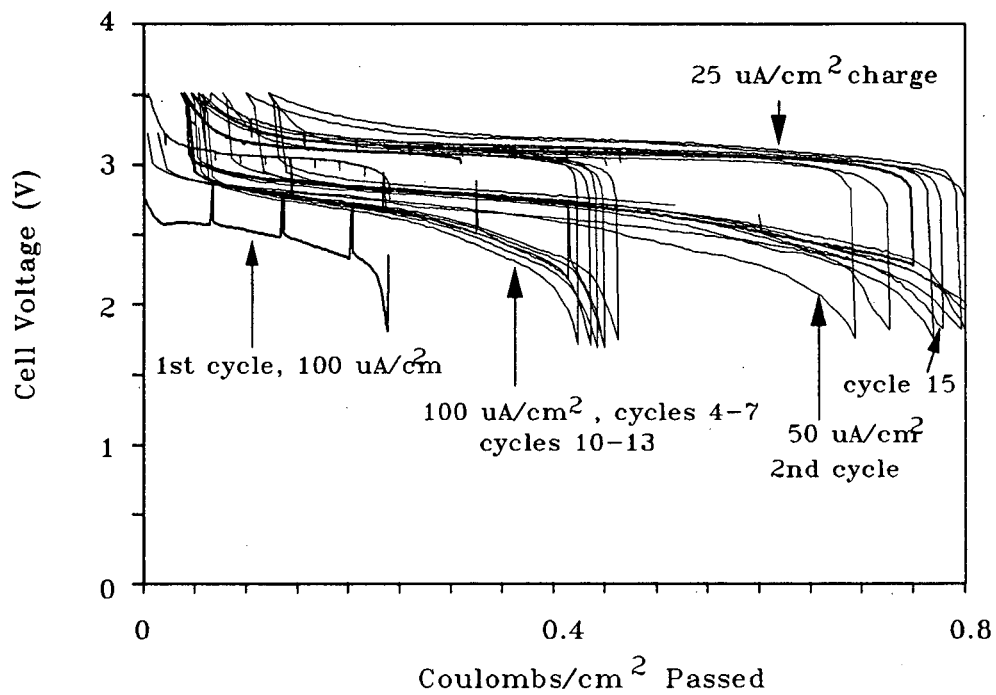

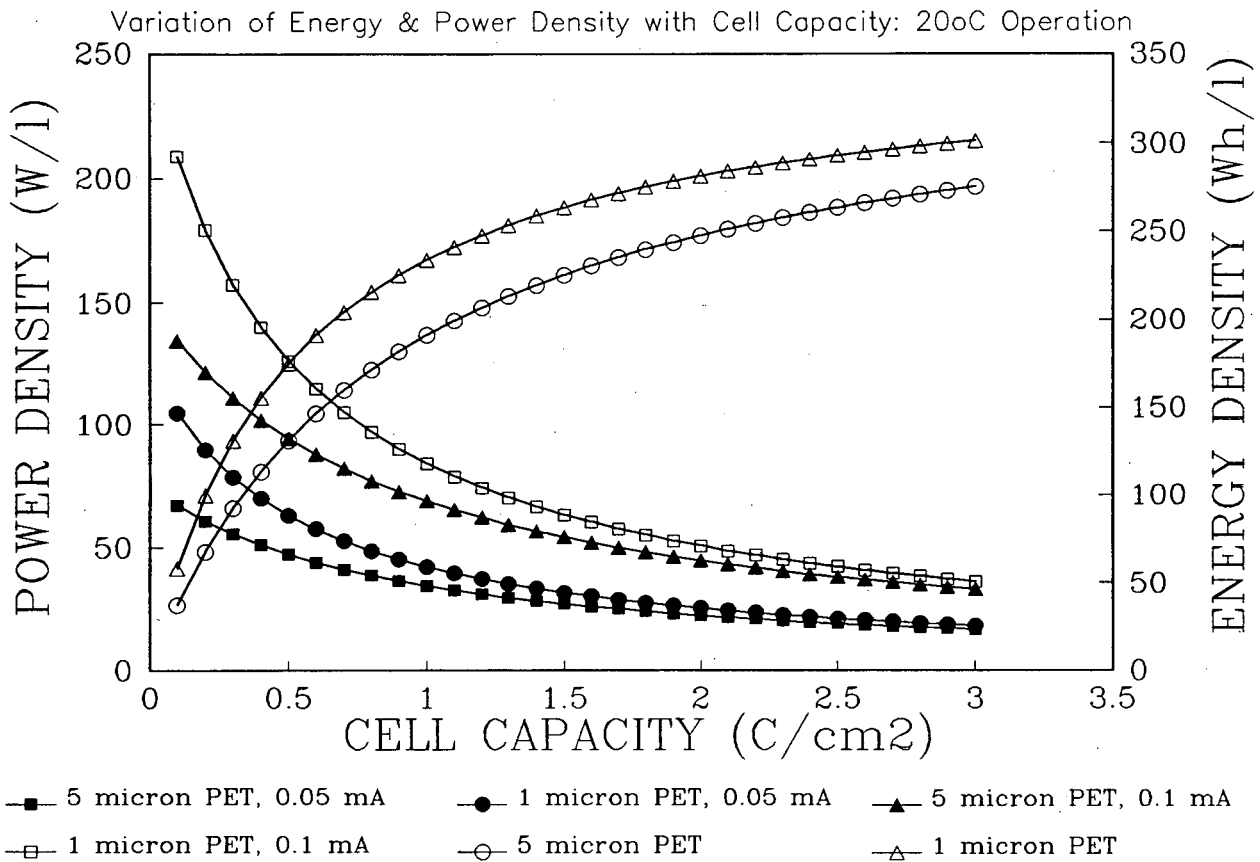Figure 4. Li/PEO/X1 cell: performance at 20°C.

