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**AEROSPACE POWER SCHOLARLY
RESEARCH PROGRAM**

**Delivery Order 0011: Single Ionic Conducting
Polymer Electrolyte**



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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. Dilithium phthalocyanine (Li2Pc) has been used in this development since it can undergo molecular self-assembly to form the ionically conducting channel. The essential features of the channel are that it is designed such that the anion matrix of the unsaturated macrocyclic forms the channel through which the lithium ions move, thus making it a single-ion conductor for lithium ions; the ionic transport of lithium depends on the electric field gradient created by the electrodes, thereby minimizing temperature dependence for ionic transport.					
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FOREWORD

The work documented in this report was performed by the University of Dayton between October 2000 and September 2004, for the Propulsion Directorate of the Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio. The effort was performed as Delivery Order 0011 on Contract No. F33615-98-D-2891, Aerospace Power Scholarly Research Program (SRP).

Technical support and direction of this delivery order was provided by Dr. Lawrence Scanlon of AFRL/PRPS. Mr. Allen Turner was the Delivery Order Principal Investigator. Mrs. Leah Lucente supported with the execution of this delivery order.

The author also wishes to acknowledge the assistance of Ms. Sheila Liskany and Mr. Jeffrey Fox of the University of Dayton Research Institute, who provided the administrative support to make this work possible. Mr. Fox is the SRP Program Manager.

1. INTRODUCTION

The present requirements for energy storage devices are for a specific energy density of 150 Whr/Kg and specific power of 300 W/Kg. Today's gel and non-aqueous lithium-ion batteries meet or exceed these energy density and specific power requirements. However, due to decomposition of the lithium salts used in non-aqueous electrolytes, present maximum operating temperatures are approximately +50°C. On the other side, performance of polyethylene oxide (PEO) based electrolytes rapidly degrade below +60°C.

The basic objectives of this program were to synthesize a single lithium ion conducting polymer electrolyte which features a constant solvent-coordination sphere for the ion (lithium-ion conducting channel) and prove the concept. Based on previous work involving computational chemistry, synthesizing the desired material could be accomplished through a molecular self-assembly process. This process takes advantage of the electrostatic attraction between lithium ions and the partial negatively charged nitrogen atoms of an unsaturated macrocyclic molecule. Dilithium phthalocyanine (Li_2Pc) was chosen as the base material. Ion transport, through the lithium-ion conducting channel, primarily depends on the electric field gradient established between the electrodes of the battery. In theory, this concept should make it possible to produce a lithium ion battery that meets the specific energy density and specific power requirements of today's batteries but without the negative temperature dependency of today's batteries.

All work was accomplished in a dry box or a dry room maintained at 1% relative humidity. As the synthesis, purification and recrystallization of Li_2Pc was accomplished and the material was received, it was characterized/evaluated using EG&G electrochemical instrumentation to determine the experimental methods that produced the best yields. A

test cell holding device was developed in which a half-cell or full electrochemical cell could be assembled, hermetically sealed via an o-ring and tested. Because of this device, specimens could be tested under various pressures while an environmental chamber was used to test the specimens at various temperatures. The electrolyte was evaluated in both the pressed pellet form as well as cast films. Lithium metal foil was used as the anode and the cathodes were cast or formed into pellets.

This final report discusses the above work and its results in detail. The latter work is discussed in a paper presented at the 205th Electrochemical Society Conference in Texas (Appendix A).

The objective of this program was achieved. Electrochemical cells using lithium metal foil as the anode, Li_2Pc as the solid-state electrolyte and various cathode materials were assembled and used to demonstrate charging and discharging behavior by way of slow scan cyclic voltammetry. Although proof of concept has been shown, the internal resistance is far too high to be practical. It is suspected that the lack of contact between solid surfaces is the problem area and by reducing or eliminating the interfacial resistance will result in a viable product.

**APPENDIX A: PREPARATION OF A THIN-FILM SOLID-STATE
ELECTROCHEMICAL CELL WITH DILITHIUM
PHTHALOCYANINE (Li₂Pc) AS THE ELECTROLYTE**

**PREPARATION OF A THIN FILM SOLID-STATE ELECTROCHEMICAL CELL WITH
DILITHIUM PHTHALOCYANINE (Li₂Pc) AS THE ELECTROLYTE**

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ABSTRACT

Electrochemical cells with lithium metal foil anodes, Li₂Pc electrolyte in the form of pressed pellets and a manganese dioxide cathode have been prepared. While these cells have stable open circuit voltages and demonstrate charging and discharging behavior via slow scan cyclic voltammograms, they have unacceptably high cell impedances. In order to address the issues of obtaining cells with low impedances and stable voltages, we have fabricated cells with slightly different configurations and have concentrated on preparing thin film solid-state electrolytes via sublimation and solution casting. These results are to be discussed in this paper.

INTRODUCTION

Dilithium Phthalocyanine (Li_2Pc) has been under investigation in our laboratory as a solid-state electrolyte for rechargeable lithium batteries (1). Theoretical modeling based on molecular dynamics and ab initio calculations illustrate the importance of molecular self-assembly in the formation of a solid-state electrolyte based on Li_2Pc (2). Different Li_2Pc crystalline forms were modeled at 300 K and lithium ion self-diffusion coefficients and ionic conductivities were calculated. These calculated results suggest that lithium ion transport in the crystalline phase can be very rapid approaching a specific conductivity of 10^{-4} S/cm at 300 K. However, these calculated results reflect ion movement via self-diffusion as determined by the field created by the self-assembly of Li_2Pc molecules, while in the actual experiment, diffusion across the electrolyte/electrode interface is driven by a difference of chemical potential and by an electric field gradient established between the electrodes of an electrochemical cell. Thus, one may expect higher specific ionic conductivities in an actual experiment, as has been reported in reference (2). Our work also shows that one can fabricate full electrochemical cells with Li_2Pc as the solid-state electrolyte and obtain cells with stable open circuit voltages(3). This has been accomplished with lithium metal foil anodes, Li_2Pc solid-state electrolyte and manganese dioxide as the cathode. Slow scan cyclic voltammograms of these cells illustrate the charging/discharging process. While these results are encouraging, current densities within these cells are very low, 10 to 20 $\mu\text{A}/\text{cm}^2$. It is suspected that high impedances at the electrode/electrolyte interface are contributing to these low current densities. In order to address the issues of obtaining cells with low impedances and stable voltages, we have fabricated cells with slightly different configurations than previously reported (3) and have concentrated on preparing thin film solid-state electrolytes via sublimation and solution casting. These results are to be discussed in this paper.

