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AEROSPACE POWER SCHOLARLY RESEARCH PROGRAM
Delivery Order 0011: Single Lithium Ion 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 (Li_2Pc) 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 macrocyc1e 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.

15. SUBJECT TERMS
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Single Lithium Ion Conducting Polymer Electrolyte

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The focus of this research was to 1) address the purification of **1** and obtain an x-ray crystallographic analysis, 2) investigate the use of thin films as well as pressed pellets as electrolyte material in a working cell, 3) investigate the low temperature performance of a cell containing **1** as the electrolyte, 4) study temperature induced crystallographic changes of **1** and 5) construct a full cell that exhibits charging and discharging.

Objective

The generation of a single-ion conducting polymer electrolyte to provide a constant-solvent-coordination sphere for lithium ion conduction. Dilithium phthalocyanine **1** (Li_2Pc), in a crystalline form, represents a molecular assembly in which the lithium atoms are held by electrostatic attraction to the partially negatively charged nitrogen atoms in the macrocycle. The three-dimensional structure of this system has been studied by computational methods and indicate that two lithium phthalocyanine molecules are held together by an energy of about 45 kcal/mole and three phthalocyanine molecules are held together by an energy of about 71 kcal/mole. These characteristics make **1** a suitable material for use as a channel material for lithium ion conduction.

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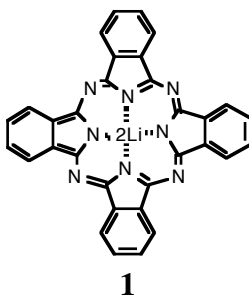
X-ray crystallographic analysis

Dilithium phthalocyanine **1** represents a self-assembled molecular channel. Its

purification and characterization as well as its stability over a wide temperature range

have been addressed. A method of purifying **1** has been discovered[1] that allows the

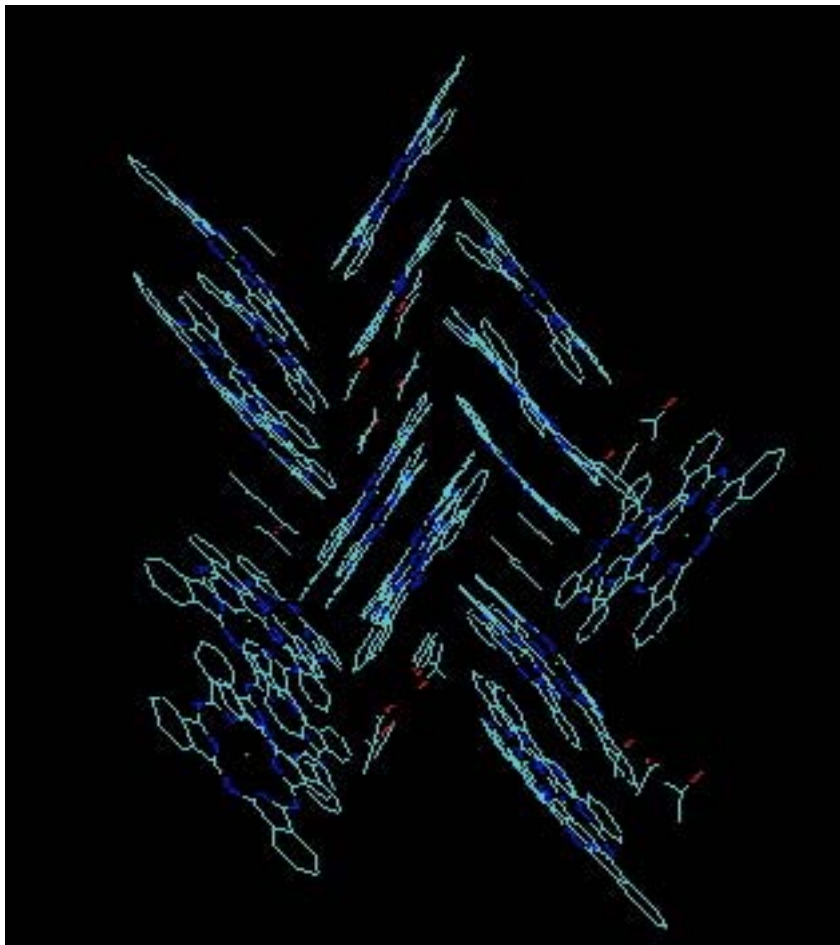preparation of reproducible batches of material for electrochemical evaluation on a small

Figure 1. X-ray crystal structure of **1.**

scale ($1cm^3$). Material suitable for X-ray structure determination was obtained after

considerable experimentation and was subjected to x-ray diffraction analysis at Argonne

National Laboratories. The structure of this system, which has not been previously

reported, is shown in Figure 1. Interestingly, one lithium resides in the center of the phthalocyanine ring while the other is present in a solvent (water and acetone) coordinated section of the unit cell. Further data collection to refine the structural parameters and additional crystallization experiments are underway to more clearly define the structural features of this molecule and determine the factors that can be used to control crystallization.

Thin Film Li$_2$Pc

The practical use of dilithium phthalocyanine **1** as a channel material will require it to be present as a thin film. In addition to the use of the neat material, a binder poly(vinylidene fluoride) (PVDF, KYNAR) was investigated. The binder material imparts flexibility to the thin films. Three approaches are envisioned. One involves the use of a solution casting technique in which a homogeneous solution is used to generate a film. A second approach is to hot press a thoroughly mixed and pulverized combination of binder and dilithium phthalocyanine **1**. A third approach is the generation of a thin film by the deposition of Li$_2$Pc by a sputtering technique.

The fabrication of cells having the electrolyte present as a thin film has been investigated with the objective of creating cells of low impedance and stable voltage.[2] Electrochemical cells with lithium metal foil anodes, Li$_2$Pc 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. The results suggested that further investigation is needed to establish an optimum method of forming thin films of Li_2Pc. The study also pointed out the need for generating optimized interfaces between the various components of the cell - anode/electrolyte/cathode.

Low temperature performance

An important advantage of using a self-assembling material like Li_2Pc as the electrolyte in an electrochemical cell is that the cell would be unaffected by temperature excursions.

Two electrode impedance measurements were made on a thin film of dilithium phthalocyanine that was deposited onto a carbon substrate.[3] The measurements were made from -50°C to + 100°C. The cell configuration used in the variable temperature experiment was: stainless steel electrode/thin film Li_2Pc cast onto carbon/thin film carbon on copper/stainless steel electrode. The total cell impedance varied from 3.4 to 4.6 Ω over this temperature range. The small change in resistance as a function of temperature suggests that a low energy of activation pathway for lithium ion transport has been achieved in the solid-state lithium ion conductor Li_2Pc. Specific conductivities are on the order of mS/cm over this temperature range.

Thermal integrity of Li_2Pc

As mentioned earlier, Li_2Pc channel single ion conductor material has been successfully purified and utilized as an electrolyte in lithium ion cells. XRD data suggests that the structure of this material is crystalline in nature, as indicated by the *hlk* reflections. *In situ* SAXS studies indicated that the molecular structure of Li_2Pc undergoes re-arrangement when the sample is heated under an inert atmosphere to

temperatures close to 200°C. Electrochemical performance is also improved at that temperature, as reflected by the increase in ionic conductivity.[4]

Complete cell

Computational chemistry calculations performed with Gaussian 98 were used to develop an experimental method that facilitates ionic connection between the solid-state electrolyte dilithium phthalocyanine (Li_2Pc) and manganese dioxide (MnO_2). The planar configuration of the phthalocyanine ring and the fact that the lithium ions are very close to the ring may sterically hinder effective ionic coupling between Li_2Pc and any potential cathode. This same argument has been used for understanding the insertion and removal of magnesium from water solutions of deuteroporphyrins. Calculated results show that lithium ions are drawn closer to the phthalocyanine ring upon formation of $(Li_2Pc)_2$ via molecular self-assembly when compared to the single-molecule Li_2Pc. However, extension of lithium ions above the planar phthalocyanine ring in $(Li_2Pc)_2$ can be enhanced through formation of a complex at the axial position above lithium. Calculations show that coroannulene at the axial position above lithium forms an asymmetric structure with $(Li_2Pc)_2$ and does extend lithium further above the ring. To test the theoretical results, an electrically conducting carbon with a curved lattice was used in the fabrication of an all solid-state electrochemical cell with a lithium metal foil anode, Li_2Pc electrolyte, and a MnO_2 cathode. Slow-scan-rate cyclic voltammograms of a Li_xMnO_2 cathode demonstrate the charging and discharging of cells.[5,6]

