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**POWER AND THERMAL
TECHNOLOGIES FOR AIR AND
SPACE**

**Delivery Order 0001: Single Ionic Conducting
Solid-State Electrolyte**



Allen Turner

**University of Dayton Research Institute
Metals and Ceramics Division
300 College Park
Dayton, OH 45469-0170**

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*//Signature//

LAWRENCE G. SCANLON, Jr. Ph.D.
Project Engineer
Electrochemistry and Thermal Sciences

//Signature//

JOHN G. NAIRUS
Chief
Electrochemistry and Thermal Sciences

//Signature//

KIRK L. YERKES, Ph.D.
Deputy for Science
Power Division

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14. ABSTRACT This report focuses on the development of a lithium-ion conducting channel as a solid-state electrolyte for rechargeable lithium batteries through the use of thin films of dilithium phthalocyanine (Li ₂ Pc) which have been solvent cast onto manganese dioxide cathodes. Experimental procedures have been developed which have resulted in the successful deposition of Li ₂ Pc with low ionic resistance. AC impedance measurements and analysis of the equivalent circuit has shown that specific ionic conductivities of 1.9 x 10 ⁻⁴ S/cm at room temperature are achievable. However, it has also been shown that Li ₂ Pc in its current configuration is also an electronic conductor. Development of a thin film insulator based on lithium nitride in conjunction with Li ₂ Pc is now in progress.						
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FOREWORD

The work documented in this report was performed by the University of Dayton between November 2003 and October 2005, for the Propulsion Directorate of the Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio. The effort was performed as Delivery Order 0001 on Contract No. FA8650-03-D-2403, Power and Thermal Technologies for Air and Space -- Scientific Research Program (SRP).

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1. Introduction

Dilithium phthalocyanine (Li_2Pc) has been under development as a solid-state electrolyte for rechargeable batteries since 1994. By the process of molecular self-assembly of Li_2Pc , an ion conducting channel is formed for lithium ion transport. Since the phthalocyanine is “locked” in place through this molecular self-assembly, the lithium ion transference number is one or there is no contribution of ionic conduction due to the anion. However, there is an electron conducting pathway associated with Li_2Pc .¹ X-ray structural analysis results show the spacing between the nearly planar rings of the phthalocyanine anions varies from 3.06 Å to 3.38 Å. Thus, you could expect an electronic pathway to exist through the pi-orbital overlap between adjacent phthalocyanine rings. Even though there is an electronic conductivity within Li_2Pc , we have been able to assemble a functioning full electrochemical cell using lithium metal foil, Li_2Pc electrolyte and manganese dioxide composite cathode.² It has been suggested that, since we were able to prepare a full electrochemical cell with stable open circuit voltage (OCV) using a pressed pellet of Li_2Pc as the electrolyte, the stable voltage could have resulted from increased separation between the phthalocyanine rings due to a reduction process taking place within the Li_2Pc upon charging and discharging of the cell.³ This charging and discharging is illustrated in figures 1 and 2. Because fabrication of the full cell involved the Li_2Pc and composite cathode in pellet form, there was

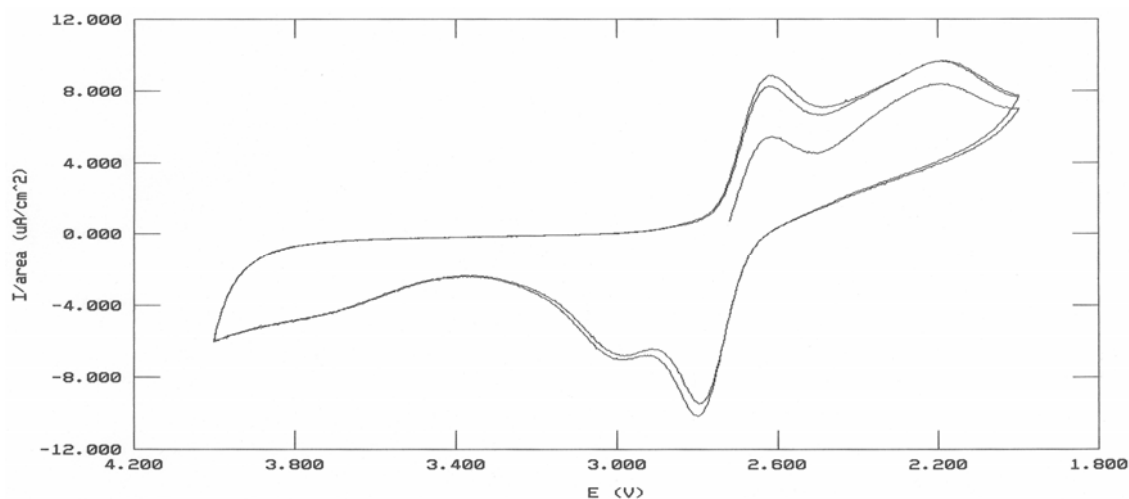


Figure 1 Cell A - slow scan cyclic voltammogram at 75° C. Full cell $\text{Li}/\text{Li}_2\text{Pc}/\text{MnO}_2$ configuration.