EXPERIMENTAL

Li_2Pc was purchased from Aldrich and recrystallized from an acetone/toluene mixture (4). The resulting microcrystalline material was dried at 130°C under a vacuum of 90 millitorr for 18 hours. Acetone, toluene, acetonitrile and cyclopentanone were purchased from Aldrich. All solvents were dried with Acros molecular sieves, 13X; 4-8 mesh. The sieves were dried under vacuum at 100°C prior to their use for drying of the solvents. MnO_2 was provided by Chemetals, Inc. (Chemically prepared gamma- MnO_2). Ultra thin iron sulfide cathode, approximately 1 μm , was prepared by electrodeposition (5). KYNAR vinylidene fluoride resin (KYNAR FLEX 2801) was purchased from Elf Atochem North America, Inc. Battery-grade lithium foil was purchased from FMC Corporation, North Carolina. The solid-state electrolyte was prepared by mixing Li_2Pc and KYNAR FLEX 2801 (8 % by wt. binder) with a Crescent WIG-L-BUG. The composite cathode was prepared by mixing MnO_2 (10.9 % by wt.), carbon (15.1 % by wt.), Li_2Pc (66.6 % by wt.), and binder (7.4 % by wt.) in a Crescent WIG-L-BUG. All electrochemical cells were prepared in a dry room where the moisture content is less than 1 percent. The mixed-composite cathode material was placed within a rubber O-ring on battery-grade aluminum foil and sandwiched between two copper plates. The cathode material was then pressed into a pellet at high pressure (3000 psi) using a Carver press. The area of the pressed cathode

was 1.6 cm^2 . Once the composite cathode was pressed, a new O-ring was positioned around the cathode pellet and the mixed electrolyte was placed on top of the cathode. Pressure was then applied to form a new layered pellet, which was a combination of electrolyte and cathode. Typical electrolyte thicknesses range in value from 400 to 700 μm . To complete formation of the galvanic cell, lithium foil approximately 150 μm thick and with an area of 0.785 cm^2 was placed on top of the pressed electrolyte/cathode pellet. The entire galvanic cell fabricated in this configuration was hermetically sealed and under pressure. An electrochemical cell with a slightly different cell configuration was fabricated where the solid state electrolyte had a sandwich construction. In this case, a 30 μm thick film of poly(ethylene oxide) (PEO) was placed adjacent to a pressed pellet of Li_2Pc . There was no lithium salt in the PEO film which was cast from acetonitrile and dried under vacuum at 100°C for 18 hours. This cell was also constructed with a 150 μm lithium foil anode and a composite pelletized MnO_2 cathode. A third electrochemical cell was constructed. The cell consisted of a lithium foil anode, thin film solid-state electrolyte and iron sulfide cathode where the ultra thin iron sulfide cathode was 100 % iron sulfide. In this case, however, the solid state electrolyte was prepared from 50 % by wt. Li_2Pc and 50 % by wt. KYNAR 2801 binder which was solution cast from acetone. The thickness of the film was 100 μm and it was dried at 100°C under vacuum. A Tenney environmental chamber was used to maintain the operating temperature of the cell. Thermocouples inside the chamber and positioned near the cell monitored the temperature. The temperature range was varied from $+21^\circ\text{C}$ to $+90^\circ\text{C}$. Alternating current (AC) impedance and cyclic voltammetry, chronopotentiometry and chronoamperometry measurements were performed using EG&G electrochemical instruments consisting of the EG&G potentiostat/galvanostat model 273A and EG&G lock-in amplifier model 5210. The amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 0.1 Hz. Both the spectrometer and the environmental chamber were located in our dry room.

Thin Film Characterization

Thin films of Li_2Pc were solution cast from cyclopentanone and toluene and deposited onto battery grade copper foil purchased from Aldrich. Pressures applied to blocking electrode cells were accomplished using a Carver model C laboratory Press. They were dried under vacuum at 100°C . Cells with copper blocking electrodes and Li_2Pc thin films, 20 μm , were used for chronoamperometry experiments where a dc bias of 10 mV was applied to a cell and the steady state current was measured. The purpose of this experiment was to measure the electronic conductivity of Li_2Pc .

Film Deposition

A 300 Å Au film was deposited onto a solution cast film of Li_2Pc using sputtering technique. The purity of Au target is 99.995%. The variable parameters were the RF power and total pressure. For this particular deposition the total pressure was 7 milli-torr and the power was 150 watts. The deposition system used to produce the Au films was a dual-gun RF sputtering system, model DV502-A, manufactured by Denton Vacuum with an RFX generator from Advanced Energy Industries. The film thickness of Au was

monitored by using an STM-100/MF Thickness/Rate Monitor from Sycon Instruments. The actual film thickness of Au was measured by using the DekTak IIIST System.

SEM

The SEM photo was taken using a JEOL 6060 SEM operated at working distance of 15mm, 20 KV, and 10,000X. The JEOL-6060 with EDX capability has the optimized resolution of 100Å.