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1. Unpublished results

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"Lithium Ion Conducting Channel as Solid-State Electrolyte for Rechargeable Lithium Batteries**,"** L. G. Scanlon, L. R. Lucente, **W.A. Feld**, G. Sandí, P. Balbuena, and A. Turner, *9th International Symposium on Polymer Electrolytes, Mragowo, Poland, August 22-27, 2004.*

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 (Li₂Pc) 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 Li₂Pc (2). Different Li₂Pc 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 Li₂Pc 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 Li₂Pc as the solid-state electrolyte and obtain cells with stable open circuit voltages(3). This has been accomplished with lithium metal foil anodes, Li₂Pc 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 $\mu A/cm^2$. 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°C to

+90°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.

<u>Thin Film Characterization</u>

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.

<u>Film deposition</u>

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.

<u>SEM</u>

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 binder100 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 $Li/Li_2Pc/MnO_2$ 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 voltamogram of a Li/PEO film/Li_2Pc/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 Li/PEO film/Li_2Pc/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 x 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

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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/Li2Pc 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.

ACKNOWLEDGEMENTS

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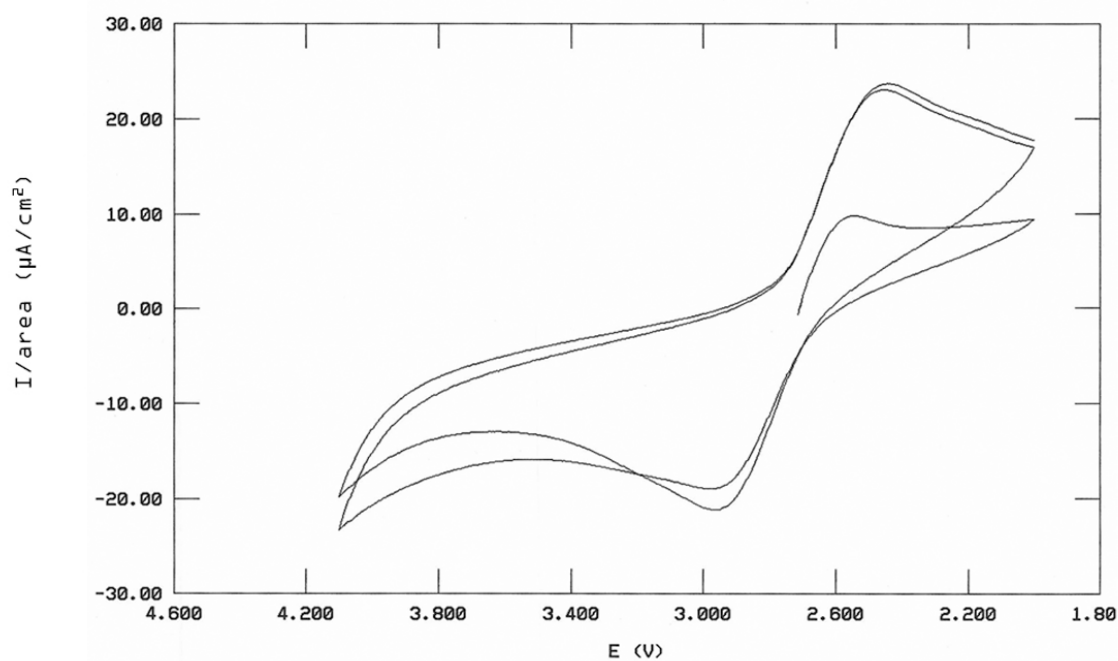8. N. Munichandraiah, private communication.

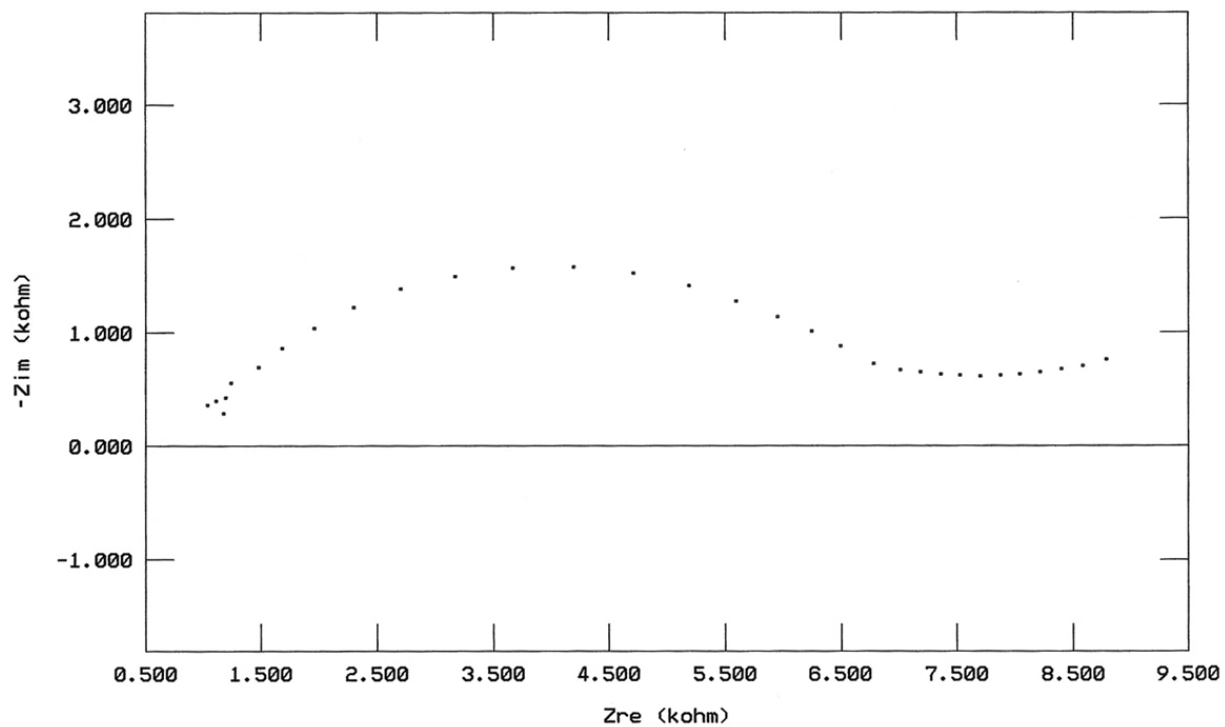**Figure 1. Cyclic voltammogram of Li/Li$_2$Pc/MnO$_2$ cell at 75°C, scan rate 280 µV/s.**