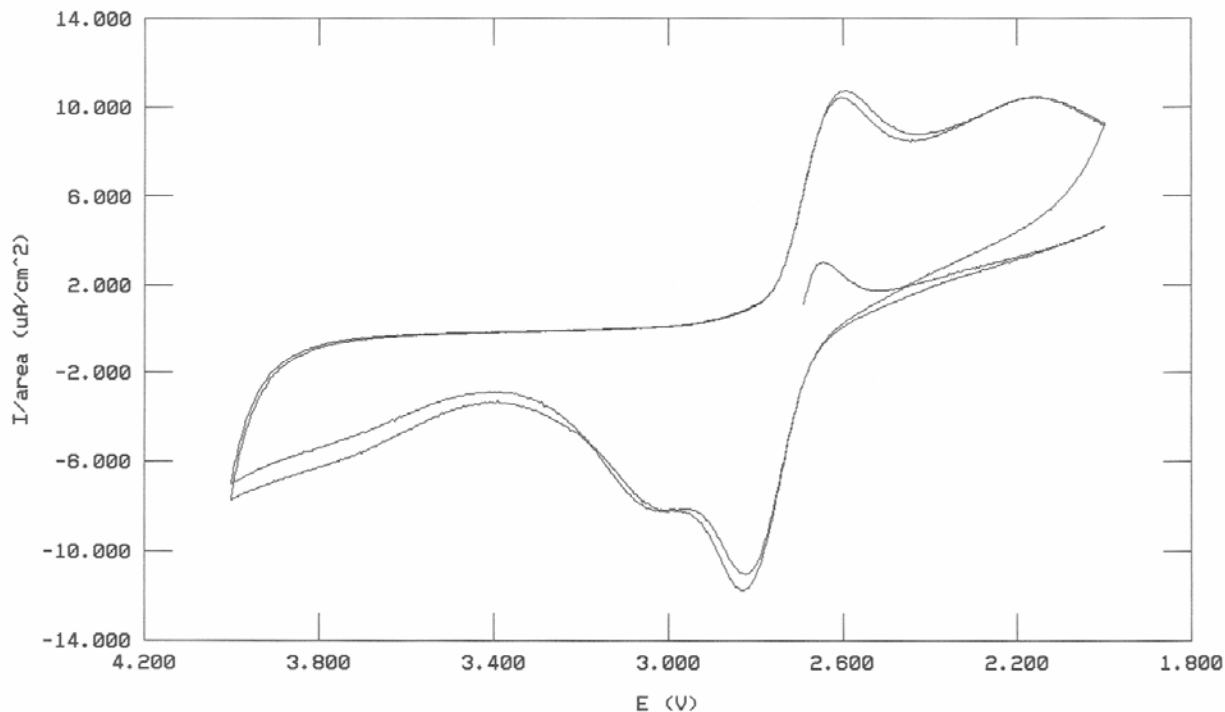


Figure 2 Cell A - slow scan cyclic voltammogram at 75° C after being maintained at 75° C for 5 days.

inherently high impedance within the cell. Ohmic resistance of the cell was approximately 5.5 k Ω with an OCV of 2.70 volts. The ionic current was approximately 12 $\mu\text{A}/\text{cm}^2$ which is unacceptable for most applications. As a verification of “proof of concept” a second electrochemical cell was prepared which consisted of a lithium anode, PEO, Li_2Pc electrolyte and a manganese dioxide composite cathode. The lithium was in the form of metal foil, PEO was a thin film containing no salts while the Li_2Pc and composite cathode were in the form of pellets. Due to the nature of PEO the electrochemical cell was operated at 50°C and although the PEO did increase the internal resistance, as expected, it also blocked the electronic pathway as the cell had an OCV of 3.32V and was cycled as illustrated in the cyclic voltammogram in figure 3.