RESULTS & DISCUSSION

Electrochemical Cell Fabrication

Three cells were fabricated with slightly different cell configurations. In the first case, pressed pellets of the electrolyte and cathode using 8 % by wt. KYNAR 2801 binder were formed. In the second case, the electrolyte was in the form of a hybrid sandwich construction which consisted of a thin film of poly (ethylene oxide) (PEO) 30 μm thick placed against a 500 μm thick pressed pellet of Li_2Pc . There was no lithium salt in the thin film of PEO. The cathode remained the same as in the first case. In case three, the electrolyte consisted of 50 % by wt. Li_2Pc and 50 % by wt. KYNAR 2801 binder 100 μm thick. In case 3, however, the cathode was 100 % iron sulfide in the form of a very thin film about 1 μm thick. Figure 1 shows the cyclic voltammogram of a $\text{Li}/\text{Li}_2\text{Pc}/\text{MnO}_2$ cell operating at 75°C (case one). The cell was tested in our lab for about two months over which time frame there was very little change either in the slow scan cyclic voltammograms or the complex impedance patterns. Figure 2 shows the Nyquist plot of the cell run after the cyclic voltammogram shown in Figure 1. One can see that there is still unacceptably high impedance within the cell since the total cell resistance is on the order of kilo-ohms. However, on a positive note, the high frequency intercept of Nyquist plots of this cell at 75°C dropped almost an order of magnitude from 7.2 kilo-ohms to 891 ohms over a two month time frame of cell testing. Figure 3 shows a slow scan cyclic voltammogram of a $\text{Li}/\text{PEO film}/\text{Li}_2\text{Pc}/\text{MnO}_2$ cell operated at 50°C (case 2), which is analogous to that showed in Figure 1. The effect of the PEO film resulted in a cell with a slightly higher open circuit voltage of 3.0 Volts compared to that in case one where the open circuit voltage was 2.7 Volts. The reason for this is, perhaps, more effective contact at the lithium metal foil/PEO/electrolyte interface. The effective contact at this interface is also reflected in the charging/discharging profiles of the $\text{Li}/\text{PEO film}/\text{Li}_2\text{Pc}/\text{MnO}_2$ cell as shown in Figures 4 and 5. During this test, the cell was charged and discharged seven times. Figures 4 and 5 show the cell after the seventh cycle. The voltage discharge profile is relatively flat out to 2200 seconds as shown in Figure 5. During the first discharge, however, this same voltage profile was relatively flat out to 2380 seconds. While this represents approximately an 8 % decrease in capacity, one must take into account that our cathode composition and configuration was most likely far from optimum.

The last cell configuration to be discussed, case 3, using the iron sulfide cathode, represents a cell we were able to fully discharge using a combination of constant current

and constant potential discharge. The initial open circuit voltage after assembling of the cell was 1.67 Volts at 21°C. By the next day the open circuit voltage was 2.14 Volts at 21°C. The cell was discharged at 90°C. The discharge profile during a portion of the discharge at constant current shows a flat voltage profile as shown in Figure 6. In order to expedite the discharge process, the cell was held at a constant potential of 1.1 Volts and discharged to a final open circuit voltage of 1.3 Volts. The measured capacity was 0.94 coulombs which is in agreement with Peled and Golodnitsky (6).

Thin Film Electrolyte Preparation and Their Properties

While the cells described above demonstrate the conduction of lithium ions through the solid-state electrolyte Li_2Pc , the total impedance of the cells are unacceptably high. In order to prepare a solid-state thin film electrolyte of Li_2Pc , sublimation was attempted. In general, metal phthalocyanines can be sublimed at approximately 400 to 500°C and 10^{-5} torr. We were unable to sublime a pellet of Li_2Pc at 700°C and 2×10^{-7} torr. Except for a very minor blemish of the surface of the pellet, no discoloration, the pellet of Li_2Pc looked as pristine as when the experiment was started. In view of this result, thin film preparation through solution casting was conducted.

The Nyquist plots of a 20 μm thick film of Li_2Pc as a function of increased pressure are shown in Figure 7. This film was obtained through solution casting from a mixed solvent of cyclopentanone and toluene and dried at 100°C under vacuum overnight. Figure 8 shows an SEM of a 20 μm thick film of Li_2Pc solution cast from cyclopentanone and toluene. There are numerous voids in this film suggesting a rather uneven surface. One can observe that as the pressure is increased, the impedance decreases perhaps through better contact between the solid particles. There are two semicircles associated with these films indicative of both ionic and electronic conduction taking place within the film (7). The dual nature of conductivity is also observed in a pressed pellet of Li_2Pc recrystallized from acetone and toluene and dried at 160°C under vacuum. The Nyquist plot for this pellet is shown in Figure 9. An unreported equivalent circuit analysis of these types of Nyquist plots for Li_2Pc based on pressed pellets concludes that the semicircles are indicative of both electronic and ionic conduction (8). To enhance the surface contact between the electrode/electrolyte interface, gold was sputtered onto the surface of films obtained from solution casting. The Nyquist plot for film 4 is shown in Figure 10. The impedance for this film is now 4.4 ohms after sputtering of gold. Two other films have low resistances after sputtering of gold. Film 5b has a resistance of 1.9 ohms and film 6c has a resistance of 2.2 ohms as measured by AC impedance. A dc voltage of 10 mV was applied to the Cu/ Li_2Pc film4/Au cell and a steady state current of 1.51 μA was measured. Since blocking electrodes are used, the resistance of 6.6 ohms is representative of electronic conduction. Films 5b and 6c after sputtering of gold also have electronic resistances of 2.7 and 3.0 ohms, respectively, as determined by applying a dc voltage of 10 mV to a blocking cell. These results may also suggest that the value of resistance as determined by impedance is a combination of ionic and electronic resistances in parallel.

CONCLUSIONS

Results suggest that good surface area contact at the electrode/electrolyte interface is important for attaining values of low resistance within cells incorporating Li_2Pc as the solid-state electrolyte. Thermal evaporation of lithium onto the surface of Li_2Pc may be important for reducing electrochemical cell resistances.