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Figure 2. Nyquist plot of Li/Li$_2$Pc/MnO$_2$ cell at 75°C.
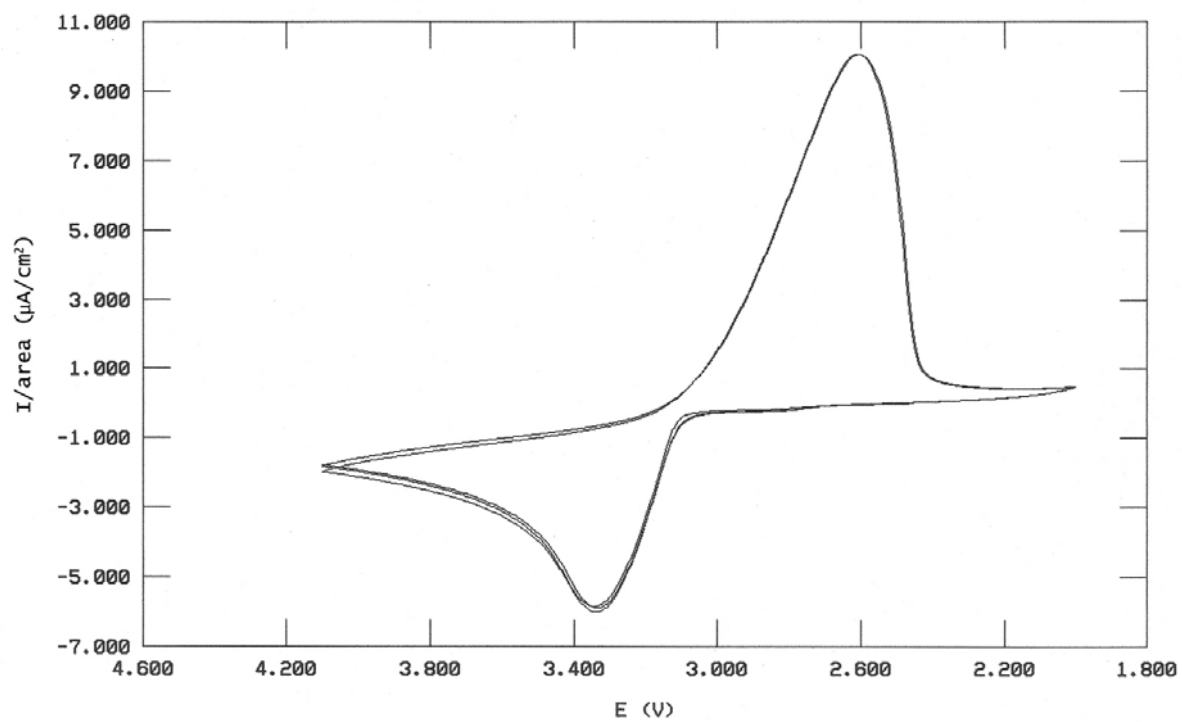
Figure 3. Cyclic voltammogram of Li/PEO film/Li$_2$Pc/MnO$_2$ cell at 50°C, scan rate 280 µV/s.
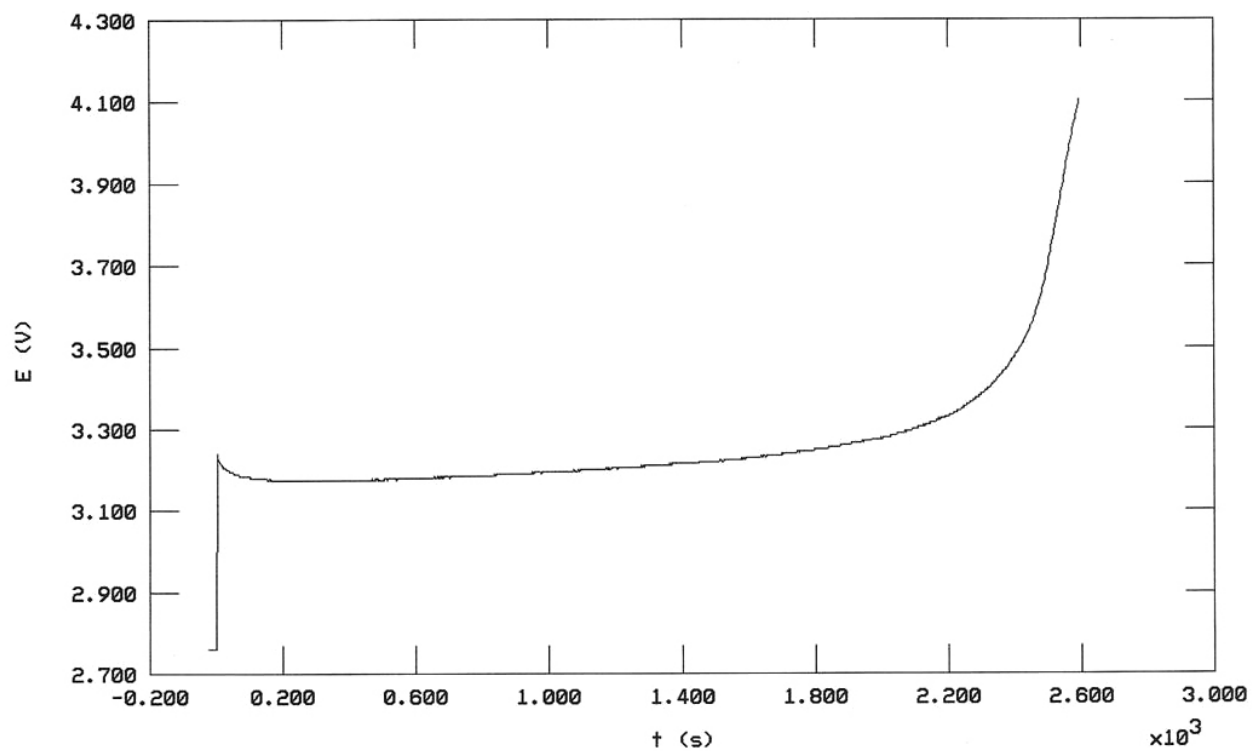
Figure 4. Chronopotentiometry of Li/PEO film/Li$_2$Pc/MnO$_2$ cell at 50°C, I = 3.2 µA/cm^2.