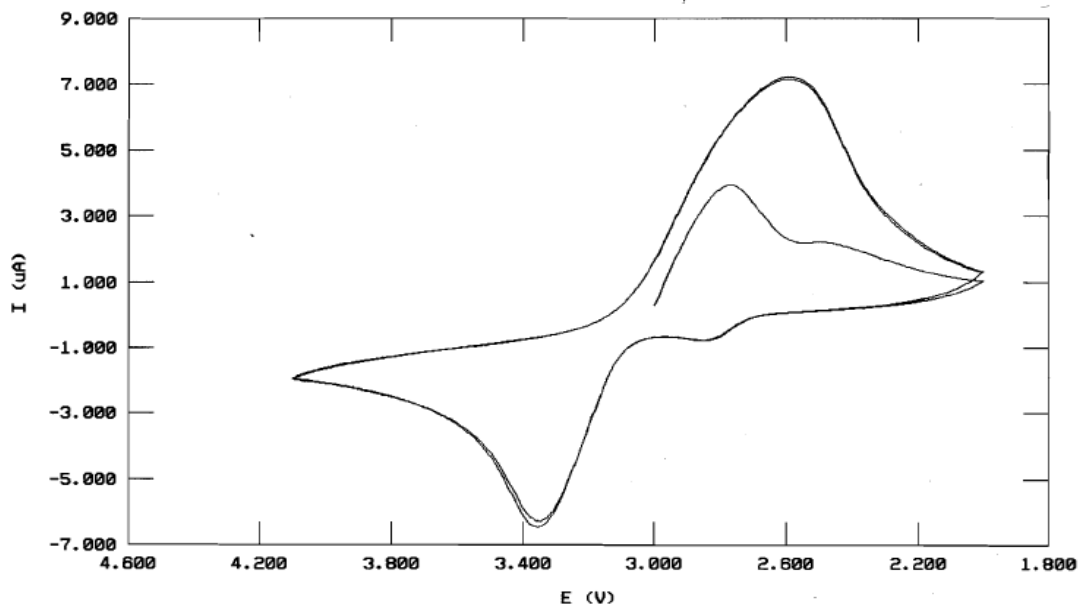


Figure 3 - Slow scan cyclic voltammogram at 50° C. Full cell Li/PEO/Li₂Pc/MnO₂ configuration - 3.32 OCV.

Thus, the task at hand was two fold. One, to reduce the internal resistance of a full cell to a more realistic number and two, to block the intrinsic electronic pathway of Li₂Pc while allowing ionic conduction. The first approach to reduce the internal resistance (IR) would be to cast a thin-film of Li₂Pc electrolyte onto a composite cathode substrate; keeping in mind the need for the Li₂Pc to be in the crystalline form. Using a cast cathode, as opposed to pelletizing, would provide a thinner (i.e. lower resistance) cathode with a smoother surface for better surface contact. At the same time casting the electrolyte onto the cathode would provide a thinner electrolyte layer with a more intimate contact at the electrolyte/cathode interface. Therefore, the thinner layers and better connectivity should lower the overall I R of the electrochemical cell. Vapor deposition and sputtering techniques were another approach to be investigated. Vapor deposition or sputtering of the components would also reduce the I R through reducing the thickness of the layers while providing good connectivity between layers.

The second area of concern, the intrinsic electronic conduction of Li₂Pc, was eliminated by the addition of a PEO film as mention previously. The PEO acted as an insulating layer or barrier to the electronic pathway but because of its physical characteristics, the PEO causes the electrochemical cell to be temperature dependent which is not desirable. What was needed was an insulating type layer formed through a

chemical reaction or applied by vapor deposition of a compound that would not create a temperature dependency but would be an electronic insulator while conducive to ionic conduction. These above investigations were conducted simultaneously but for brevity will be discussed separately in this report

2. **Experimental**

Electrolyte Casting

All work was accomplished in a dry room capable of maintaining a relative humidity of < 2 % or in a dry box capable of keeping the moisture at < 5 ppm and the O₂ level at < 10 ppm. For a list of equipment used in this work see table 1. The bulk dilithium phthalocyanine used was purchased from Aldrich and then purified and recrystallized from acetone and toluene. Information about the other chemicals used in this work can be found in table 2.

To cast the Li₂Pc electrolyte a solvent system and procedures would have to be developed and to take advantage of the ionic conducting channel, the casting process would have to result in the electrolyte layer of Li₂Pc to be in the form of crystals. All solvents were dried with molecular sieve. Cyclopentanone and acetone were chosen as solvents for the Li₂Pc while hexane and toluene were chosen as the possible recrystallizing agents. The initial process was accomplished on battery grade copper and aluminum as the substrate. The substrate material was placed in a ventless fume hood located in the dry room. Small quantities of Li₂Pc were dissolved in cyclopentanone and acetone and by way of an eyedropper, the Li₂Pc solutions were placed on the substrates followed immediately by drops of hexane, toluene and a hexane/toluene mixture to the Li₂Pc solutions on the substrate and allowed to air dry. When dry, the samples were examined using a microscope. The results of this process were unsatisfactory and inconclusive possibly because of the substrate materials and rapid evaporation rate. However, the results did lead to the use of a hexane/toluene mixture opposed to hexane or toluene separately as the best chance of producing crystals. Therefore, it was proposed that solutions be prepared of Li₂Pc dissolved in cyclopentanone and acetone as before but use only a toluene/hexane mixture to aid recrystallization. Two Li₂Pc solutions were made using acetone and cyclopentanone as before and a hexane/toluene mixture was

prepared. However, a prefabricated cathode received from Argonne Laboratories was used as the substrate in place of the copper and aluminum substrates previously used. To slow the evaporation rate, separate substrates were placed in individual containers along with a beaker containing the proper solvent (cyclopentanone or acetone) and the container was covered with parafilm containing a small hole. The casting process was then accomplished by applying the constituents to the substrate with a hypodermic syringe and needle and the samples were allowed to dry in the container with the beaker of solvent over several days. When the samples were dry, both were examined by scanning electron microscope (SEM). Although coverage was not optimum in either sample, the Li_2Pc in acetone solution (figure 4) contained more crystalline structures than the cyclopentanone solution (figure 5).