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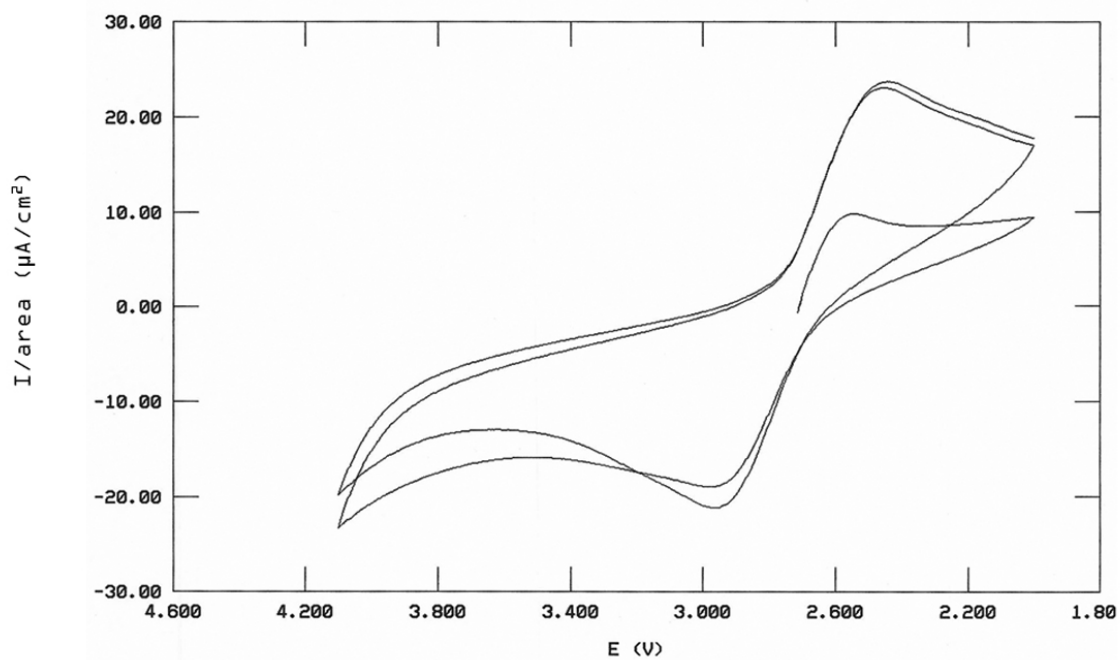


Figure 1. Cyclic voltammogram of Li/Li₂Pc/MnO₂ cell at 75°C, scan rate 280 μV/s.

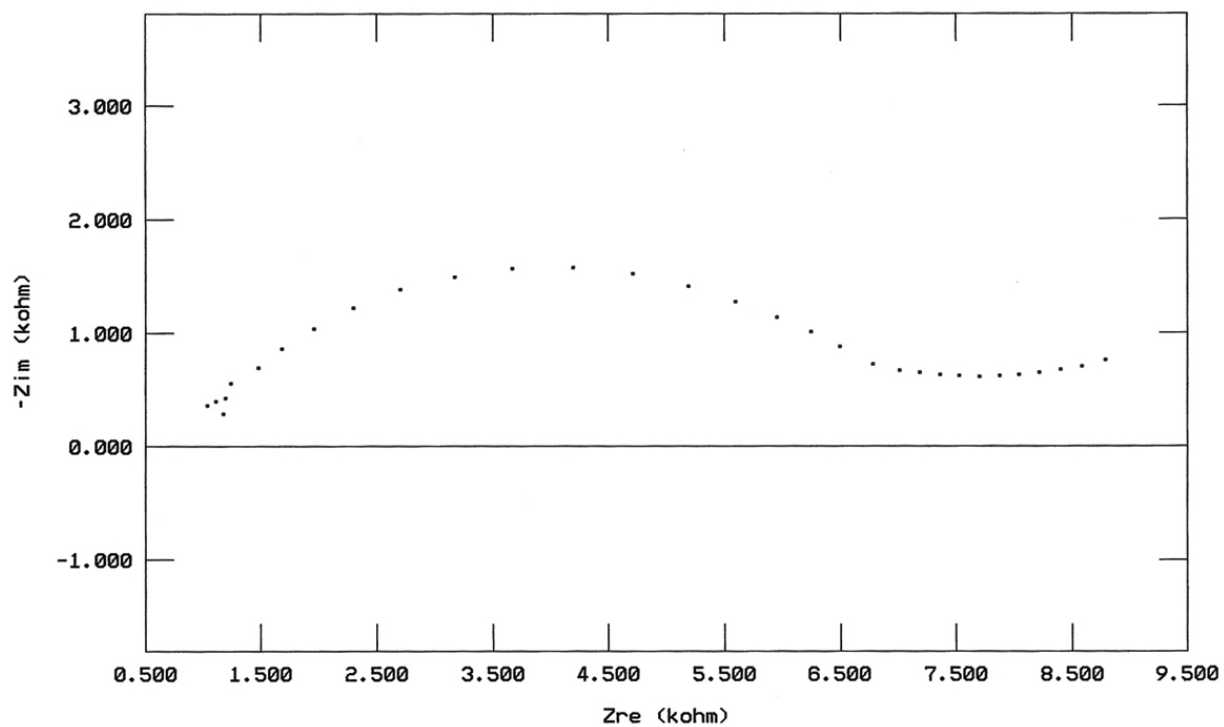


Figure 2. Nyquist plot of Li/Li₂Pc/MnO₂ cell at 75°C.