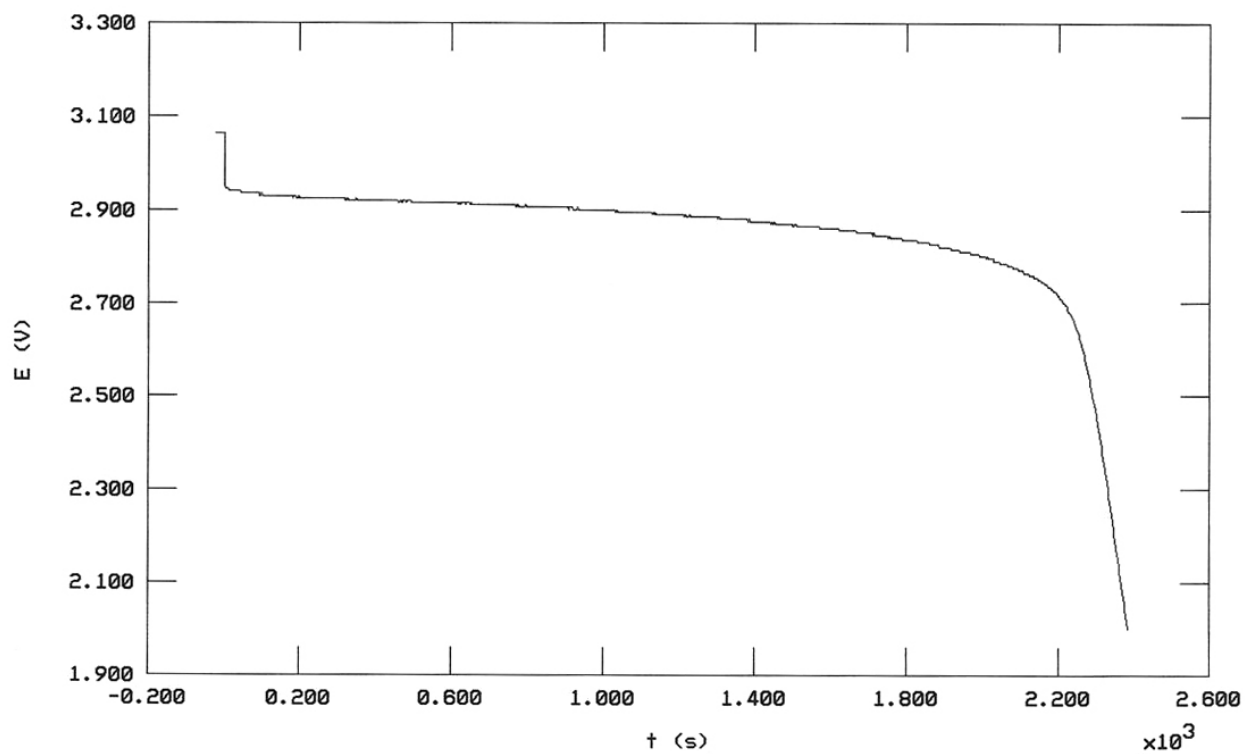
Figure 5. Chronopotentiometry of Li/PEO film/Li$_2$Pc/MnO$_2$ cell at 50°C, I = 3.2 µA/cm^2.
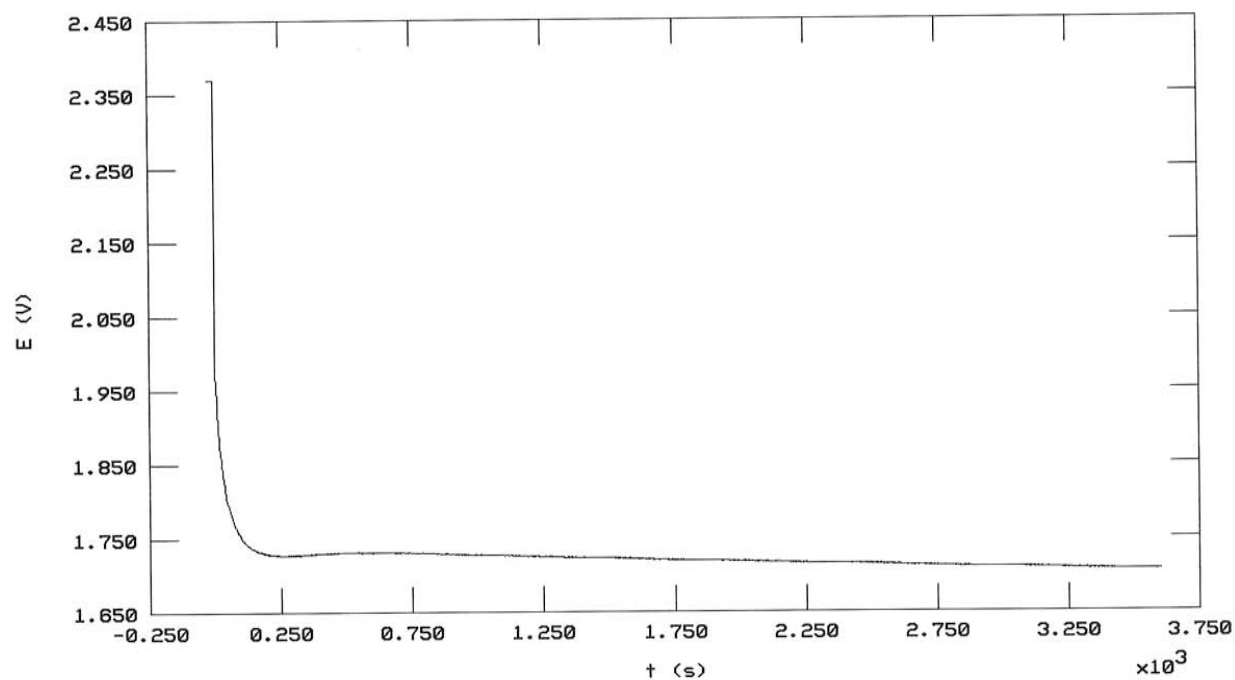
Figure 6. Chronopotentiometry of Li/Li$_2$Pc:pvdf/Fe$_x$S$_y$ cell at 90°C, I = 3.8 µA/cm^2.
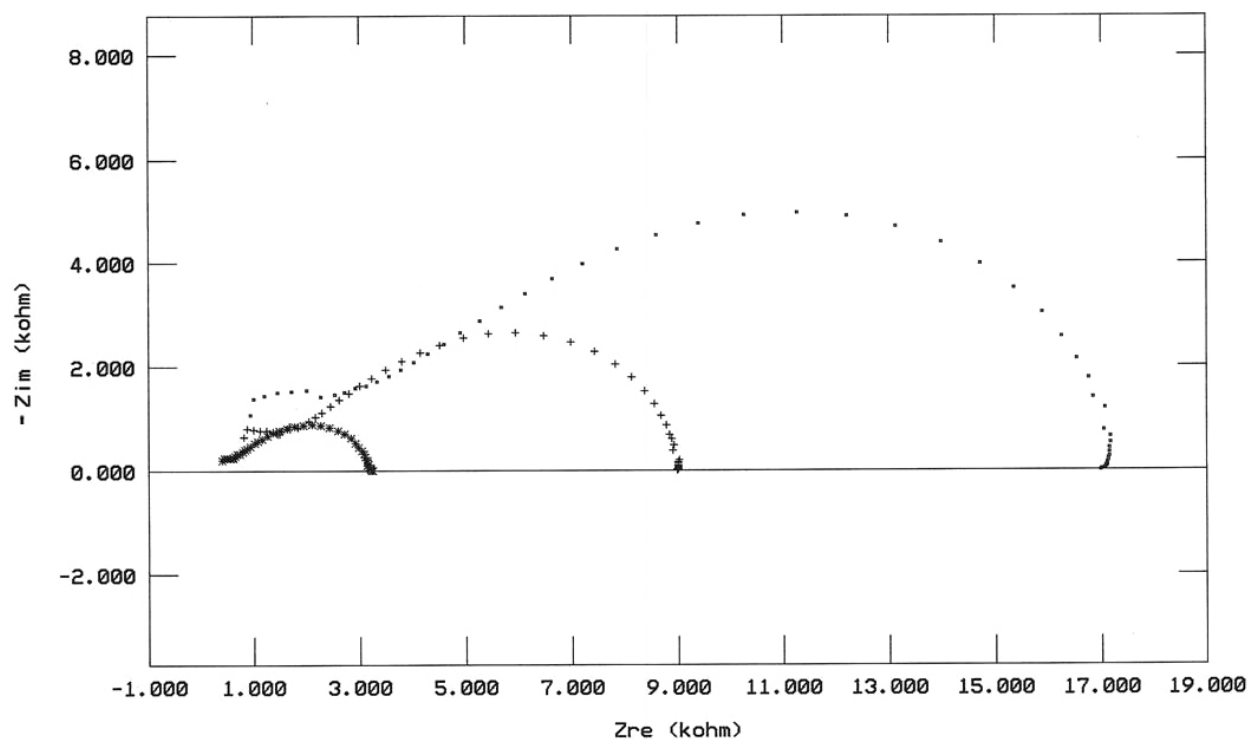
Figure 7. Nyquist plots of Cu/Li$_2$Pc(Sol. Cast 20µm film 4)/Cu cell at 21°C and pressures of 24,000 psi, 12,000 psi and 8,000 psi.