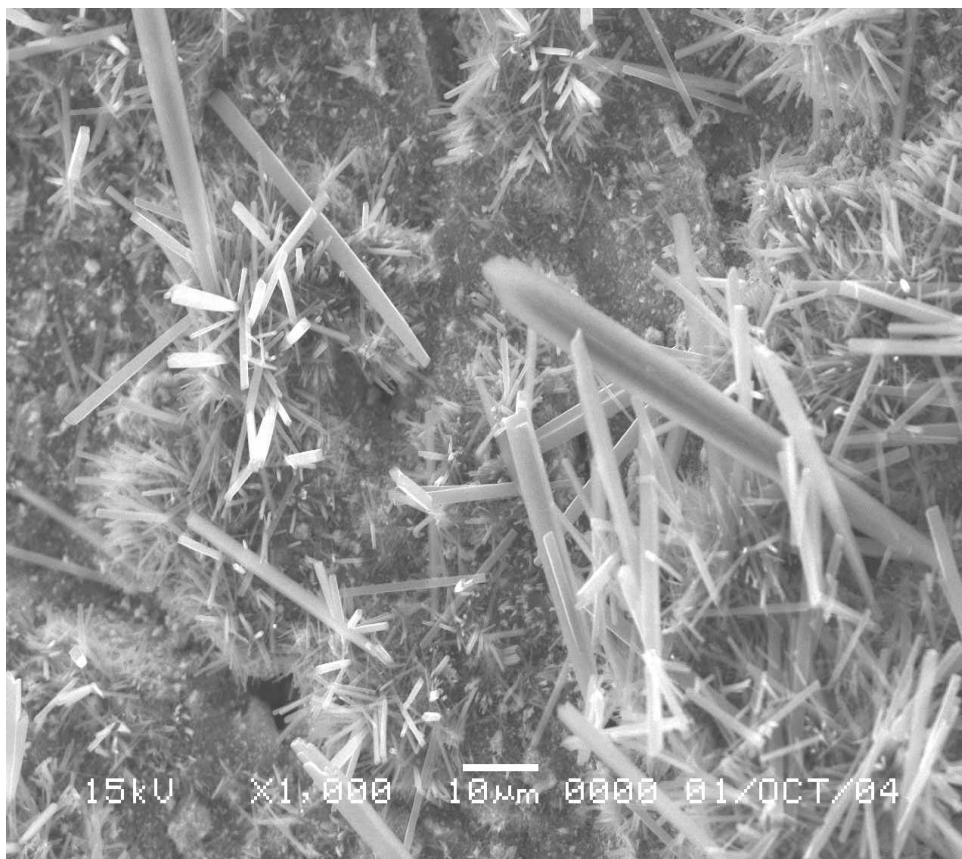


Figure 4 - SEM of solvent cast Li_2Pc on cathode substrate. Acetone/hexane/toluene solvent system.

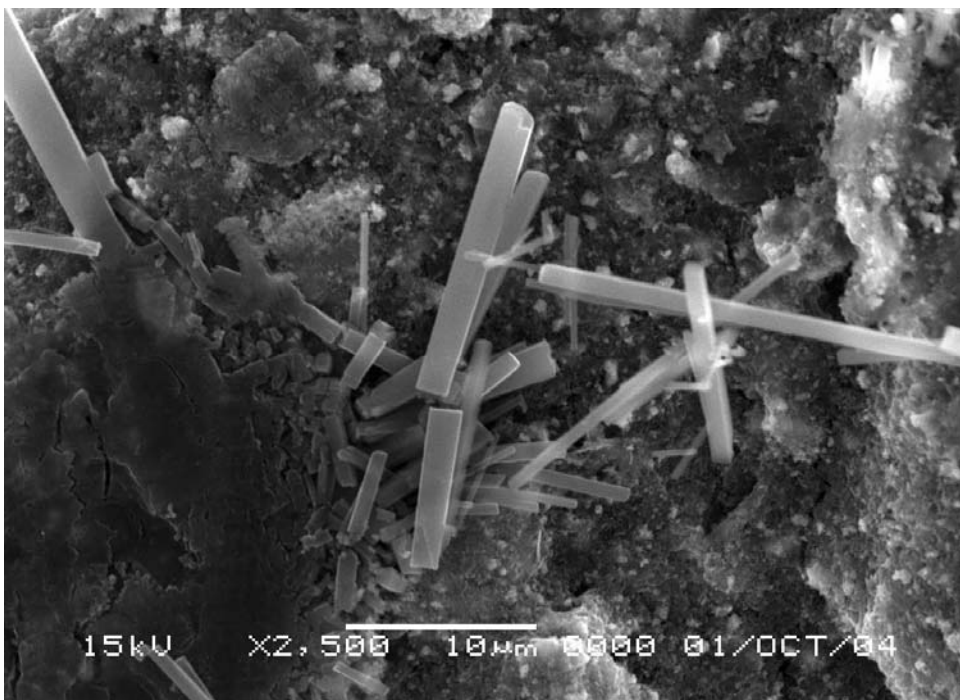


Figure 5 - SEM of solvent cast Li₂Pc on cathode substrate. Cyclopentanone/hexane/toluene solvent system.