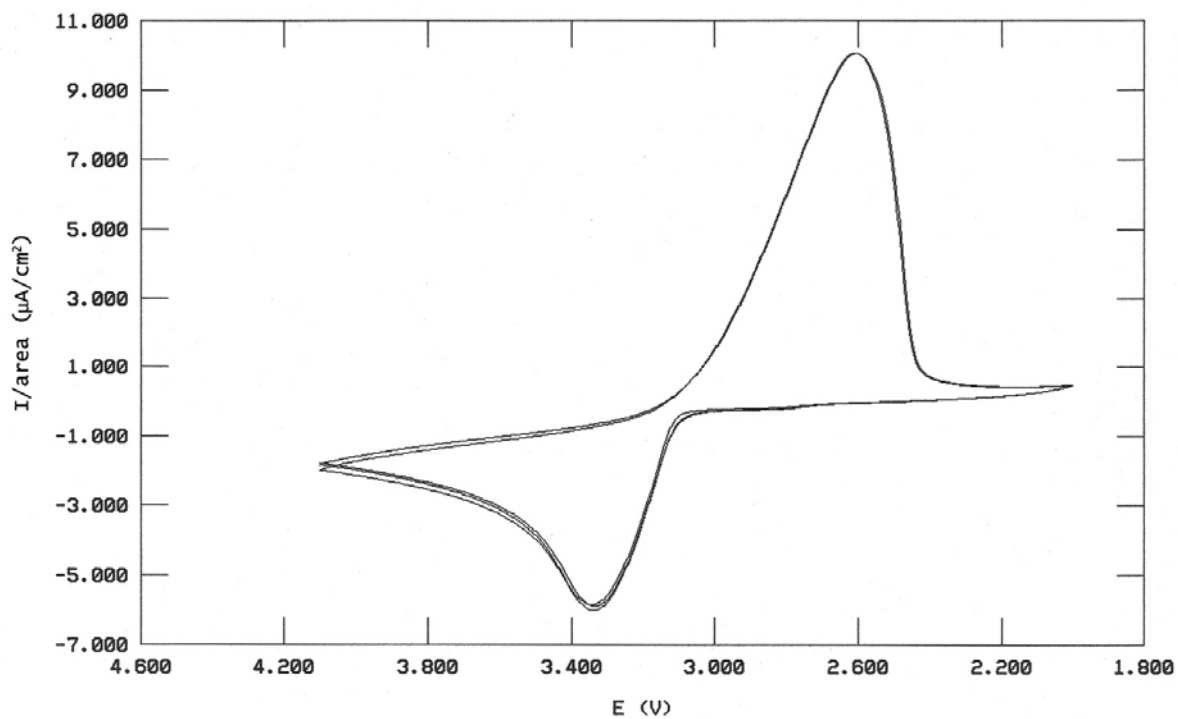


Figure 3. Cyclic voltammogram of Li/PEO film/Li₂Pc/MnO₂ cell at 50°C, scan rate 280 μV/s.

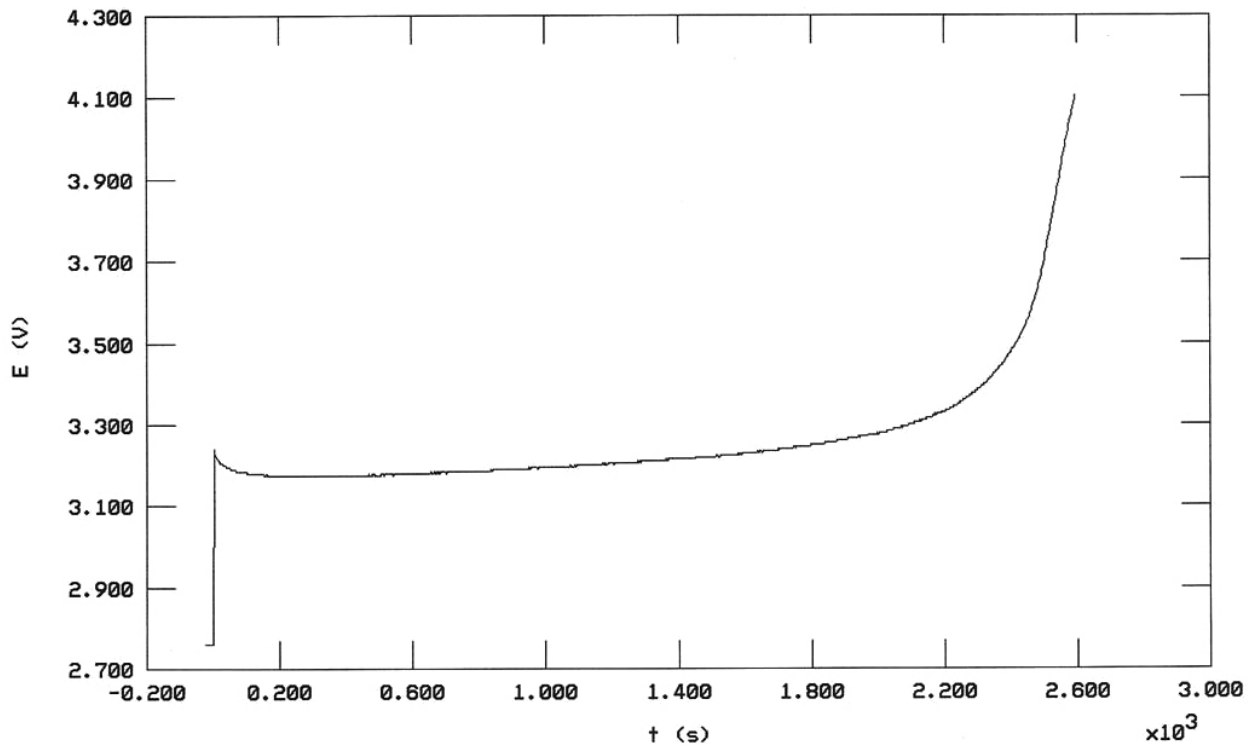


Figure 4. Chronopotentiometry of Li/PEO film/Li₂Pc/MnO₂ cell at 50°C, $I = 3.2 \mu\text{A}/\text{cm}^2$.