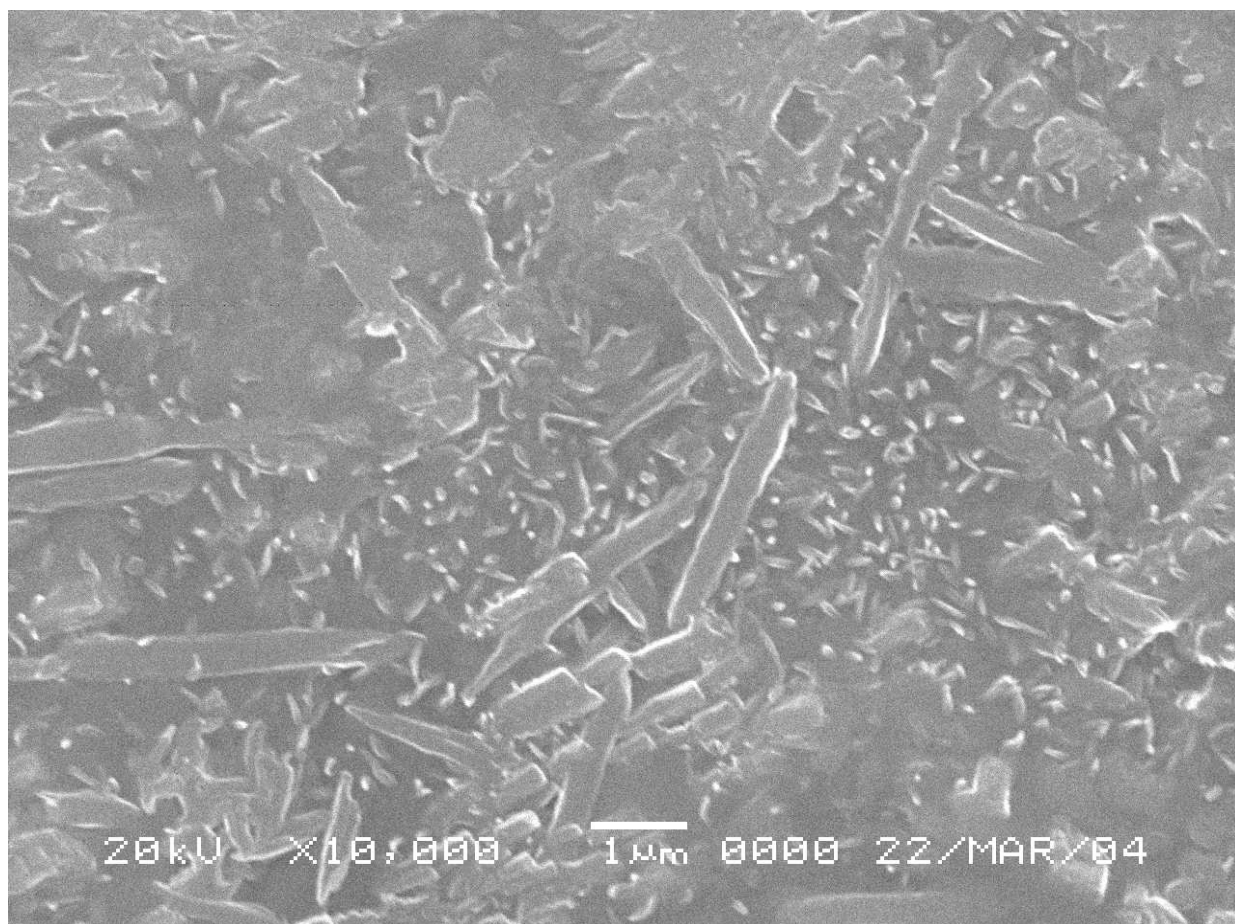
Figure 8. SEM of 20μm thick film of Li$_2$Pc solution cast from cyclopentanone and toluene.
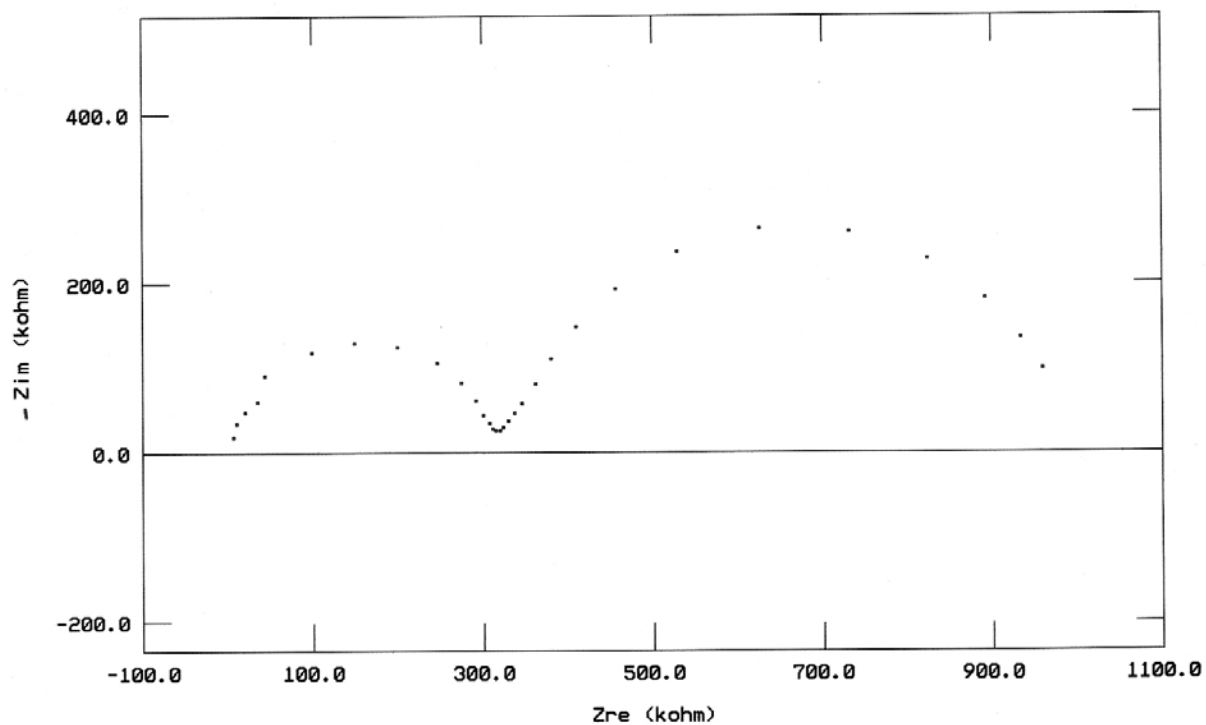
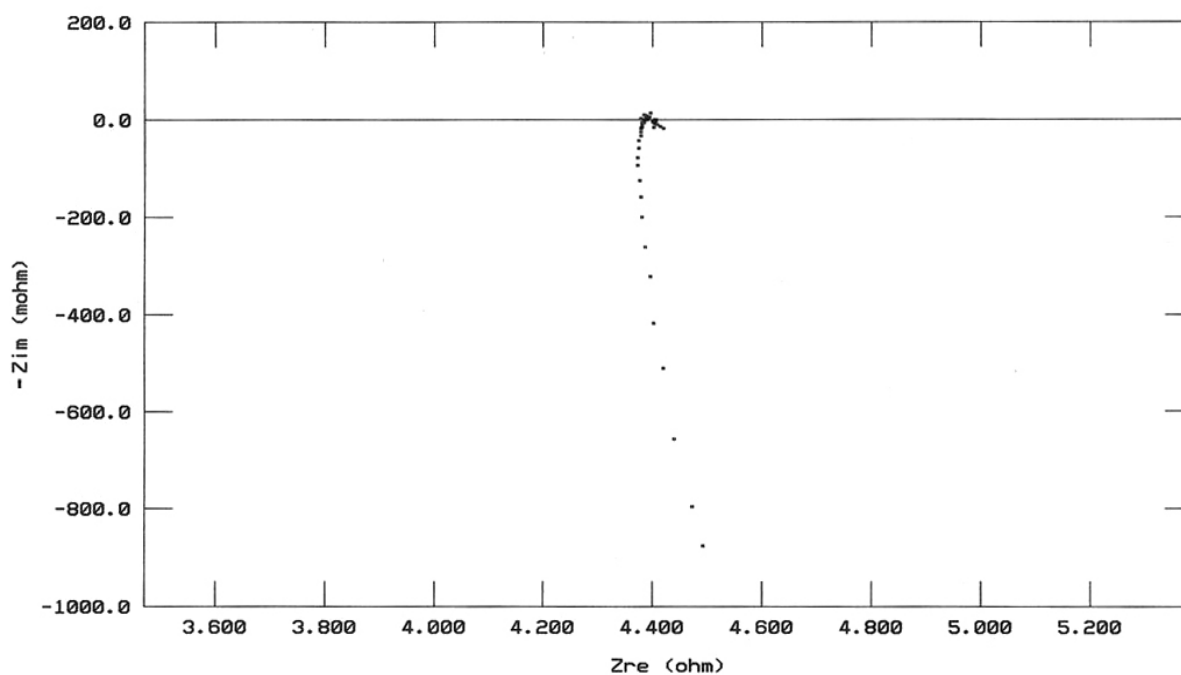**Figure 9. Nyquist plot for a pressed pellet of Li$_2$Pc recrystallized from acetone and toluene and dried at 160°C under vacuum.**