After analysis of the samples, the procedure was refined and only the Li₂Pc in acetone solution would be used for the rest of the work. The next step was to try for complete coverage, better crystal growth and to verify the process. A small amount of Li₂Pc/acetone solution was prepared and added to a clean bottle. Then, the hexane/toluene mixture was added to the Li₂Pc solution. The final solution was agitated and allowed to set for approximately 20 minutes. A cathode substrate was placed in a container with a larger beaker of acetone than previously used. The container was covered with parafilm as before but the hole in the parafilm was decreased in size. The layers of solution were applied using a hypodermic needle and drying time between layers was increased. After applying multiple layers of the solution, the substrate with electrolyte was allowed to dry over several days in the container and then examined by SEM (figure 6). As can be seen, coverage was not very good. The sample was then placed in a sealed sample holder and examined by AC impedance. As expected, due to the poor coverage and lack of nice crystal structure the impedance results were not very satisfactory.

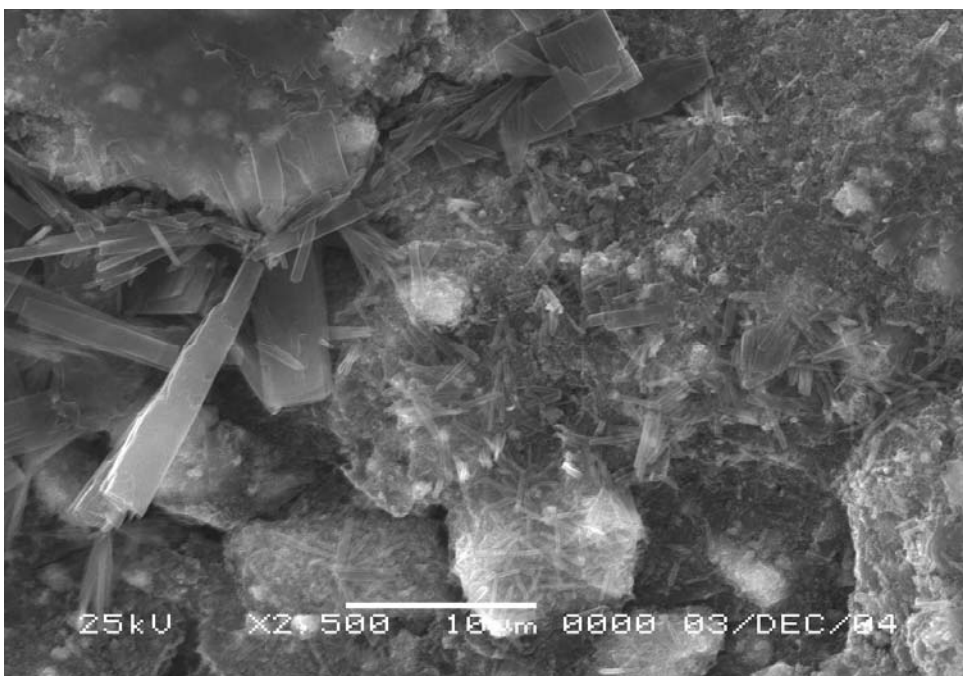


Figure 6 SEM of solvent cast Li₂Pc after refining techniques. Acetone/hexane/toluene solvent system.

Based on the previous results, the process seemed viable but the procedures/techniques still needed refined. Therefore, another sample was prepared using the basic process outlined above but with minor changes and refinements to the application of layers, time between layers and total drying time. Again, the sample was examined by SEM and the results can be seen in figures 7 and 8.

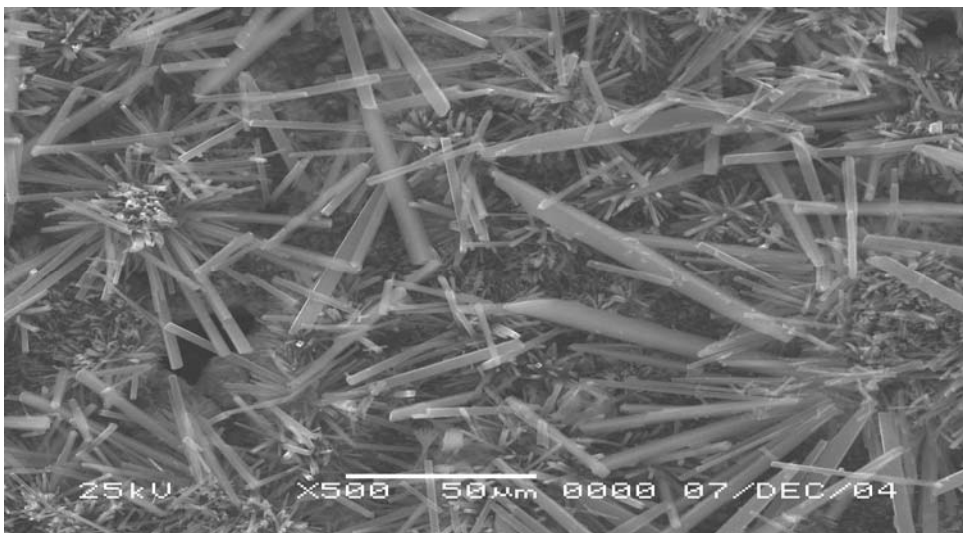


Figure 7 Sample 11-26, SEM of solvent cast Li₂Pc on cathode substrate.