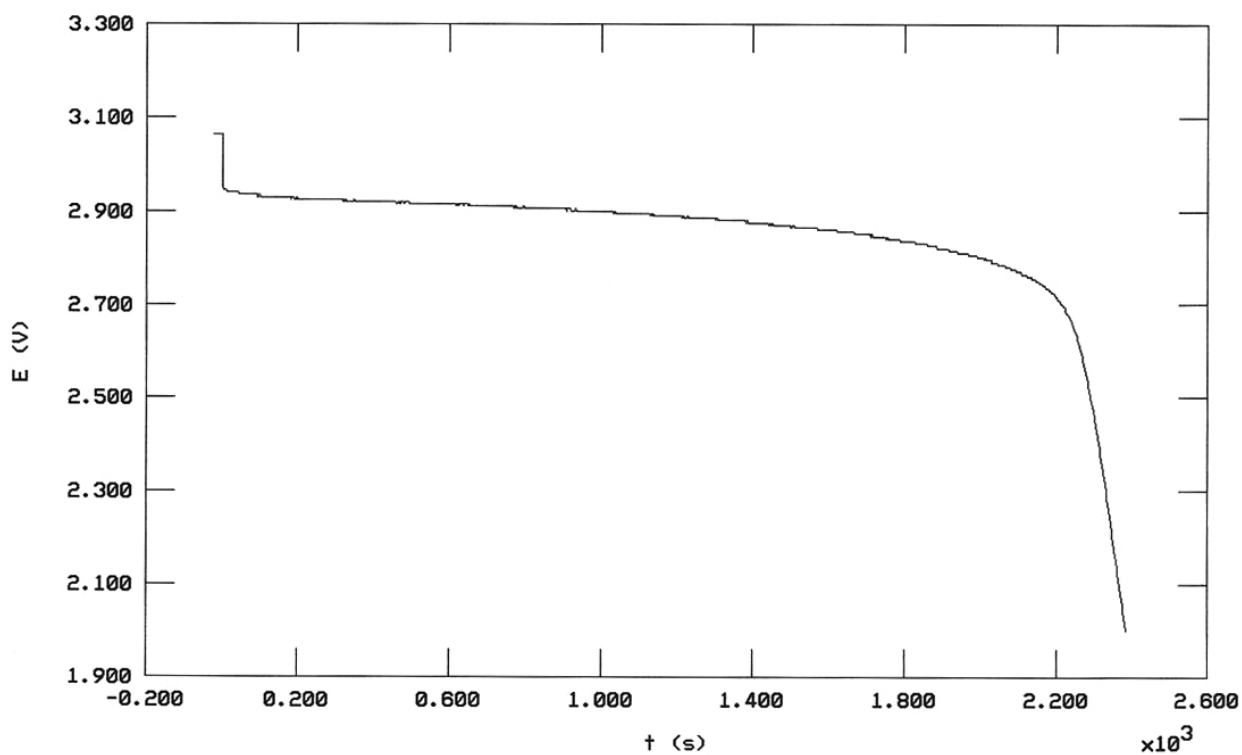


Figure 5. Chronopotentiometry of Li/PEO film/ $\text{Li}_2\text{Pc}/\text{MnO}_2$ cell at 50°C , $I = 3.2 \mu\text{A}/\text{cm}^2$.

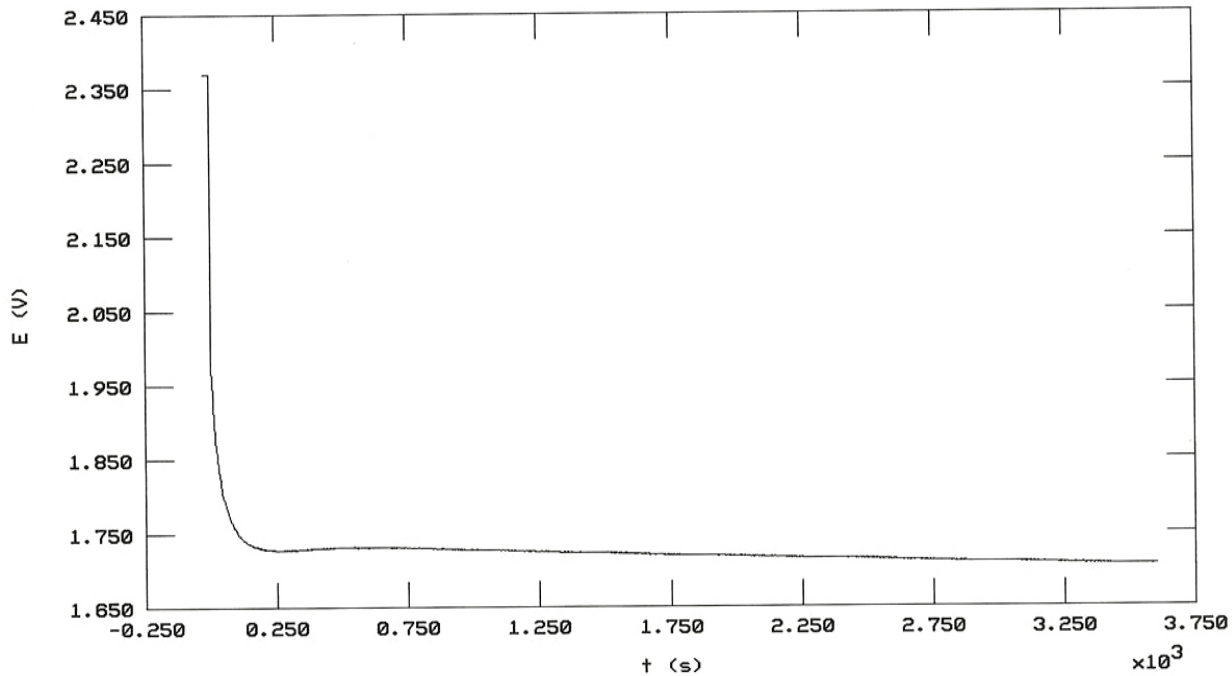


Figure 6. Chronopotentiometry of Li/ $\text{Li}_2\text{Pc}:\text{pvdf}/\text{Fe}_x\text{S}_y$ cell at 90°C , $I = 3.8 \mu\text{A}/\text{cm}^2$.