Figure 5. Dependence of volumetric energy and power density on cell capacity; ambient temperature solid-state cell.

The performance of Li/PEO/SRPE cells operating at higher temperatures, 70 to 90°C, have been reported previously[2,7]. In particular, Li/PEO/X1 cells have demonstrated energy and power densities that meet the demands of electric vehicle applications. At these elevated temperatures the solid-state lithium cells are routinely cycled at current densities of 0.5 mA/cm^2, and have demonstrated current densities of up to 10 mA/cm^2 for over 80% of the available capacity. As mentioned previously (figure 3), the energy density of these cells does not improve dramatically beyond 3C/cm^2, and consequently the majority of the laboratory cells were constructed with composite cathodes having capacities of 2 to 4 C/cm^2. Li/PEO/X1 cells were cycled at 0.5 mA/cm^2 for over 300 cycles at a nominal discharge voltage of 2.6 volts[2,7], corresponding to energy densities of 190 Wh/l (160 Wh/kg) and power densities of 140 W/l (120 W/kg) as described pre-viously, and indicated in figure 6. Furthermore, these cells could deliver much high power densities and still attain high capacity utilization. As shown in figure three, at a current density of 2 mA/cm^2, a cell with a positive electrode capacity of 3 C/cm^2 can provide power densities of over 500 W/l. The gravimetric and volumetric specific energy and power of solid-state Li/PEO/SRPE batteries makes them an attractive system for electric vehicles. In addition, the low cost of raw materials and low estimated cost of fabrication, makes these batteries economically viable for electric vehicle use as well as other applica-tions where large specific energy and power are required.
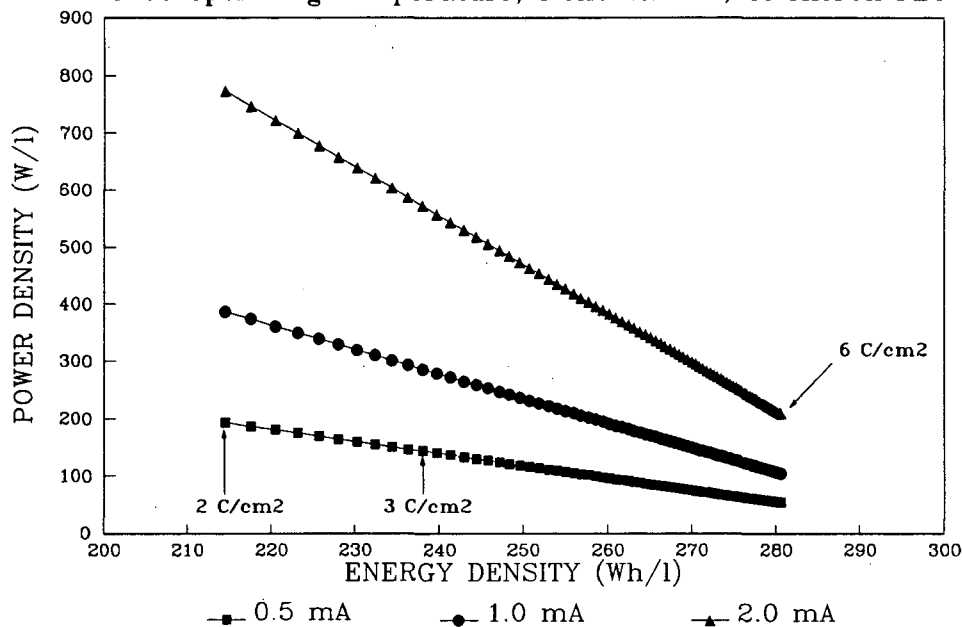
Figure 6. Intermediate temperature cell, 70 to 90°C; variation of energy and power density as a function of cell capacity and current density; each marker indicates increments of 0.1 C/cm^2 from 2 to 6 C/cm^2 (left to right).