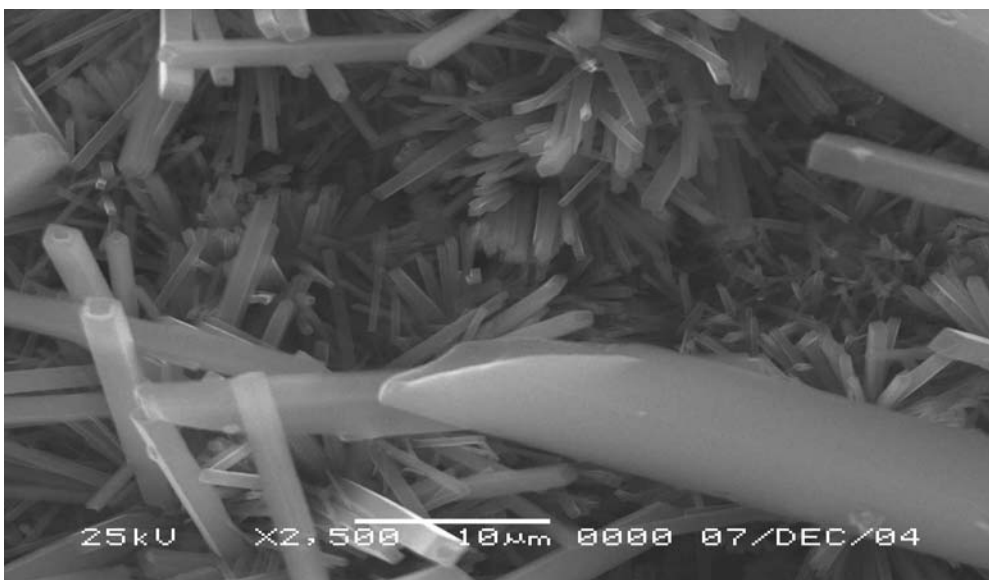


Figure 8 Sample 11-26, Same view as Figure 7 under increased magnification.

The coverage was much better than in previous attempts and crystal growth was much more successful. This sample was also placed in a sealable holder, placed under 1000 pounds force and examined by AC impedance from 199 KHz to 100 mHz at 21° C (figure 9) and analyzed by equivalent circuit fit (see figure 2C, ref#1). The results of the equivalent circuit fit are in table 3.

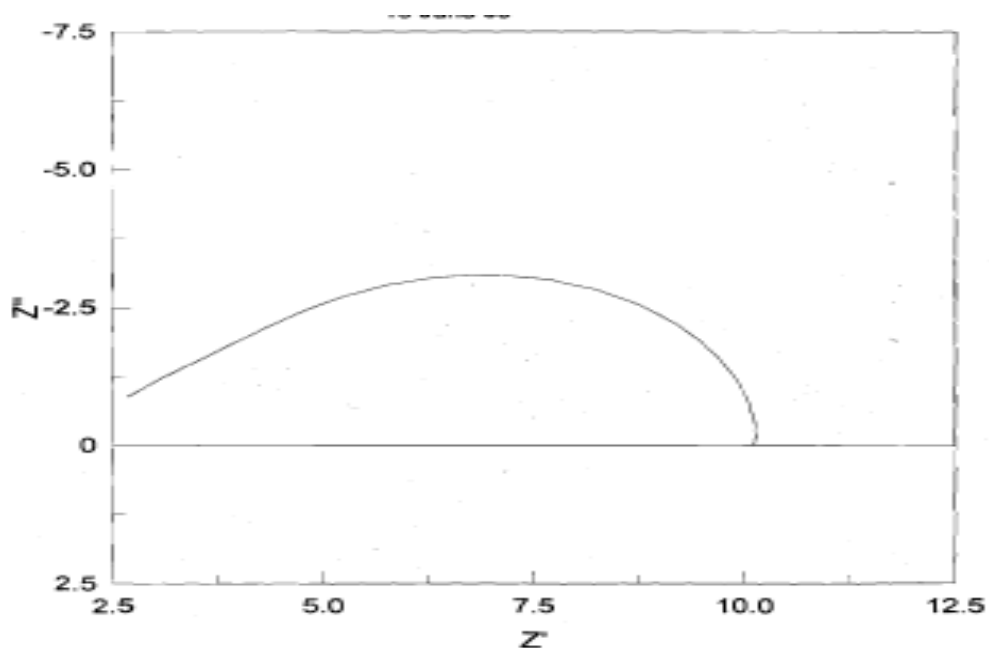


Figure 9 Sample 11-26 AC Impedance of cast Li_2Pc on cathode substrate, 1000 lbs. Force, at 21° C, 199 KHz to 100 mHz.