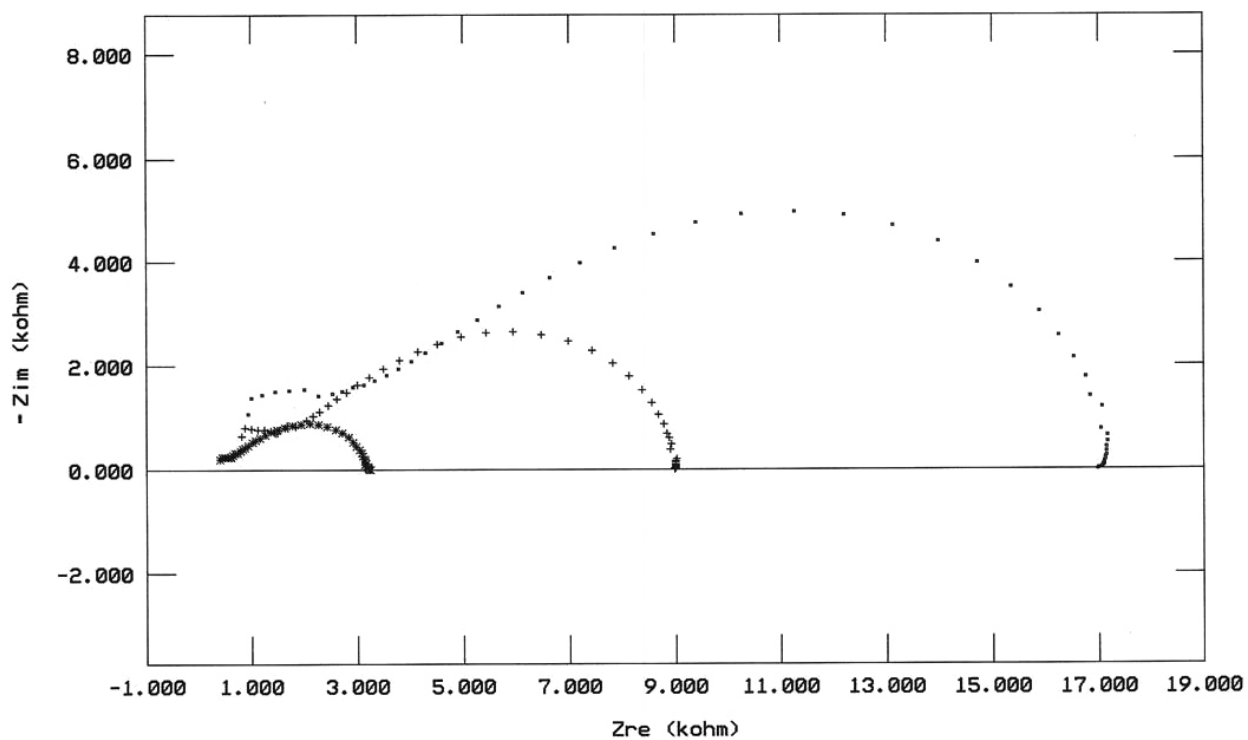


Figure 7. Nyquist plots of Cu/Li₂Pc(Sol. Cast 20μm film 4)/Cu cell at 21°C and pressures of 24,000 psi, 12,000 psi and 8,000 psi.

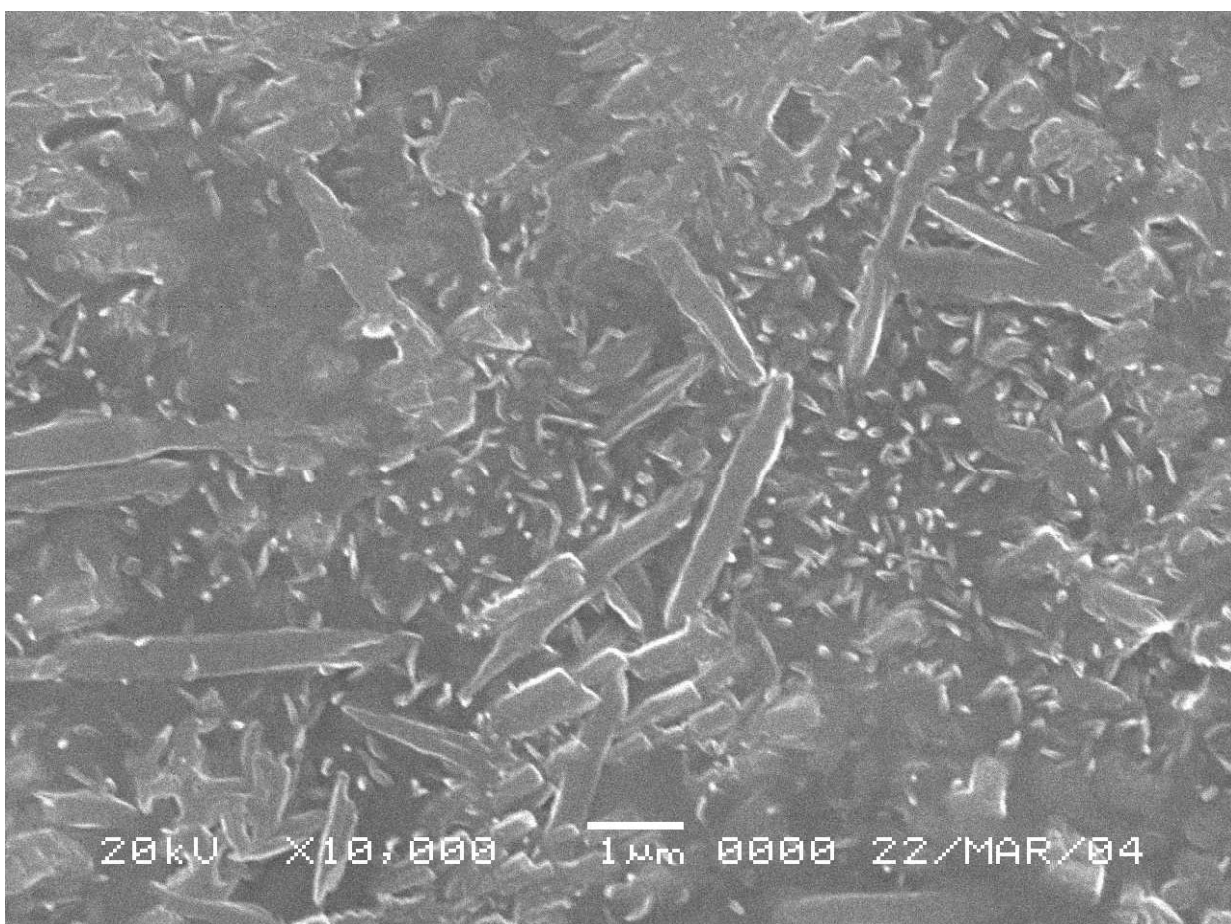


Figure 8. SEM of 20µm thick film of Li₂Pc solution cast from cyclopentanone and toluene.

