CHARACTERIZATION OF GLASS FIBER SEPARATOR MATERIAL FOR LITHIUM BATTERIES

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ABSTRACT

Characterization studies were carried out on a glass fiber paper that is currently employed as a separator material for some $LiSOCl_2$ primary cells. The material is of the non-woven type made from microfilaments of E-type glass and contains an ethyl acrylate binder. Results from extraction studies and tensile testing revealed that the binder content and tensile strength of the paper were significantly less than values specified by the manufacturer. Scanning electron micrographs revealed the presence of clusters of impurities many of which were high in iron content. Results of emission spectroscopy revealed high overall levels of iron and leaching, followed by atomic absorption measurements, revealed that essentially all of this iron is soluble in $SOCl_2$.

INTRODUCTION

This work was carried out in collaboration with S. Subbarao (see Figure 1) who is a Resident Research Associate for NASA.

As indicated in Figure 2 the effort is part of NASA's Primary Lithium Battery Program wich is aimed at developing flight quality $Li-SOCl_2$ cells by FY86. One element of this program is being directed towards development and characterization of the components of as well as complete $Li-SOCl_2$ cells. The specific subject of this investigation is characterization of the separator material that is commonly employed in this type of cell. The separator is made by Mead Paper Company and is a non-woven paper made from micro filament glass fibers supplied by Johns Manville.

RESULTS AND DISCUSSION

Overall physical properties of the paper are given in Figure 3. The binder content was determined by extraction with dichloromethane and also verified by ignition described later. The tensile strengths were measured with an Instron Tensile Tester. Results shown therein reveal that the observed values for binder content and tensile strength are appreciably lower than those specified by the manufacturer.

Since the specific type of binder was not specified by the vendor, a sample of it was analyzed by Fourrier Transform Infrared Analysis. The resultant spectra is given in Figure 4. Comparison of this spectra with known spectra in the literature (1) revealed that the binder is an acrylic.

Samples of the material were examined by Scanning Electron Microscopy. Analyses revealed that the glass filaments are randomly oriented and their diameters range in size from approximately 0.2 to 2 microns. Further it was found that the material contains small clusters of impurities as shown in Figure 5. These particles are located throughout the roll of the paper. Energy Dispersive Analysis (EDAX) of these particles revealed that most of them contain appreciable amounts of iron as shown in Figure 6.

Emission Spectrographic Analysis of the material revealed that its overall iron content was 0.48%, as shown in Figure 7, and this value is somewhat higher than that claimed by the manufacturer. Although this amount of iron is low in terms of percentages, it is high from a contamination point of view in that very low levels of iron in the parts per million range can adversely affect performance of Li-$SOCl_2$ cells. Figure 7 also shows that the amount of material "lost on ignition" was 3.04% and this should correspond to the binder content. This value is in good agreement with the binder content determined by extraction as given in Figure 1.

Samples of the material were also leached in $SOCl_2$ solution for 24 hrs and the extract was analyzed for iron by Atomic Absorption. Results showed that essentially all the iron is soluble in $SOCl_2$.

Based on the above findings calculations were carried out to estimate the amount of iron that the separator would contribute to a typical "D" size Li-$SOCl_2$ cell. Results indicated that the amount of iron would correspond to about 150 ppm which is quite high in regard to tolerable levels of iron in these cells (2).

CONCLUDING REMARKS

As indicated in Figure 8, this separator material does not conform to the manufacturer's specifications, has low physical strength, and also contains impurities that are known to be deleterious to operation of Li-$SOCl_2$ cells. In its present form the separator would not be classified as of high enough quality for aerospace applications. Further, the manufacturer has not indicated a willingness to develop a high quality separator. On this basis it will be necessary to locate another manufacturer that can supply the desired high quality material. Investigations are currently underway to locate such a manufacturer.