The normalized or specific ionic conductivity of this sample was 1.9×10^{-4} S/cm. This data was compared to results of a study ⁴ involving known crystals of Li_2Pc which had been pressed into a pellet, placed between gold electrodes, placed under 3000 pounds of force and analyzed at 21° C (table 4). In this case, the specific ionic conductivity was 1.6×10^{-4} S/cm. The ionic conductivity of our sample was in good agreement with the data of known Li_2Pc crystals which indicated the solvent cast sample had resulted in a thin layer of crystalline structure with good ionic conductivity.

During the effort to refine the casting process, it was discovered after a couple of attempts that the Li_2Pc appeared to have been “soaking” into or being absorbed by the substrate. The only major change had been the use of the second sheet of cathode material. This occurrence has not been fully understood as both sheets of cathode material were said to be the same per Argonne Laboratory personnel. However, this brought about the decision to attempt casting cathode substrates in-house. The ingredients used for the composite cathode work are listed in table 2. The formula used was suggested by personnel of Argonne Laboratory. After several attempts the locally cast cathodes resulted in satisfactory substrates that were used for the continuing casting process, as well as, the vapor deposition work to be covered next.

Vapor Deposition

It had been proposed that the process of vapor deposition could also solve the connectivity and high internal resistance problems as well as a method of introducing the insulating layer to block the intrinsic electronic pathway. From previous work,⁴ it had been determined that sublimation of Li_2Pc was not viable. However, deposition of Li_2Pc by electron beam (e-beam) had not been investigated. For the initial investigation, 0.001 gram of Li_2Pc , previously purified and recrystallized, was placed in a crucible inside the deposition system (table 1) under a vacuum of 1×10^{-7} torr. Copper foil 0.025 mm thick was used as the substrate on which to deposit. After deposition of the Li_2Pc , the layer was analyzed by AC impedance. The resultant resistance of the Li_2Pc layer was approximately 3 M ohms which was unacceptable and pointed to the fact that the deposition may no longer be Li_2Pc . The decision was then made to cast the electrolyte

onto a cast composite cathode and use the combination as the substrate for the rest of the investigation.

Trials were made to deposit lithium metal onto copper and nickel substrates as well as, cast electrolyte/cathode substrates. All attempts to protect the lithium from reacting with the moisture in the air were not successful due to the nature of lithium and the process. The same was true of lithium iodide (LiI) which was proposed as an electronic blocking layer but lithium iodide proved to be too hygroscopic. The next approach was to substitute lithium nitride (Li_3N) in place of the lithium iodide. Lithium nitride was vapor deposited by e-beam onto a cast electrolyte/cathode substrate and steps taken to protect it from the environment. This sample was examined by AC impedance. The impedance results were not very encouraging and a post mortem examination revealed the copper foil placed between the Li_3N layer and the current collector had reacted. Zinc, copper, gold and silver were investigated as possible sealing agents. Li_3N would be deposited by e-beam onto the electrolyte/cathode substrate and then zinc, copper, gold or silver would be deposited to seal the deposition from the environment. Due to equipment and adhesion problems with the zinc, copper, gold and silver these trials were not successful. Attempts were also made to vapor deposit a full cell by vapor deposition of Li_3N on an electrolyte/cathode substrate followed by deposition of lithium metal and sealed with gold. These attempts have not been successful and it has been suggested that the use of e-beam may have ripped apart the Li_3N molecule and the deposited layer is no longer in the form of Li_3N . An analysis to determine the composition of the layer has not been accomplished.

3. Summary and Conclusions

Dilithium phthalocyanine has been under development as a solid-state electrolyte for rechargeable batteries since 1994. The “proof of concept” had been accomplished but there were a couple of undesirable characteristics, such as the high internal resistance (IR) and intrinsic electronic conduction of the Li_2Pc solid-state electrolyte. The purpose of this work was to solve the IR and electronic problems. To that end we developed procedures that resulted in thin-film Li_2Pc electrolyte layers on composite cathode substrates. The key point was maintaining the crystalline structures of the Li_2Pc layers.

Through developing the thin electrolyte layer and maintaining the crystal structure, the process resulted in a decrease in the IR from hundreds of K ohms to ohms.

The other part of the project was the blocking of the electronic pathway. To that end we were not successful. There were unavoidable problems with the equipment which could have also led to some of the adhesion problems. The problems with adhesion were not consistent and we never got a good understanding of the problem. The equipment for the e-beam is such that exposure of materials to the environment could not be avoided and this was always a problem. The investigation of Li_3N was not completed and left perhaps more question than answers but theoretically should block the electronic pathway. Another question not resolved was whether the e-beam destroyed or ripped apart the Li_3N . It would perhaps be better to form the Li_3N layer in place through a chemical reaction. Another method of deposition that should be investigated is that of resistive heating. This method should be more benign to the materials we have been involved with.