Figure 10. Nyquist plot of Cu/Li$_2$Pc(Sol. Cast 20μm film4)/Au cell at 21°C and 4,000 psi.

Specific Conductivity as a Function of Temperature for Dilithium Phthalocyanine (Li$_2$Pc) from -50°C to +100°C

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Abstract

Two electrode impedance measurements were made on a thin film of dilithium phthalocyanine that was deposited onto a carbon substrate. The measurements were made from -50°C to + 100°C. The cell configuration used in the variable temperature experiment was: stainless steel electrode/thin film Li$_2$Pc cast onto carbon/thin film carbon on copper/stainless steel electrode. The total cell impedance varied from 3.4 to 4.6 _ over this temperature range. The small change in resistance as a function of temperature suggests that a low energy of activation pathway for lithium ion transport has been achieved in the solid-state lithium ion conductor Li$_2$Pc. Specific conductivities are on the order of mS/cm over this temperature range.

Keywords: Lithium-ion; Conductivity; Impedance

1. Introduction

Metal phthalocyanines can function as organic semiconductors because of overlap of the π molecular orbitals between adjacent molecules. It has been found that phthalocyanines with orthorhombic crystal structures have poor π-π overlap and therefore electronic conductivity is low, ranging in values from 10^{-13} to 10^{-11} S/cm (1). Electronic conductivities for polycrystalline materials H$_2$Pc, CuPc, and NiPc range from 10^{-14} to 10^{-9} S/cm (2,3). One-dimensional coordination polymers composed of metal phthalocyanines bridged with μ-axial ligands can have conductivities between 10^{-5} to 10^{-2} S/cm after doping with iodine. In these bridged structures, the μ-axial ligand is unsaturated and can provide a pathway for conduction (1). Octakis-substituted metal phthalocyanines with donor or acceptor groups can have electronic conductivities in the range of 10^{-9} to 10^{-8} S/cm (1). After doping these molecular systems with either iodine or lithium, the conductivities are increased to 10^{-6} – 10^{-4} S/cm. The molecular system in our investigation, Li$_2$Pc, is used to form a lithium ion conducting channel via molecular self-assembly (4). A schematic of a one dimensional single ion conductor for lithium ions as shown in Figure 1 illustrates this point. The macrocyclic ring in this figure is an unsaturated macrocyclic complex such as dilithium phthalocyanine. It is by design that one uses an unsaturated macrocyclic complex because with it, there is electron delocalization around the

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ring that keeps the lithium ion centered within the macrocycle. Correspondingly, this is where the negative electrostatic potential is at a maximum. It is through proper spacing of the unsaturated macrocyclic rings, with respect to one another, that allows one to create a channel where the negative electrostatic potential remains relatively constant throughout the molecular system but where there is sufficient macrocyclic ring separation to preclude electronic
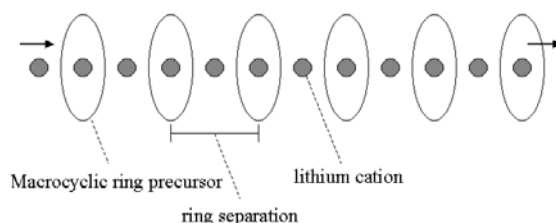

Fig.1. Schematic diagram for a one-dimensional single-ion conductor for lithium ions.

conduction. It is the relatively constant negative electrostatic potential that is primarily responsible for changing the lithium ion transport mechanism from one that depends primarily on polymer segmental motion as found in oxygen based polymer electrolytes, to one that depends upon the electric field gradient established between the electrodes of a cell. In this fashion, the temperature dependence for ionic conduction is minimized and one can expect high ionic conductivity at ambient and subambient temperatures. An additional benefit associated with the lithium ion channel is that the transference number for lithium is one and therefore under high current loads any voltage drop across the electrolyte is minimized. The transference number of one for lithium is by design since the anion matrix that forms the lithium ion conducting channel is immobile.

2. Experimental

Dilithium Phthalocyanine was purchased from Aldrich and recrystallized from an acetone/toluene mixture. The crystals were dried at 90°C under a vacuum of 90 millitorr for 18 hours. Thin films of Li_2Pc, 25 μm thick, were cast onto a carbon thin film that was 152 μm thick. A polyvinylidene binder was used in both the Li_2Pc and carbon films. The carbon film was prepared by casting onto a copper substrate and dried before the casting of Li_2Pc. The cell configuration used in the variable temperature experiment was: stainless steel electrode/thin film Li_2Pc cast onto carbon/thin film carbon on copper/stainless steel electrode. The electrode area was 1.23 cm^2. A Tenney environmental chamber was used to vary the temperature of the cell placed inside the chamber. Thermocouples inside the chamber and positioned near the cell monitored the temperature. The temperature range was varied from -50°C to +100°C. The experiment was conducted over a two day time frame with the high temperatures experiments on the first day and the low temperature experiments on the second day. After the chamber reached the desired temperature, the cell was equilibrated for an additional 30 minutes before the resistance of the cell was measured. Resistance was measured by using an EG&G impedance spectrometer model 398 software interfaced with an EG&G potentiostat/galvanostat model 273A

and EG&G lock-in amplifier model 5210. The amplitude of the alternating current 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 where the relative humidity is less than 1%.

Gaussian 98 was used to perform geometry optimizations for Li_2Pc and $(Li_2Pc)_2$ (5). Density Functional Theory was used for these optimizations since it includes the effects of electron correlation which is important for phthalocyanine because of electron delocalization. The specific method of calculation was Becke-style 3-Parameter Density Functional Theory (B3LYP) with a 3-21G and 6-31G(d) basis sets.

The Differential Scanning Calorimetry (DSC) measurements were carried out using a TA Instruments model 2010 at a heating rate of 10^oC/min, under a nitrogen atmosphere. Temperature and enthalpy calibration of the calorimeter was initially performed using pure indium and tin as standard material with the same heating rate of 10^oC/min. Approximately 5 mg of the dried sample in a hermetically sealed aluminum pan was used in the experiment.

The morphology of the Li_2Pc was determined using the Hitachi S4700 Field Emission Gun Scanning Electron Microscope (FESEM) at the in the Electron Microscopy Collaborative Research Center at Argonne National Laboratory. Samples were prepared by sprinkling powder on conducting tape on aluminum stubs. Samples were uncoated. Secondary electron images were recorded with the FESEM operating at 10kV.

At Argonne National Laboratory, carbonaceous materials with enhanced lithium capacity have been derived from ethylene or propylene upon incorporation in the vapor phase in the channels of sepiolite, taking advantage of the Brønsted acidity in the channels to polymerize olefins (6). Sepiolite is a phyllosilicate clay insofar as it contains a continuous two-dimensional tetrahedral silicate sheet. However, it differs from other clays in that it lacks a continuous octahedral sheet structure. Instead, its structure can be considered to contain ribbons of 2:1 phyllosilicate structure, with each ribbon linked to the next by inversion of SiO_4 tetrahedra along a set of Si-O-Si bonds. In this framework, rectangular channels run parallel to the x-axis between opposing 2:1 ribbons, which results in a fibrous morphology with channels running parallel to the fiber length. Channels are 3.7 x 10.6 Å in sepiolite (they are 3.7 x 6.4 Å in palygorskite). Individual fibers generally range from about 100 Å to 4-5 microns in length, 100-300 Å width, and 50-100 Å thickness. Inside the channels are protons, coordinated water, a small number of exchangeable cations, and zeolitic water. Carbon fibers (1-1.5 microns long) are obtained whose orientation and shape resemble that of the original clay. The SAED pattern of the carbon fibers shows diffuse rings typical of amorphous carbon; no diffraction spots were observed

Carbon Synthesis

Ethylene and propylene (AGA, 99.95%) were loaded in the sepiolite samples and pyrolyzed in the gas phase in one step. A three-zone furnace was used. Quartz boats containing sepiolite were placed within a quartz tube. The tube was initially flushed with nitrogen for about 3 hours. The gas was then switched to propylene or ethylene and the gas flow was kept about

5 cm³/min. The temperature of the oven was gradually increased from room temperature (about 5EC/min) to 700 EC. The oven was then held at that target temperature for 4 hours. The clay from the loaded/pyrolyzed sepiolite sample was removed using HF, previously cooled at 0EC to passivate the exothermic reaction. The resulting slurry was stirred for about one hour. It was then rinsed to neutral pH and refluxed with concentrated HCl for 2 hours. The sample was washed with distilled water until the pH was > 5 to ensure that there was no acid left. The resultant carbon was oven dried overnight at 120 °C.