ACKNOWLEDGEMENT

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NASA GODDARD SPACE FLIGHT CENTER BATTERY WORKSHOP

JPL

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Figure 1

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CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL
INTRODUCTION

- NASA SPONSORED PRIMARY LITHIUM BATTERY PROGRAM
- QUALIFY $Li\text{-}SOC\ell_2$ CELLS FOR FLIGHT BY FY-86
- PROGRAM ELEMENTS
    - RESEARCH ON CHEM RELATED SAFETY ISSUES
    - DEVELOPMENT OF PROTOTYPE CELLS / 1st GENERATION CELLS FY-84
    - DEVELOPMENT OF FLIGHT CELLS
- COMPONENT CHARACTERIZATION PART OF PROTO CELL DEVELOPMENT
- UNCOVERED PROBLEM AREAS WITH EXISTING SEPARATORS

Figure 2

CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL
OVERALL PHYSICAL PROPERTIES

		VENDOR CLAIM
THICKNESS	3.5 mil	
WEIGHT/AREA	3.5 gms/ft^2	
DENSITY	0.43 gms/cc	
POROSITY	80%	
BINDER CONTENT	3%	8%
TENSILE STRENGTH $\perp$	152 TO 174 psi	300 psi
TENSILE STRENGTH =	159 TO 170 psi	300 psi

Figure 3

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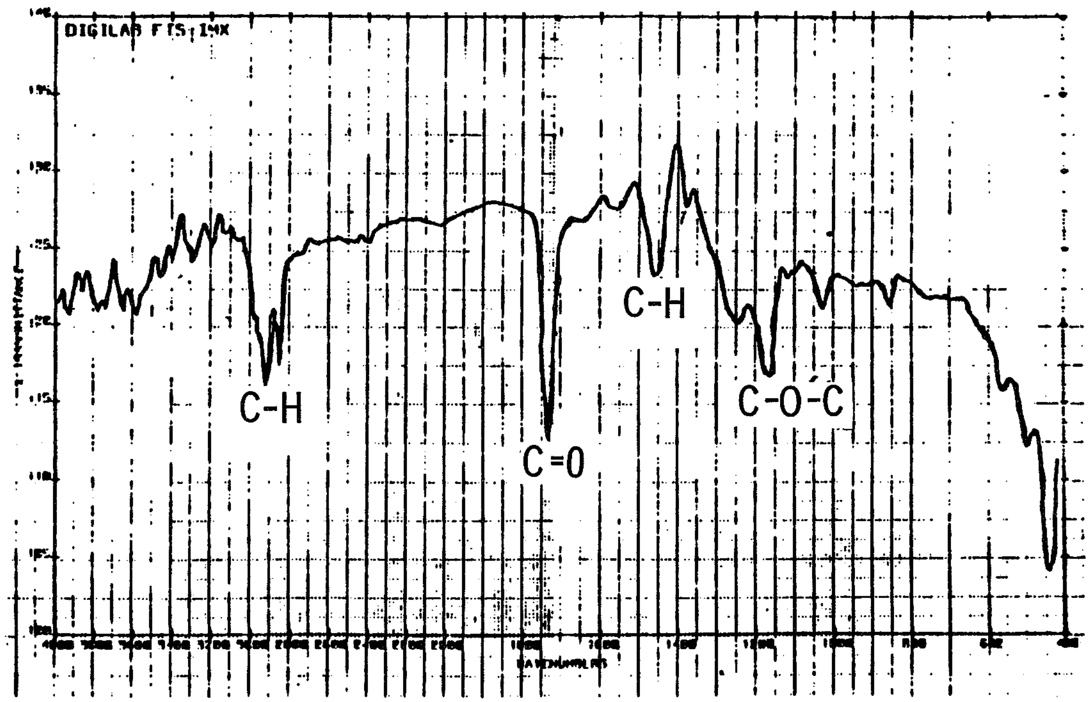
CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL
ANALYSIS OF BINDER

- BINDER REPORTED TO BE SOME TYPE OF ACRYLIC BY VENDOR
- REMOVED BINDER BY EXTRACTION WITH DICHLOROMETHANE AND RAN FTIR ON EXTRACT
- RESULTS