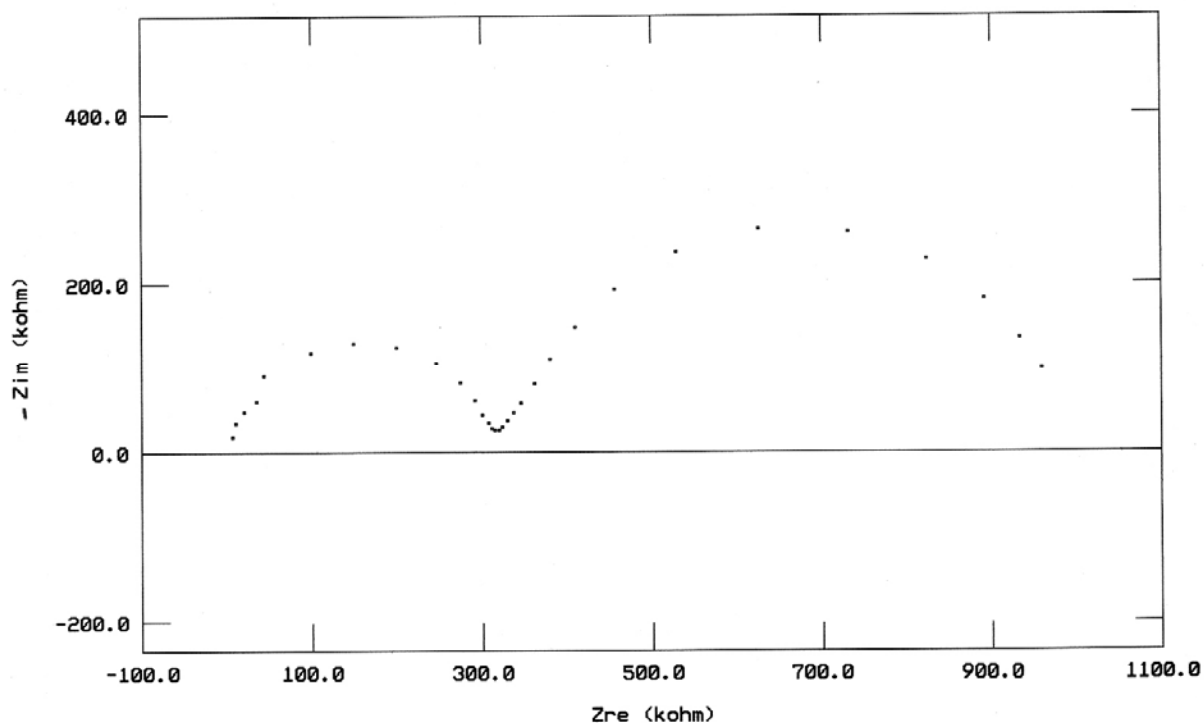


Figure 9. Nyquist plot for a pressed pellet of Li₂Pc recrystallized from acetone and toluene and dried at 160°C under vacuum.

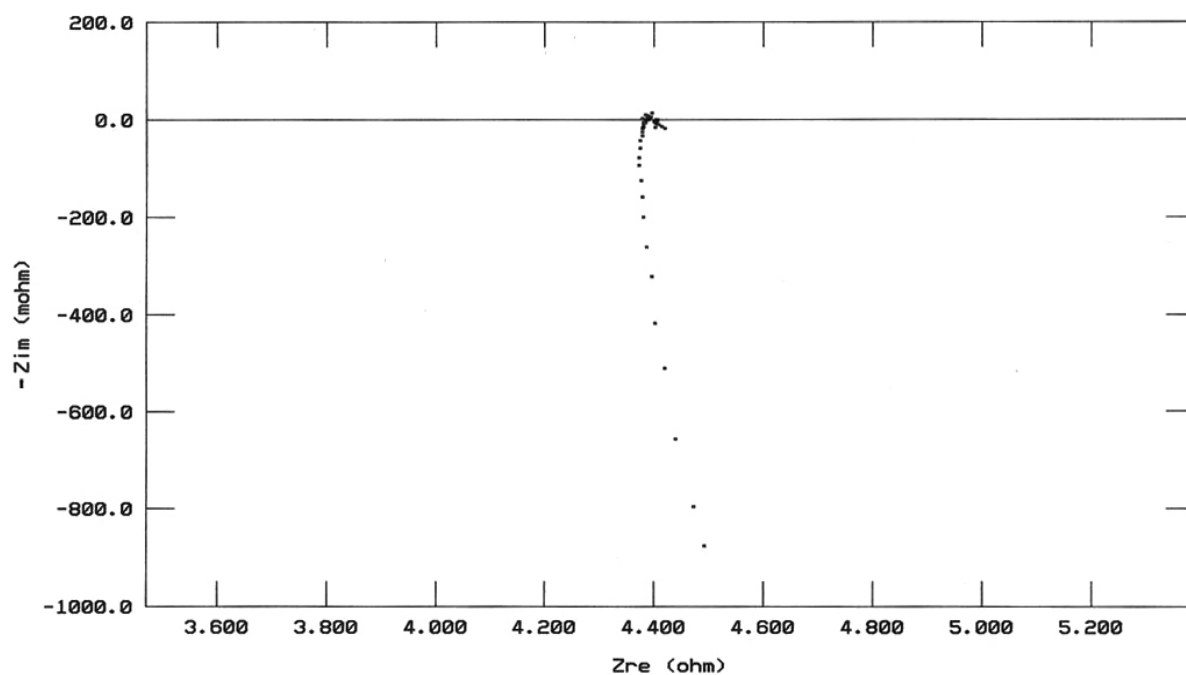


Figure 10. Nyquist plot of Cu/Li₂Pc(Sol. Cast 20µm film4)/Au cell at 21°C and 4,000 psi.