3. Results and Discussion

In order to test the concept of a lithium ion conducting channel based on Li₂Pc, the molecular structures for Li_2Pc and $(Li_2Pc)_2$ were calculated using Density Functional Theory.
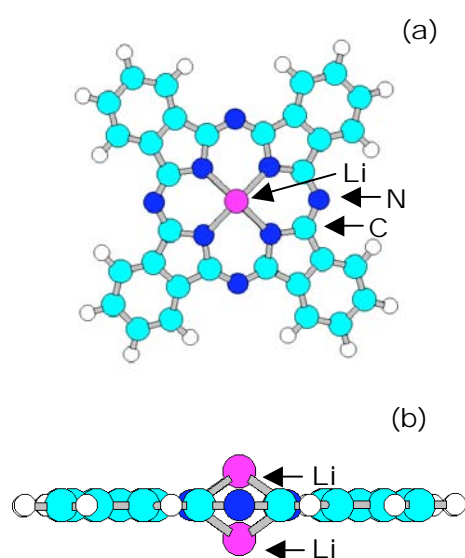
Fig. 2. Optimized geometry for (Li₂Pc)
(a) top and (b) side views using the
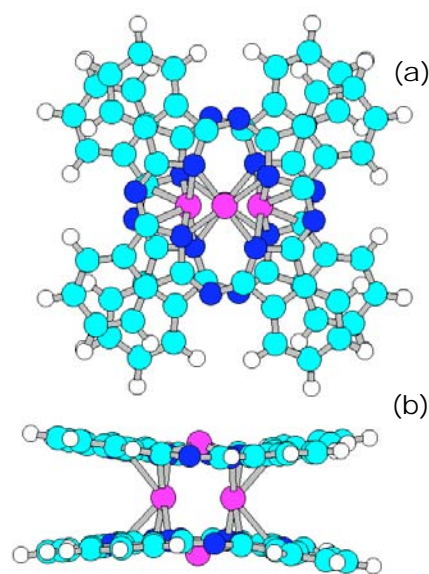3-21G basis set for optimization.

Fig. 3. Optimized geometry for (Li₂Pc)₂
(a) top and (b) side views using the 3-21G
basis set for optimization.

Figures 2 and 3 show the calculated structures using the 3-21G basis set. The separation between lithium ions in Li_2Pc is 1.945 Å. Lithium nitrogen bond distances are 2.18 Å. The calculated electronic energy for Li_2Pc at 0 K is − 1673.0644527 Hartrees (1 Hartree=627.51 kcal/mol). $(Li_2Pc)_2$ represents the molecular structure after two adjacent molecules of Li_2Pc have combined through electrostatic forces attributed to the partial positive and negative charges on the lithium and nitrogen atoms, respectively. The calculated electronic energy for $(Li_2Pc)_2$ at 0 K is -3346.2021385 Hartrees. The calculated bond energy between the two phthalocyanines as a result of the electrostatic attraction is 45.95 kcal/mole. The separation between lithiums that are almost in the plane of the phthalocyanine rings is 4.29 Å. The phthalocyanine rings are staggered by approximately twenty degrees. The separation between the rings is approximately 3.75 Å. This value was measured between one of the inner most carbons of the corresponding six membered rings.
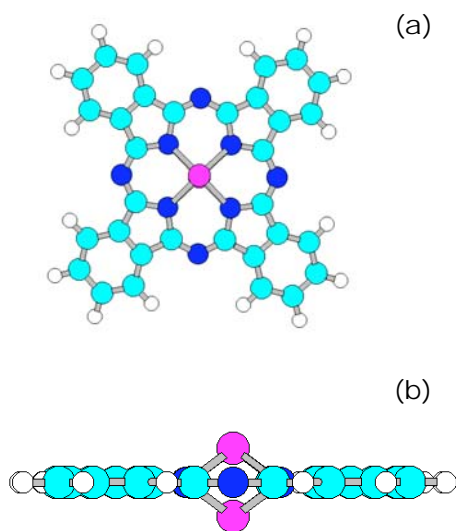
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Fig. 4. Optimized geometry for (Li₂Pc)
(a) top and (b) side views using the
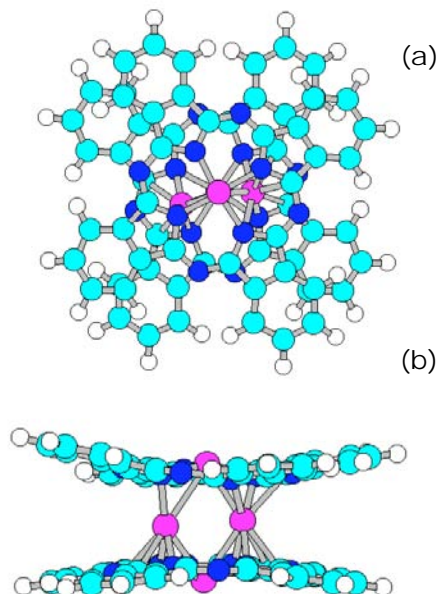6-31G(d) basis set for optimization.

Fig. 5. Optimized geometry for (Li₂Pc)₂
(a) top and (b) side views using the
6-31G(d) basis set for optimization.

Figures 4 and 5 show the calculated structures using the 6-31G(d) basis set. The separation between lithium ions in Li_2Pc is 1.991 Å. Lithium nitrogen bond distances are 2.18 Å. The calculated electronic energy for Li_2Pc at 0 K is – 1682.3574567 Hartrees. $(Li_2Pc)_2$ as shown in Figure 4 represents the molecular structure after two adjacent molecules of Li_2Pc have combined through electrostatic forces. The calculated electronic energy for $(Li_2Pc)_2$ at 0 K is -3364.743437 Hartrees. The calculated bond energy between the two phthalocyanines as a result of the electrostatic attraction is 17.90 kcal/mole. The separation between lithiums that are almost in the plane of the phthalocyanine rings is 4.47 Å. The phthalocyanine rings are staggered now by approximately thirty degrees. The separation between the outer benzene rings varies from 3.94 to 4.89 Å. These values were measured between the two carbons that overlap one another on the outer benzene rings. The importance of these calculated results suggest that molecular self-assembly can be important in the formation of the lithium ion conducting channel and one might expect high electronic resistance due to poor orbital overlap between the π molecular orbitals.

The scanning electron microscopy (SEM) photomicrograph of Li_2Pc is shown in Figure 6.
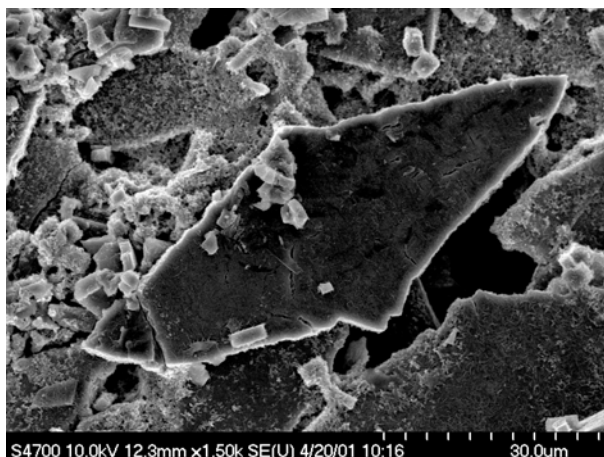
Fig. 6. SEM photomicrograph of Li_2Pc.