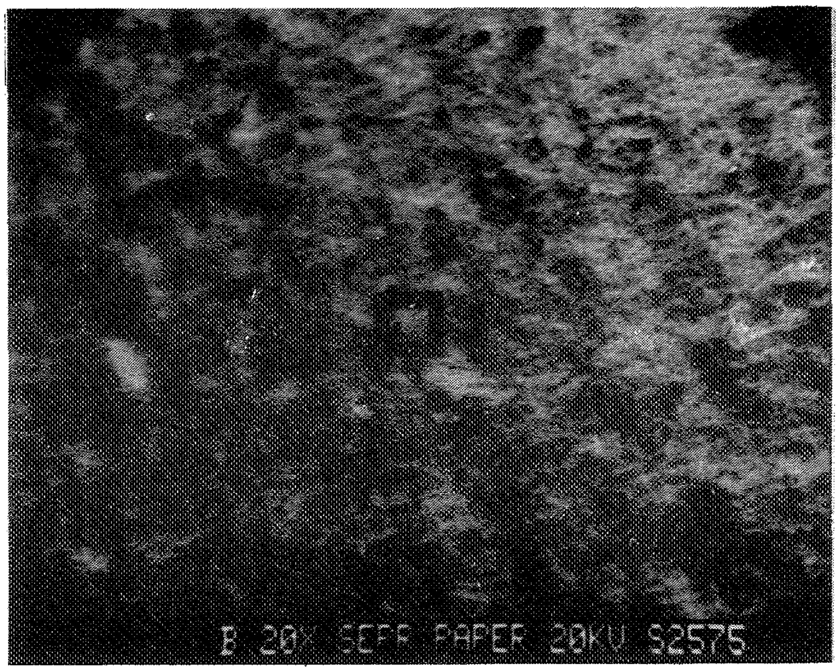


- CONCLUSION: BINDER IS ETHYL ACRYLATE - $(CH_2\text{-}\underset{\displaystyle COOC_2H_5}{\underset{|}{CH}})_n$