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3. R. Gerald and R. J. Klinger, Argonne National Laboratory, unpublished results.
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APPENDIX A: TABLES

TABLE 1 - List of equipment used for this work.

EQUIPMENT LIST			
ITEM	MODEL NO.	MANUFACTURE	USE
Dry Box	DLX-001-D-P	Vacuum Atmosphere Inc.	Inert environment.
- Drying bed and controls.	NEXUS 400300	Vacuum Atmosphere Inc.	Inert environment.
Tumbler	A	Thumbler Tumbler	Ball milling.
Tumbler	TB-050	Ikohe Inc.	Ball milling.
Ductless Fume Hood	AU-250E	Misonix	Solvent casting in dry room.
Electrochemical System	N/A	Princeton Applied Research	Electrochem. studies/analysis
- Potentiostat	273A	Princeton Applied Research	Electrochem. studies/analysis
- Lock-in Amplifier	5210	Princeton Applied Research	Electrochem. studies/analysis
Electrochemical System	N/A	Solartron Analytical	Electrochem. studies/analysis
- Electrochemical interface	SI 1287	Solartron Analytical	Electrochem. studies/analysis
- Frequency Response Anal.	1255B	Solartron Analytical	Electrochem. studies/analysis
Wig-L-Bug	C32010B	Crescent	Mixing/Blending.
Environmental Chamber	JUJr	Tenny	Temperature control of test samples.
Vacuum Oven	1410M	Sheldon Mfg. Inc.	Material drying.
Carver Lab. Press	3912	Carver Inc.	Pellet fabrication, pressure effects.
Scanning Electron Microscope	JSN-6060	JEOL	Surface examinations.
Deposition System	306	BOC Edwards	E-beam deposition.
Dual Gun Sputtering System	DV-502A	Denton Vacuum (Custom)	Vapor deposition
Microscope, stereomaster II	SPT-ITH	Allied Fisher Scientific	Initial solvent casting.

TABLE 2 - List of chemicals used for this work.

Chemicals Used			
NAME	PURPOSE	PARTICULARS	SOURCE
Dilithium Phthalocyanine	Electrolyte Casting	N/A	Aldrich
Acetone	Electrolyte Casting	Chromasolv® HPLC Grade	Aldrich
Cyclopentanone	Electrolyte Casting	99%	Aldrich
Hexane	Electrolyte Casting	Anhydrous	Aldrich
Toluene	Electrolyte Casting	99.8 %, anhydrous	Aldrich
Manganese Dioxide	Cathode Casting	CMD gamma MnO ₂	Provided by Chemetals, Inc.
Acetylene Carbon Black	Cathode Casting	99.9 + % (metals basis)	Alfa Aesar
Polyvinylidene Fluoride Resin	Cathode Casting	PVDF KYNAR FLEX 2801	Elf Atochem, North American, Inc.
1-methyl-2-pyrrolidinone	Cathode Casting	N,M,P 99.5 % anhydrous	Aldrich
Molecular Sieve	Solvent Drying	13 X	Aldrich
Lithium Metal Foil	Anode	Battery Grade	FMC Corporation, North Carolina
Polyethylene oxide (PEO)	Insulating film	Mol. Wt. 1 M.	Aldrich

TABLE 3 - Impedance results for sample 11-26, 199 KHz to 100 mHz.

Freq. Range	Element	Value	Error	% Error	Chi-Square	Wt. Sum
199 KHz - 100 mHz	Re	10.1	0.0060812	0.06021		
	Ri	5.511	0.098017	1.7786		
	CPE-T	1.4494E-07	8.5797E-09	5.9195		
	CPE-P	0.96856	0.0044384	0.45825	0.019465	2.4137

TABLE 4 - Impedance results for a pellet composed of single crystals of Li₂Pc sandwiched between gold electrodes. The pellet is 710 µm thick with an area of 1.6 cm². Results are for data collected at 21° C.

Freq. Range	Element	Value	Error	% Error	Chi-Squared	Wt. Sum
1 MHz-0.1 Hz	Re	1523	1.5716	0.10319		
	Ri	290.7	5.617	1.9322		
	CPE-T	8.4058E-09	4.3867E-10	5.2187		
	CPE-P	0.79863	0.0037035	0.46373	0.012809	1.7677
398 KHz - 0.1 Hz	Re	1526	0.23204	0.015206		
	Ri	268.4	2.2063	0.82202		
	CPE-T	1.0899E-08	1.2036E-10	1.1043		
	CPE-P	0.77808	0.00082148	0.10558	0.00031265	0.040645
199 KHz - 0.1 Hz	Re	1526	0.12414	0.008135		
	Ri	274.8	2.679	0.97489		
	CPE-T	1.1060E-08	9.113E-11	0.82396		
	CPE-P	0.77675	0.00063919	0.08229	0.0001068	0.013244