The cost of raw materials is an important factor in assessing the economic feasibility of any product. The materials cost can be examined as a function of cell dimensions. Figure 7 shows the estimated cost in dollars/kWh for raw materials as a function of cell capacity. As one can see from the trends in figure 7, the raw materials costs will most likely be dominated by the cost of lithium above a surface capacity of 2 C/cm^2, whereas, below 0.5 C/cm^2 the cost of materials is probably dominated by the current collectors. Although it is premature to estimate the manufacturing costs of Li/PEO/SRPE cells, crude estimates based on current industrial film-processing lines indicates that fabrication costs may be as low as 1/10 of the raw materials cost. In addition to the low cost of the solid-state Li/PEO/SRPE system, the problems associated with disposal of the batteries should be minimal owing to the low toxicity and environmentally inert nature of the electrodes and electrolyte. The reported toxicity (LD_{50}) of the mercaptan precursor to the X1 polymer is essentially the same as that reported for caffeine.

Cost Breakdown in $/kWh as a Function of Cell Capacity
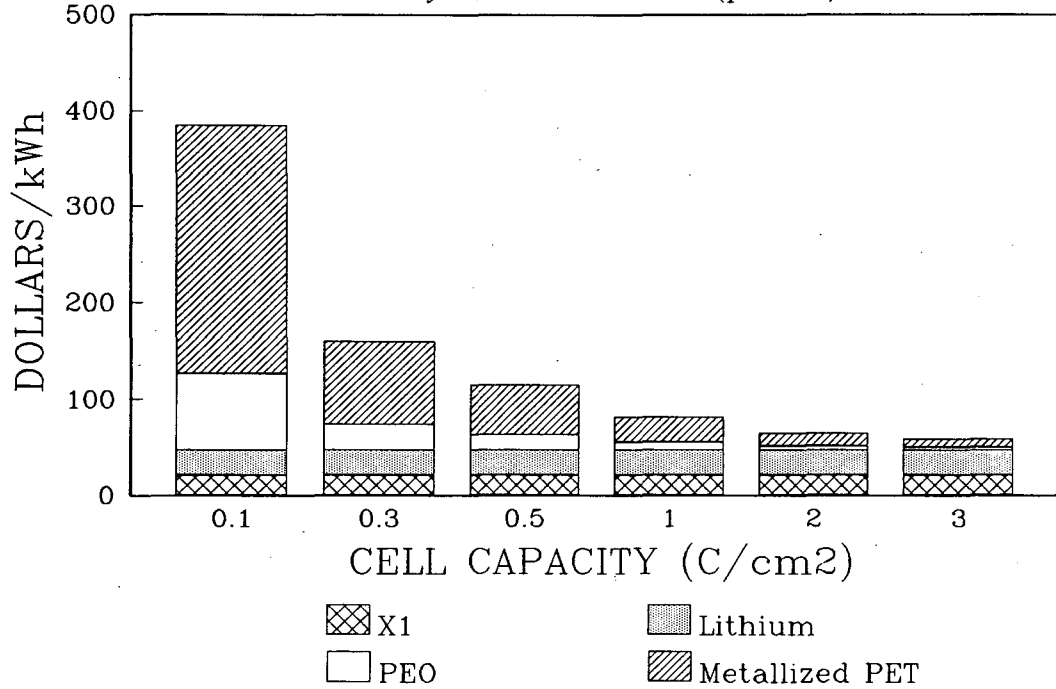### 10 Microns PEO Electroyte, 5 Micron PET (plastic) Current Collectors

Figure 7. Cost of raw materials in solid state Li/PEO/X1 cells as a function of cell capacity (electrode thickness).

4. Conclusions

All-solid-state lithium batteries based on polyorganodisulfides offer reliable and safe energy storage for applications ranging from medium power demand at ambient temperatures to high rate applications at intermediate temperatures. These thin-film systems should be economically competitive with existing systems, yet offer the advantages inherent in solid-state technology. Furthermore, Li/PEO/SRPE cells avoid the problems associated with disposal of toxic heavy metals, and/or the safety hazards attributed to the use of flammable organic electrolytes.

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