Figure 4

CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL
SEM ANALYSES

SEM PHOTO REVEALS CLUSTERS OF FOREIGN PARTICLES



MAGNIFIED SEM PHOTO OF A TYPICAL PARTICLE

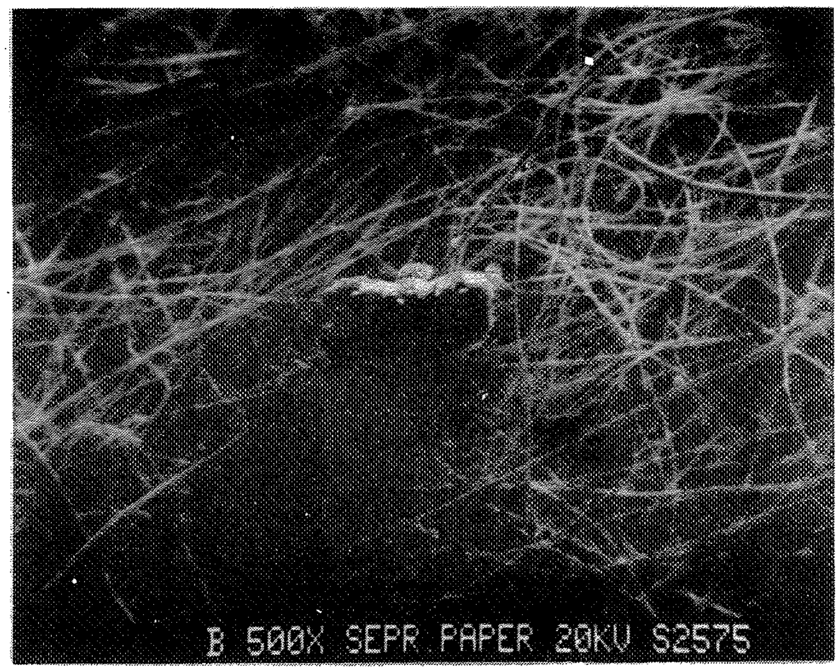


Figure 5

CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL

EDAX ANALYSIS OF TYPICAL FOREIGN PARTICLE

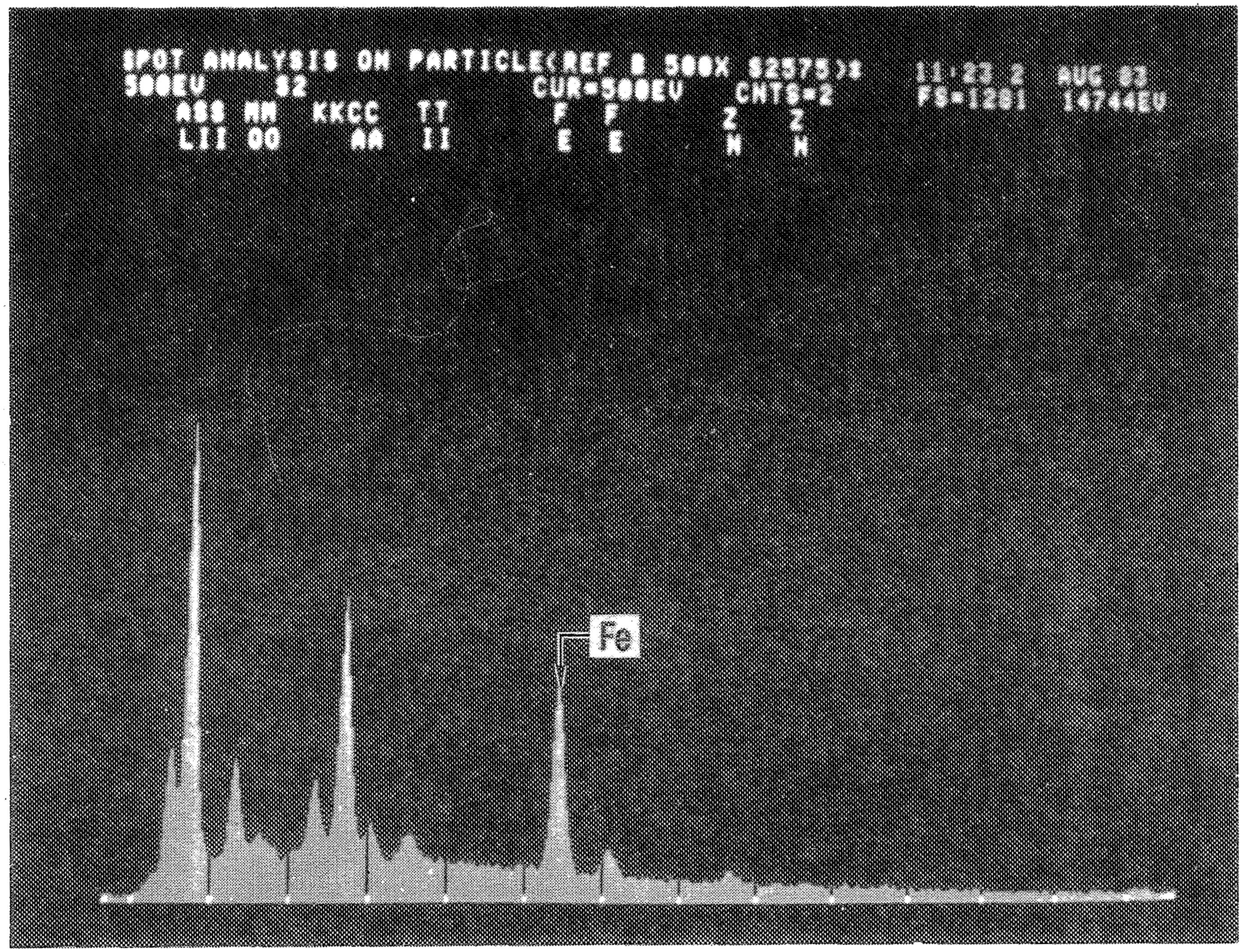


Figure 6

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CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL

SPECTROGRAPHIC ANALYSIS

SEMIQUANTITATIVE ANALYSIS

Si	21.%	
Al	13.	
Ca	14.	
Mg	1.3	
Sr	0.090	
B	0.72	
Mn	0.023	
Pb	0.018	
Ba	0.46	
Fe	0.48	← VERY HIGH (VENDOR CLAIMS $Fe_2O_3 < 0.3\%$)
Ga	0.0099	
Ni	0.014	
Na	0.87	
Cu	0.0014	
Zn	0.35	
Ni	0.0021	
Zr	0.029	
Co	0.0041	
K	TR < 0.10	
Cr	0.0024	
OTHER ELEMENT	nil	
LOSS ON IGNITION	3.04%	← BINDER

Figure 7

CHARACTERIZATION OF GLASS FIBRE SEPARATOR MATERIAL
SUMMARY AND CONCLUSIONS

- LOW BINDER CONTENT
- LOW TENSILE STRENGTH
- CLUSTERS OF IMPURITIES THROUGHOUT
- IMPURITIES HIGH IN IRON
- THE IRON READILY DISSOLVES IN $SOC\ell_2$ (YIELD 150 ppm IN CELL) AND WOULD CAUSE SEVERE VOLTAGE DELAY
- DUE TO INFERIOR CHEMICAL AND PHYSICAL PROPERTIES THIS MATERIAL DEEMED UNSUITABLE FOR AEROSPACE CELLS
- AVAILABILITY OF QUALITY MTL UNCERTAIN

Figure 8

Q. Roth, NASA HQ: I was wondering - this is more of a general question - not only to ask yourself but of the people here. What you said about the ability of NASA to get supplies to give them the type of materials they want is an across-the-board problem. And I'm just wondering - is it that significant a problem that it's going to cause trouble now and in the future - and I guess I'm asking everybody here the same question. We don't buy much of anything in high quantities.

A. Frank, JPL: I guess that's a good subject. I'm just running into it now at this level. Perhaps someone else wants to address it. Well I know that, from JPL's point of view, it's the same thing. Small quantities we are not interested in - one has to get the right source eventually if the problem is indeed one that would demand that it can be done one way or another and that's what we're in the process of doing here.

Q. Roth, NASA HQ: Did you ever get the feeling you might want to do it yourself?

A. Frank, JPL: Yes, we are doing it ourself. We tried for example to eliminate these impurities by dissolving them. But if we can devise a process and then go to some other company and have them use our procedures. We will do it - either that or by obtaining a better source. So we're looking at both avenues here on this particular problem.

Q. Osterhoudt, Eastman Kodak: What price are you paying for this per square foot?

A. Frank, JPL: Actually we pay for it by the pound. It's something like $10 a pound or in that range. But we're not interested in the cost.

Q. Osterhoudt, Eastman Kodak: What you be willing to pay for something that would work? No I'm serious - premium price for premium quality?

A. Frank, JPL: Yes, yes of course for manned space flight.

Q. Osterhoudt, Eastman Kodak: I didn't understand that part.

A. Frank, JPL: Yes, if it could not be obtained in a condition suitable for NASA, we would be considering a small developmental contract to obtain the necessary quality.

COMMENT

Unidentified: I would like to comment - if you go back 14 years, this battery workshop got started because nickel cadmium cells were framing during charge - for the OAO spacecraft - a very serious problem for NASA. There were some other problems as well, and the battery separator manufacturer was present. And we asked him about that problem and he had put in some wetting agent because somebody had asked him to do it. There were some other basis of the problem. But he also got up and made the same statement - "You tell us what you want and we'll give it to you." And we're still using the same separator today.

Q. Levy, Sandia National Lab: Have you noted any specific problems due to this separator or are you just conjecturing that this might cause some problems.

A. Frank, JPL: We're in the process of doing that right now, Sam. We are building the prototype cells and we are going to make the voltage measurements. From, well first of all the physical properties are quite evident. One could not use this in fabricating the cells. When you go to the rolling operations the strengths would be inadequate and that's most likely related to the binder. A direct answer to your question is no, but we are in the process of doing it. And in the literature there is evidence that these levels of iron cause severe voltage regulation problems. So we'll be verifying it shortly.

Q. Allvey, Saft America, Inc.: Your 150 ppm of iron seemed high so I assume that's a spiral round configuration.

A. Frank, JPL: Yes.