It suggests that there are two crystalline phases present as represented by the arrow-head and columnar structures. The columnar structure is consistent with the calculated results reflecting a strong molecular electrostatic bonding predominately along one axis. As an additional collaboration of the calculated results, a DSC was run on Li_2Pc since it was expected that one should have an endotherm peak reflecting the molecular self-assembly process. The DSC results showed a broad endotherm at 89.4°C with an absorption energy of 202.9 J/g. The calculated bond energies described above correspond to 182.6 and 71.1 J/g. The DSC is shown in Figure 7. Upon cooling there is no observance of an expected exotherm peak. However, when the DSC was run the next day, the endotherm at 89.4°C was again observed.
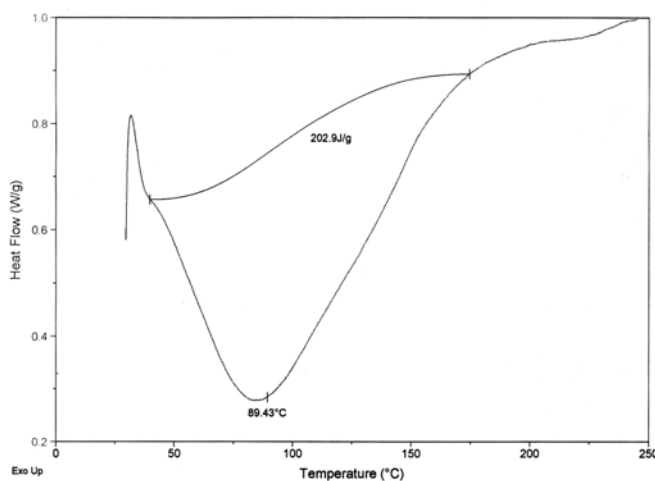

Fig. 7. DSC of Li_2Pc.

In our earlier investigations, Li_2Pc was used in the form of a pellet approximately 500 μm thick and in the presence of a lithium metal anode (4). Electrochemical cells assembled at Argonne National Laboratory under high pressure, with lithium metal anodes, solid-state Li_2Pc purified by our lab as the electrolyte and copper as the working electrode have open circuit voltages of 1.8 V

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under no load conditions. A DC current of 200 µA which was passed through these cells did not result in shorting of the cells (7).   These results suggest that there is poor electronic transport throughout the molecular system. Solid-state Lithium 7 NMR results have shown that lithium is stored within Li_2Pc as ionic lithium (7). This result is consistent with that reported by Yamaki who has shown through X-ray diffraction analysis that there is lattice expansion along the b axis of a phthalocyanine cathode material during discharge (8). He suggested that lithium is stored between the layered phthalocyanine molecules and correspondingly internal resistance is decreased because of the lattice expansion. In view of precluding any possible effects due to lithium doping, it was decided to investigate Li_2Pc in the absence of any lithium metal. This was accomplished by depositing a layer of Li_2Pc onto a thin film of carbon anode material prepared by Giselle Sandi. A two electrode cell configuration was used in these experiments as already described. Figures 8 and 9 show the Nyquist plots for thin film Li_2Pc cast onto carbon as a function of temperature. These plots are primarily composed of a high frequency inductive tail indicative of a porous media. For example, the Nyquist plot for a lithium ion battery is comprised of an inductive tail at high frequency followed by two semicircles at the medium and low frequencies. (9) The inductance behavior of the lithium ion battery is attributed to the porous features of the electrodes. For our solid state system under investigation, the Nyquist plots would suggest that the difference in ohmic resistance of the electrolyte and total cell resistance is very slight.
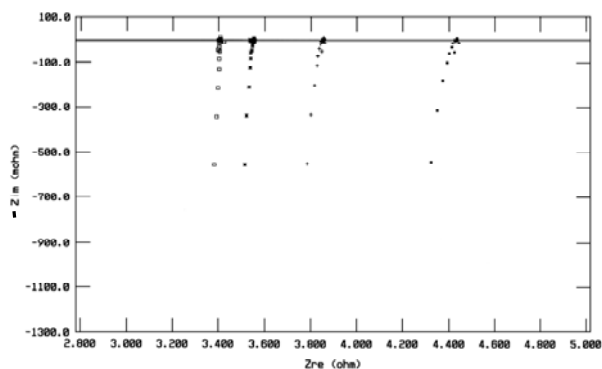

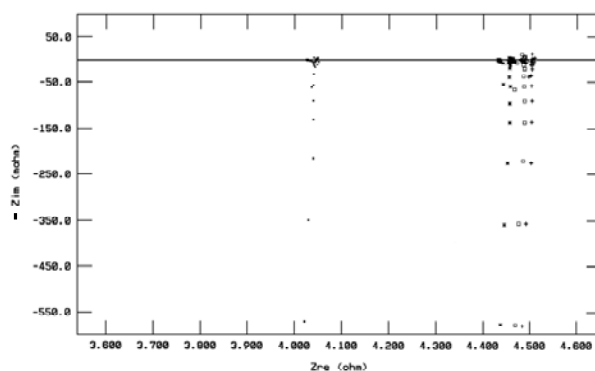Fig. 8. Nyquist plots for thin film Li_2Pc cast onto carbon at (a) □, 25°C, (b) ·, 50°C, (c) +, 75°C and (d) ■, 100°C.

Fig. 9. Nyquist plots for thin film Li_2Pc cast onto carbon at (a) ■, 21°C, (b) +, 0°C, (c) ·, -25°C and (d) □, -50°C.

The resistances shown in Table 1 were determined where the high frequency inductive tail intercepts the real axis of the Nyquist plot and it represents the ohmic resistance of the Li_2Pc electrolyte.

Table 1
Specific Conductivity from -50°C to +100°C for thin film Li_2Pc cast onto carbon

Temp °C	Resistance	σ (mS/cm)
25	3.4	0.60
50	3.5	0.58
75	3.9	0.52
100	4.4	0.46
21	4.05	0.50
0	4.5	0.45
-25	4.45	0.46
-50	4.5	0.45
20	4.6	0.44
21	0.95[a]	2.1
21	2.35[b]	1.7

a Initial Value prior to variable temperature experiment
b Sandwich configuration of thin film Li_2Pc cast onto carbon, pressure applied to cell.

As discussed in the experimental section, the variable temperature experiment was conducted over two days. The high temperature experiments were conducted on the first day and are shown as the first four values in Table 1. Upon completion of this set of experiments, heating was discontinued, and the cell was allowed to cool overnight to room temperature. The ohmic resistance prior to the start of the low temperature experiments was 4.05 _ at 21°C. The slight changes in resistance as reflected in the high and low temperature regime could be due to slight changes in pressure or force on the electrochemical cell since the electrochemical cell was not spring loaded to provide a constant force. In a separate experiment with this same cell configuration we were able to obtain an ohmic resistance of 0.95 _ at 21°C. In order to test this idea, a new electrochemical cell was constructed with a sandwich configuration using the same material that was cast onto carbon for the variable temperature experiments. This was done by taking two test samples from different areas of the original cast film and placing the top surface areas of Li_2Pc face to face. Pressure exerted on the cell was varied by tightening the screw-type Teflon cell that housed the stainless steel electrodes. The stainless steel electrodes did not move during this procedure. The impedance of the cell was run after each tightening of the cell and the ohmic resistance was shown to decrease. The lowest value for the ohmic resistance obtained by this procedure was 1.7 _.

4. Conclusion

The slight change in resistance as a function of temperature suggests that a low energy of activation pathway has been achieved in the solid-state lithium ion conductor Li_2Pc. Specific conductivities are on the order of mS/cm over this temperature range.

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